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A NOVEL ALTERNATIVE ETCHANT FOR MILD STEEL USING VALENCIA ORANGE (*Citrus sinensis*) PEEL EXTRACT

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ABSTRACT

Etching potential of Valencia orange peel extracts (VOPE) on mild steel was investigated using one-step etching process method. The etchant was extracted through solid state fermentation (SSF) method and 1 liter of crude extract was obtained. Water was extracted from the crude extract to make it anhydrous and 8g/ litre of anhydrous solid crude removed VOPE was obtained. The etchant organic contents were determined using volumetric acid-base titration method which confirmed the predominant presence of citric acid as the major organic acid contained in the crude extract VOPE with 78% / litre of extract (VOPE) produced in weight percent (wt%) concentration. The etching performance of crude extract (VOPE) on mild steel was studied using two level (2^2) factorial Design. The metallography of mild steel was carried out using 2.5% concentration of crude extract VOPE etchant and 2 minutes etching time was used which gives the best positive yield. The result of microstructures reveals that: newly produced and developed organic etchant VOPE gives better quality of microstructures than the conventional mild steel etchant of Nital solution.

Keywords: Mild steel; Etchant; Orange peel extract; Citric acid; Microstructure

1.0 INTRODUCTION

Valencia Orange (*Citrus sinensis*) (VO) is a common fruit (Li *et al.,* 2013). It is well known and consumed locally as food/juice. The world citrus production was estimated at 89 million tons in 2014 and the amount of world industrial waste of citrus is estimated to be 15million tons. (M'hiri*etal.,* 2015). Citrus is the most abundant crop of fruit trees in the world, with an annual production of approximately 115.5 million tons, among which the most important are oranges (70.6 million tons) (Marey and Shoughy, 2016), and citrus can be used to generate several value added products such as the organic acids mentioned, among others. It was earlier reported by some researchers that citric acid is contained in plant extracts. Amenaghawon *et al.* (2017) extracted citric acid from yam peel and obtained 66 grams per litre of citric acid concentration by using solid state fermentation (SSF) method.

It was earlier reported by Erukainure *et al.* (2016) that orange peel contained predominance of citric acid, fatty acid methyl Esters in hexane extract, and that it also contains soluble sugar, proteins and minerals from fatty acid methyl Esters.

Torado *et al.* (2011) extracted citric acid from orange peel using solid state fermentation (SSF) method and obtained large quantities of citric acid amounting to 193.2 mg/g dry orange peel. In their findings orange peel also contains simple sugars such as: glucose, fructose, sucrose and galacturonic acid.

Extracts from plants may be better corrosion facilitators as etchants due to low cost of production and availability. In this present work, we report Valencia Orange (*Citrus sinensis*) peel Extracts (VOPE) as an efficient corrosion facilitator or etchant for low carbon steel.

Li *et al.* (2013) also identified orange peel extracts among four common vegetal biomasses and it was affirmed by Jamil *et al.* (2015) that orange contains citric acid and Forcas *et al.* (2015) reported that a

smaller number of fatty acids are contained in orange fruits.

The most commonly used etchants for steel are hydrochloric acid (HCl), and Nitric acid (HNO_3) diluted with distilled/deionized water and the reactants ratiowere reported as follows:1ml.cc.HCl + 3ml.cc.HNO_3 + 1ml of glycerol (Oyetunji*et al.,* 2013); 10ml.cc.Hcl + 3ml.ccHNO_3 + 100ml.dist.H_2O (Tunimu*et al.*,2013); 10ml.cc.HCl + 10ml.cc.HNO_3 + 80ml.dist.H_2O. (Muhammad *et al.,* 2016); 10g$CuSO_4$ + 50ml.HCl + 50ml.H_2O (Roy *et al.,* 2014); acetic glyceregia15ml.HCl +10mlHNO_3 Nitric acid HNO_3 +10ml ethanol + 2drop.glycerol (Roy *et al.,* 2014); 3mlHCl +2ml nitric acid + 2ml.accetic acid (Reddy *et al.,* 2014); Marble's reagents. 10g $CuSO_4$ + 50ml HCl + 50ml dist.H_2O (Mishra *et al.,* 2014); Marble's reagents 15mlHCl + 10ml HNO_3 + 10ml ethanol (Mishra *et al.,* 2014). However, the above mentioned chemical and inorganic reagents are dangerous and injurious to human health (Schorr and Valdez, 2016). It is observed also that all these inorganic chemical reagents are expensive and the processing routes are costly (Radwan*et al.*, 2018). Therefore, the choice of Valencia orange peel extracts (VOPE) as an etchant is due to its low cost of production and easy processing route.

