"Science Stays True Here"
Biological and Chemical Research (ISSN 2312-0088), Vol.7, 61-69 | Science Signpost Publishing

Corrosion Inhibition of Mild Steel in Acidic Media by *Citrus Microcarpa* (Calamansi) Leaf Extract

Christine Bolo[1], Archie P. Amba[1], Geelyn Raeanne C. Rellin[1], Jayfe Anthony Abrea[1]

1. Philippine Science High School, 6021, Argao, Cebu, Philippines

Received: February 17, 2020 / Accepted: March 22, 2020 / Published: May 25, 2020

Abstract:

Corrosion inhibition is usually done through means of commercialized products such as paint. However, due to the desire in finding a close substitute, green inhibitors were made and tested through means of experimentation. The corrosion inhibition efficiency of *Citrus microcarpa* (Calamansi) leaf extract on mild steel in 1.0 M hydrochloric acid was investigated under ambient temperature. Different concentrations of the leaf extract were prepared (0.02, 0.04, 0.06, 0.08 g/mL) alongside with 1.0 M hydrochloric acid as the control solution. The mild steel samples were immersed in these solutions, monitored in a 192 – hour duration and the corrosion inhibition efficiencies were calculated using the mass loss method. The results showed significant inhibition efficiencies greater than 70% for all extract concentrations with respect to the control. The highest obtained inhibition efficiency was 97.40±0.218% at 0.08 g/mL extract concentration. This corrosion inhibition was implied to undergo chemisorption mechanism process with adsorption isotherm models that fit to both from Lanmguir and Freundlich (R^2 values > 0.99). The results also showed that the corrosion and its inhibition process fit best in zero – order kinetics where the residual mild steel mass is proportionate with time (R^2 values > 0.98). The *Citrus microcarpa* (Calamansi) leaf extract therefore serves as an effective corrosion inhibitor of mild steel in hydrochloric acid media.

Key words: corrosion, mild steel, calamansi, weight loss

1. Introduction

The mild steel corrosion is inevitable. This greatly affects the industrial performance of petrochemical, leather, sugar, textile, food and paper-industries especially when this alloy is in contact with acidic environments. Mild steel is a metal alloy which is a mixture of different metals and non-metal, such as chromium, manganese,

Corresponding author: Jayfe Anthony Abrea, Curriculum and Instruction Services Division (CISD), Philippine Science High School – Central Visayas Campus, Argao, Cebu, Philippines,

iron, and other elements, and is known to have high carbon content that is very prone to rusting because of its high carbon content [1]. The corrosion reaction may be able to reduce the quality of steel and may highly affect its use of the metal thus causing it to lose its strength and capability to hold things when used in construction [2].

However, corrosion can be inhibited. A present way of inhibiting corrosion is by applying paint to the material. Other ways to inhibit corrosion are mixing other elements into the metal and applying an oxide layer on the material.

Numerous studies have already been conducted which aimed on investigating corrosion inhibitors sourcing out from plant extracts. However, some of the samples used for the inhibitors only grow in specific areas. Plants that can be easily grown and are widely cultivated are better samples to be tested as corrosion inhibitors. Leaves of plants are considered to be good corrosion inhibitors together with some other parts of a plant like seeds, bark, roots, etc. [3]. One of those plants is *Citrus microcarpa* (Calamansi).

Calamansi plant belongs to the family of Rutaceae. Its small fruit is usually green in color, has a sour taste and is used to enhance the flavor of food [4]. This fruit has been widely cultivated in the Philippines and is domestically bought in public markets and supermarkets. Its fruit is used for medicinal purposes such as treatment to itchy scalp, heal insect bites and remedy for cough. It can also remove heavy stains on fabrics [5].

This primary investigation reveals such potential of the 1M HCl – extract from Calamansi leaves in inhibiting the corrosion of mild steel where it explores the efficiency, its kinetics and its adsorption modelling inclination

2. Materials and Methods

2.1 Sample Collection

Mild steel strips were gathered from a mild steel company found in the province of Cebu. Mild steel strips with the least signs of corrosion, determined by physical examination, were purchased. The mild steel strips were cut into coupons with a dimension of 1 inch x 0.75 inch x 1mm each. The samples were polished with emery paper or sand paper and were then pre-weighed.

2.2 Extraction Process of Citrus microcarpa (Calamansi) Leaves

Citrus microcarpa (Calamansi) leaves were obtained from Argao, Cebu, Philippines. Before the collection of extracts, the *Citrus microcarpa* (Calamansi) leaves were air-dried for 2 days to enrich the active principles in them and for faster and easier blending due to absence of water. The presence of water on the leaves was used to determine whether the leaves were ready to be blended or not. The dried leaves were pulverized using a blender. A stock solution was made out of the *Citrus microcarpa* (Calamansi) leaves. Sixty-five (65) grams of the powdered leaves was immersed in 200 mL of 1M HCl. After 3 hours the solution was filtered, placed in a 500 mL volumetric flask, diluted to mark and obtained the concentration of 0.13 g leaves per mL extract. The extraction process of *Citrus microcarpa* (Calamansi) leaves was patterned from the study of Vimala et al. (2011) with slight modifications such as type of extract, extract concentration, and duration of extraction [3].

2.3 Preparation of Solutions

Five (5) different concentrations were used including the control solution. The concentration of leaf extract varied in different beakers in order to compare the effect of the amount of leaf extract on the rate of corrosion of mild steel.

A hundred (100) mL of 1M HCl was prepared in a beaker which will serve as the control solution. Before immersing the mild steel into the final solution or test media, 100 mL of different concentrations of the leaf extract was prepared in different beakers. The different extract concentrations were obtained from the stock solution. Amounts of the stock solution were transferred to different 100 mL volumetric flasks in different volumes and were then diluted up to the mark. Each solution contains a mixture of the extract and HCl with a total volume of 100 mL per solution. The concentrations used were 0.02, 0.04, 0.06, and 0.08 g leaves per 1 mL HCl solution and were chosen accordingly to determine whether there is a significant difference of the values of inhibition efficiency despite the very small difference (0.02-interval) between plant extract concentrations. Each solution was stored in a beaker and was covered with foil.

2.4 Mass Loss Technique

The mass loss technique was patterned from similar methods done by research groups led by Abiola [6, 7, 8]. Before the samples were tested, they were pre-weighed using KERN ABS 120-4 Analytical Balance. These masses were recorded as their initial mass. One (1) sample was immersed in the control solution and the other four (4) samples were immersed in beakers with different concentrations, maintained at ambient temperature of 27 ±1°C. After 48 hours, the samples were taken out from the test solutions and were cleaned based on the ASTM G1 1-90 standard [9]. The samples were immersed in sodium hydroxide solution to prevent further corrosion reactions. The samples were brushed under running water several times to remove products of the corrosion reaction prior to air – drying. The dried samples were then weighed and the mass obtained was recorded as the final mass. After re-weighing, the samples were immersed in the same solutions and were re-weighed every 48 hours for the whole 192 – hour duration. Initial masses and final masses were compared and mass loss of the metal was recorded.

2.5 Data Analysis

Using the data gathered, the inhibition efficiency was calculated. The Equation 1 below was used to calculate inhibition efficiency, % E [10],

$$\%\boldsymbol{E} = \frac{\boldsymbol{\Delta M_c - \Delta M_A}}{\boldsymbol{\Delta M_c}} \boldsymbol{x\ 100} \qquad \text{Equaiton 1}$$

Where ΔM_C is the mass loss of metal immersed in the control solution and ΔM_A is the mass loss of metal immersed in solution with plant material.

Statistical analyses, including the data normalities, were done using Statistical Package for Social Sciences® (SPSS) Statistics under the license of Philippine Science High School – Central Visayas Campus. One-way ANOVA was used to determine the significance of the trends of inhibition efficiency in different concentrations and different contact time with the assumption that the data was normally distributed. It was used to test the significance of the values of the inhibition efficiencies with time and varieties of extract concentration. In cases of violation of assumption of normality, Kruskal-Wallis test was used. Significant values indicate that there is a significant relationship between inhibition efficiencies given different concentrations of extract and between inhibition efficiencies with time in each replicate. Post-hoc analysis was used to test multiple comparisons between variable groups.

Linearity tests were based on the resulting Pearson r correlations for curve fitting models in adsorption isotherms and kinetic rate laws.

3. Results and Discussion

3.1. Mass Loss and Inhibition Efficiency

Difference in the samples' initial and final masses with respect to concentration and time means that corrosion had occurred. Average mass loss of samples immersed in control solution (no inhibitor) is shown in Table 1.

Table 1 Average mass loss, in g, of mild steel at different extract concentrations

Time	Concentration (g/mL)				
(hours)	0.00[a]	0.02[b]	0.04[c]	0.06[d]	0.08[e]
48[f]	0.5984 ± 0.051[a]	0.0398 ± 0.002[a]	0.0315 ± 0.002[a]	0.0241 ± 0.001[a]	0.0209 ± 0.002[a]
96[f]	0.7446 ± 0.05 [a]	0.0356 ± 0.001[a]	0.0283 ± 0.003[a]	0.0222 ± 0.001[a]	0.0193 ± 0.0006[a]
144[f]	0.6124 ± 0.075[a]	0.0374 ± 0.001[a]	0.0289 ± 0.003[a]	0.0239 ± 0.002[a]	0.0217 ± 0.002[a]
192[f]	0.2243 ± 0.053[a]	0.0479 ± 0.010[a]	0.0389 ± 0.002[a]	0.0323 ± 0.002[a]	0.0268 ± 0.001[a]

a – Significance value above 0.05 based on concentration

b,c,d,e – Significance value below 0.05 based on concentration

f – Significance value above 0.05 based on time

As shown in Table 1, the mass loss of mild steel immersed in the control solution tends to decrease because the surface area of the samples immersed in the control solution were observed to decrease distingtively especially after the 192nd hour. Parts of the metal are converted to rust in the process of corrosion which are removed before re-weighing, resulting in a decrease in mass loss. With respect to the control solution, mass loss in all extract concentrations are statistically different (Significance value < 0.05). This means that the leaf extract effectively inhibited corrosion by lowering the mass loss of the steel samples.

Overall, mass loss of each extract concentration over time does not have a significant difference (Significance value > 0.05). With respect to extract concentration, mass loss of samples do have a significant difference (Significance value < 0.05). The results also showed a decrease in mass loss of the *Citrus microcarpa* (Calamansi) leaf extract – treated samples against 1.0 M HCl. From the mass loss of the samples, the inhibition efficiency was derived using Equation 1. Average inhibition efficiencies of samples in different concentrations as contact time increases is shown in Table 2.

Table 2 Average percent inhibition efficiency of samples in different extract concentrations

Time (hours)	Concentration (g/mL)			
	0.02 g/mL	0.04 g/mL	0.06 g/mL	0.08 g/mL
48	93.33 ± 0.578 [a,c]	94.72 ± 0.258 [a,c]	95.96 ± 0.300 [a,d]	96.49 ± 0.478 [a,d]
96	95.25 ± 0.288 [a,c]	96.17 ± 0.652 [a,c]	97.01 ± 0.107 [a,d]	97.40 ± 0.218 [a,d]
144	93.82 ± 0.935 [a,c]	95.21 ± 1.01 [a,c]	96.05 ± 0.687 [a,d]	96.42 ± 0.547 [a,d]
192	77.85 ± 6.495 [b,c]	81.74 ± 5.749 [b,c]	85.05 ± 3.770 [b,d]	87.59 ± 2.887 [b,d]

a – Significance value greater than 0.05 based on time

b – Significance value less than 0.05 based on time

c – Significance value greater than 0.05 based on concentration

d – Significance value less than 0.05 based on concentration

Based on Table 2, inhibition of mild steel with different *Citrus microcarpa* (Calamansi) leaf extract concentrations show positive results in inhibiting the corrosion of mild steel ranging from 70% to 98% inhibition efficiency. However, the inhibition efficiency at extract concentrations 0.02 g/mL have no significant differences with inhibition efficiencies at extract concentrations 0.04 g/mL (Significance Value > 0.05) therefore have relatively similar effectivity in inhibiting corrosion of mild steel. Inhibition efficiencies in concentration 0.02 g/mL are significantly different to the inhibition efficiencies at concentrations 0.06 and 0.08 g/mL (Significance value < 0.05) whereas the inhibition efficiencies between the concentrations 0.06 and 0.08 g/mL have no significant difference (Significance Value > 0.05). This means that their effectivity in inhibiting corrosion of mild steel is relatively similar.

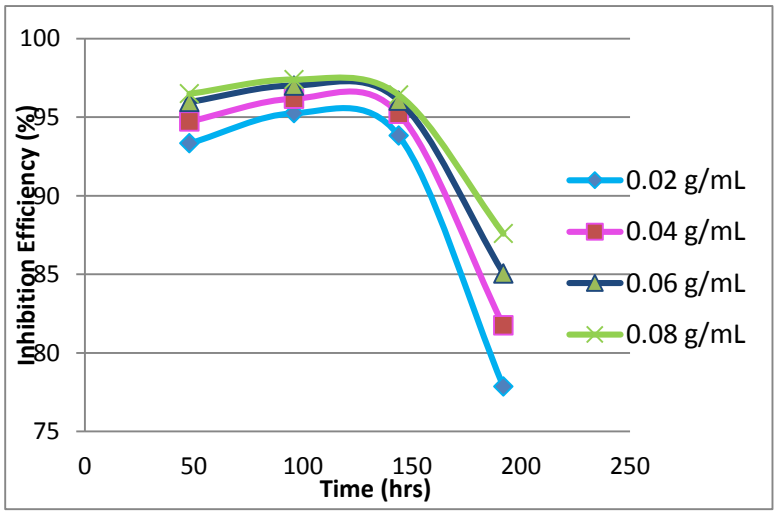

Fig. 1 Inhibition Efficiency versus Time line graph

Figure 1 shows inhibition efficiency decreases as time increases. Inhibition efficiency before the 144th hour at each extract concentration is not significantly different from each other thus having relatively similar effectivity in inhibiting corrosion of mild steel. There is a significant variation in inhibition efficiency after the 144th hour; that as contact time increases, inhibition efficiency decreases significantly.

In this study, the best corrosion inhibition performance for mild steel was observed with 0.06 g/mL extract concentration. Based on statistical analysis, inhibition efficiency increased significantly with extract concentration after 0.04 g/mL and significantly decreased after the 144th hour. The inhibitor gains or loses its effectiveness the longer it is exposed to the corrosive environment during the process of corrosion [13]. In this study, the extract of *Citrus microcarpa* (Calamansi) leaves reduced its effectiveness after 144 hours as contact time increased. This corrosion inhibition trends are similar with other related studies of corrosion inhibitors from biological sources [11, 12, 13].

3.2. Adsorption Isotherm Modelling

The decreased corrosion rate of the *Citrus microcarpa* leaf extract can be attributed to the adsorption of the inhibitor phytochemicals to the mild steel surface. This process produces a good barrier from the attack of oxidizing agents in the aqueous solution. This is possible due to the presence of various high molecular weight compounds like tannins, flavonoids, and phenolic compounds that contains many heteroatoms like oxygen, nitrogen and sulfur that are capable of forming multiple bonds available for attachment to the mild steel surface [14]. The inhibition efficiencies were used to generate the corresponding degree surface coverage, θ, of different extract concentrations at each contact time given this relationship [6]:

$$\boldsymbol{\theta = \frac{\%E}{100}} \qquad \text{Equation 2}$$

This θ parameter, along with the extract concentration, C, were used to produce a curve fitting linear graphs for the 2 common adsorption isotherm models: the Langmuir and Freundlich models [15, 16]. Both graphs show a very high correlation with all of their corresponding Pearson R^2 values greater than 0.99 (as shown in Figure 2 and Figure 3). These are suggestive that the adsorption mechanism of the extracts to the mild steel follows both of these adsorption models. Also, these good correlations manifest that the adsorption process is generally chemisorption, wherein strong attracting interactions mainly involved stronger perturbation of the molecular electronic structure with formation of chemical bonds with the metal.

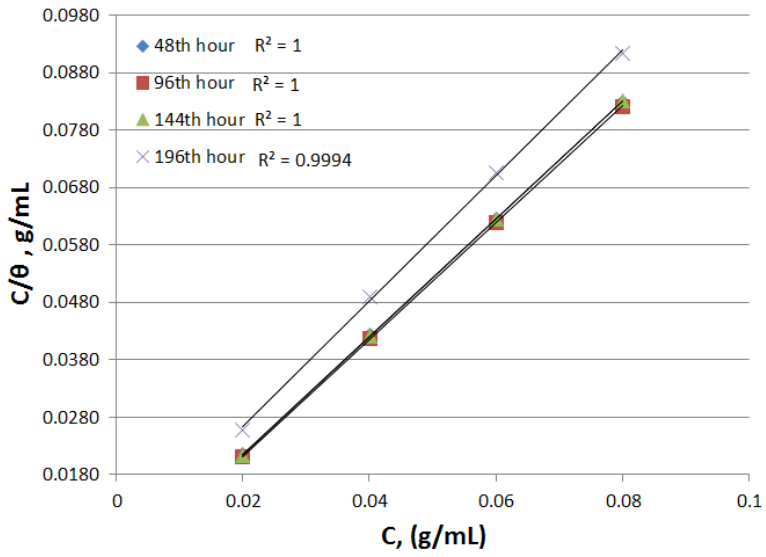

Fig. 2 Langmuir adsorption plots of mild steel in 1M HCl medium with different *Citrus microcarpa* extract concentrations at 27 ±1°C.

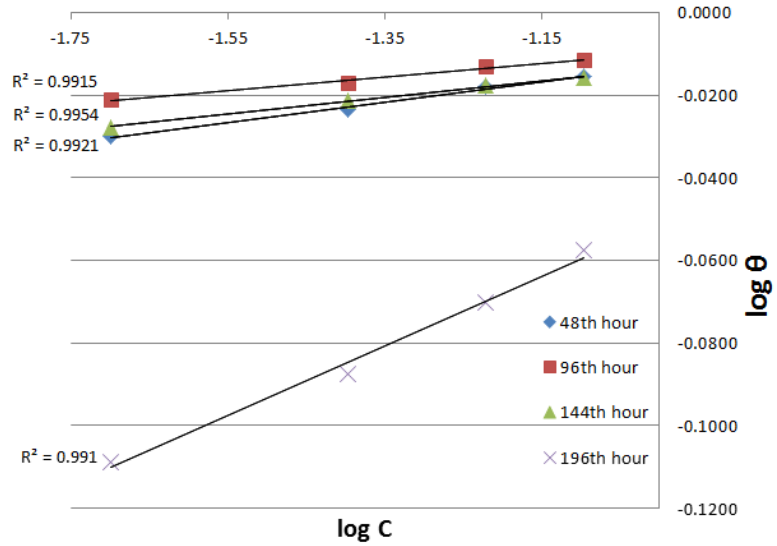

Fig. 3: Freundlich adsorption plots of mild steel in 1M HCl medium with different *Citrus microcarpa* extract concentrations at 27 ±1°C.

3.3 Kinetics Considerations

The dependence of the corrosion process with time was evaluated under ambient temperature by fitting a corrosion data into different known kinetic rate laws: namely zero – order, first – order and second – order rate laws. The resulting linear correlation coefficients, R^2, were used to determine the best rate law for the mild steel corrosion.

The corrosion data was determined to fit best in the zero – order reaction rate law with given equation [17]:

$$M_f = -\frac{k}{2.303}t + M_i \quad \text{Equation 3}$$

where M_f is the residual mass (in g) of the mild steel coupon at time, t (in hours); M_i is the initial mass (in g) of the mild steel coupon before immersion and k is the first – order constant.

The R^2 (as shown in Figure 3) for both control solution and with different extract concentrations were greater than 0.99 that is suggestive of the direct proportionality of the residual mild steel left uncorroded with respect to time. The linearity of the curves in the absence and presence of the extract implies that its presence does not change the kinetics of the corrosion reaction though it significantly reduces its rate as presented in Table 1 [6]. This zero – order kinetics process verification is in agreement with other mild steel corrosion inhibition studies done by group of Obot and Musa [18, 19].

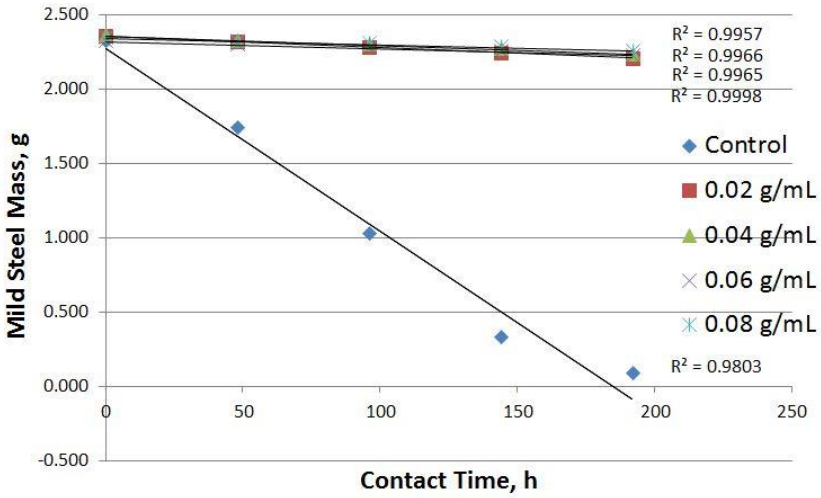

Fig. 3 Variation of mild steel masses immersed in 1M HCl with and without *Citrus microcarpa* leaf extract solutions at different contact time.

4. Conclusion

This study aimed to determine the potential of *Citrus microcarpa* (Calamansi) leaves in inhibiting the corrosion of mild steel through mass loss method with these significant results and conclusion:

- The results showed a significant increase in inhibition efficiency to extract concentration after 0.04 g/mL extract concentration with increasing concentration and a significant decrease in inhibition efficiency to time of immersion after the 144th hour.
- In this experiment, solution with 0.08 g/mL concentration of Citrus microcarpa (Calamansi) showed the highest potential in inhibiting the corrosion of mild steel with 97.40±0.218% inhibition efficiency.
- When immersed in *Citrus microcarpa* (Calamansi) leaf HCl-extract, rate of corrosion of mild steel was reduced.
- Curve fitting modelling of the corrosion data reveals that the adsorption process obeys both Langmuir and Freundlich adsorption isotherm and its rate law follows zero – order kinetics.

- Based on the results, it can be concluded that *Citrus microcarpa* (Calamansi) leaf extract has the potential to inhibit corrosion.

Acknowledgments

The researchers would like to thank the Philippine Science High School – Central Visayas Campus and family for the wholesome and admirable support given to them.

References

[1] Phatak, O. (2011). Mild Steel Properties http://www.buzzle.com/articles/mild-steel/properties.html
[2] Nimmo, B., Hinds, G. (2003). Beginners Guide to Corrosion
[3] Vimala, J.R., Rose, A.L., Raja, S., Cassia auriculata extract as corrosion inhibitor for mild steel in acid medium. Int.J. ChemTech Res. 3 (2011) 4
[4] Stuart, G., Santiago, A.S., Flores, M.L.S. (2012). Philippine Medical Plants: Kalamansi http://www.stuartxchange.com/Kalamansi.html
[5] Lyles, M. (2009). Calamansi, a great citrus fruit to know and grow http://www.examiner.com/article/calamansi-a-great-citrus-fruit-to-know-and-grow
[6] Abiola, O. K., Aliyu, A.O.C., Phillips, A.A. , Ogunsipe, A.O., J. Mater. Environ. Sci. 4 (2013) 3
[7] Abiola, O. K., Otaigbe, J. O. E., Corros. Sci. 51 (2009) 2790.
[8] Abiola, O. K., Oforka, N. C., Angaye, S. S., Materials Letters 58 (2004) 3461.
[9] ASTM. (1999). "Standard practice for preparing, cleaning, and evaluating corrosion test specimens." ASTM G 1-90, West Conshohocken, Pa.
[10]James, A.O., Akaranta, O., Res.J.Chem.Sci. 1 (2011) 1
[11]Loto, C.A., Loto, R.T., Popoola, A.P.I., Int. J. Phys. Sci.Vol. 6 (2011) 15
[12]Hasan, S.K., Sisodia, P., RASAYAN J. Chem. 4 (2011) 3
[13]Kesavan, D., Gopiraman M., Sulochana N., Che Sci Rev Lett 1 (2012) 1
[14]Kawaii, S., Tomono, Y., Katase, E., Ogawa, K., Yano, M., Koizum, M., Ito, C., and Furukawa, H., J. Agric. Food Chem. 48 (2000) 9
[15]Freundlich, H., J. Z Phys. Chem. 57 (1906) 385
[16]Langmuir, I., J. Am. Chem. Soc. 40 (1918) 1361
[17]Brown, T.L., Lemay, Jr., H.E., Bursten, B.E., Burdge, J.R. (2004) Chemistry: The Central Science. Pearson Education Inc.
[18]Obot, I.B., Obi-Egbedi, N.O., Odozi, N.W., Corros. Sci. 52 (2010) 3
[19]Musa, A. Y. , Khadom, A. A. , Kadhum A. A. H. , Mohamad, A. B. , Takriff, M.S.,Journal of the Taiwan Institute of Chemical Engineers 41 (2010) 1