2.0 METALLOGRAPHY

Ji *et al.*(2011) have observed that metals and alloys react with corrosive media to form stable compounds and metal or alloy surfaces get corroded. In this process, oxides of metals or alloys are formed as stable compounds. Etching process in metallography is a mechanism of corrosion; therefore, it should be performed on steel so that it may be subjected to microscopy examination to reveal the different phases and surface morphologies of metals and alloys, during metallurgical inspection and tests on materials to ensure quality control before steel products are supplied to meet the high demands in the market. (Kumar *et al.,* 2018).

2.1 Etchants used for Mild Steel

Nital solution is made up of Nitric acid and distilled water or ethanol for mild steel and reported as:

5% cc Nitric acid HNO_3 + 95% dist. H_2O (Reddy *et al.,* 2014); 70% Nitric acid HNO_3 + 30% dist. H_2O (Moslemi*et al.,* 2015); 2% of nital solution was used by Kong *et al.* (2014); 3% of Nitric acid was used (Pikalite*et al.,* 2015); 2% of Nital solution was used by Bouzouni and Papae*et al*, (2017); 6% cone. $FeCl_3$ + 18% cone HCl, 10g oxalic acid + 100ml distil H_2O (Tabish*et al.,* 2014).

2.1.1 Etching

Etching in metallography is a corrosion mechanism. El-Lateef *et al.* (2015) pointed out that corrosion occurs on low carbon steel exposed to acidic medium. Etching process may be one-step (swabbing) or multiple (immersion) process (Herenio*et al.,* 2011), (Tamadon*et al.,* 2016) and (Ye *et al.,* 2009). In this research work, one-step (swabbing) process was used.

Cao *et al.* (2015) reported etching process by using dark field mask method in the fabrication of TaN thin film resistors applied in microwave circuits. In their findings there was a problem of narrow alignment window of optical microscopy which resulted in inconsistency and poor yield.

Clark *et al.* (2009) reported: aqueous etching that produces Si (100) surfaces near atomic flatness, at room temperature. The result shows that no contrast of surface morphology was observed after microscopy. Huang *et al.* (2011) present anisotropic and isotropic etching behaviour of Si under various conditions. Tamadon *et al.* (2017) developed a vibrant non organic etchant which improved the microstructures of the substrate used.

2.2 Mild Steel

The Mild steel used has chemical composition as shown in Table 1 (Ji *et al.,* 2011).

Table 1: The chemical composition of mild steel

Elements	Fc	C	Si	P	Mn	S	Al
% in mass	99.21	0.21	0.38	0.08	0.05	0.05	0.01

(Belkaid*et al.,* 2012).

3.0 MATERIALS AND METHODS

Orange (*Citrus sinensis*) peels were collected from a local fruit seller in the Federal University of Technology, Minna Niger State, Nigeria, and were the source of the citric acid used as etchant in this experimental research work. The peels were washed with deionized water to remove dirts and keep free of germs and sundried for two days under weather temperature of 34^0C for day 1 and 39^0C for day 2. The dried peels were then ground to fine particle size 0.05µm, and 567g of the particles were obtained.

3.1 The Sieve Analysis of the Particles

The particle size analysis of the orange (*Citrus geines*) peel particles was carried out in accordance with B51377.1990 (Chira*et al.,* 2014) by using British Standard sieve of BSS particles; 567g obtained after milling was placed unto a set of sieves arranged in descending order of fineness and shaken for 15minutes which is the recommended time to achieve complete classification (Chira *et al.,* 2014). The particles that were retained in the BSS 0.05µm(VOPE) were used in this experimental work.

3.2 Microorganism

Aspergillusniger used for this work was isolated from soil obtained from Federal University of Technology, Minna, and was used throughout the research as an organism used for solid state fermentation and Potatoe dextrose was prepared with deionized water.

3.3 Inoculum Preparation

Spore inoculums were prepared by using potatoe dextrose broth with deionized water and shaking vigorously for seconds. The potatoe dextrose again was sterilized at 100^0C by the use of autoclave machine for 20 minutes and cultured for 48hours at 25^0C, to obtain maximum spore production.

3.4 Culture of Organism

The Aspergillus Niger isolated from soil was transferred in to the slant of cultured potatoe dextrose agar and further cultured for 72 hours at 28^0C. The grown Aspergillus niger was then dissolved in deionized water, lightening the environment by the use of burnsen burner to prevent the presence of any organisms, so as to leave only Aspergillus niger alone in the slant domain.

The Aspergillus niger in deionized water was shaken vigorously for seconds and also sterilized in autoclave machine at 120^0C for 20minutes and then cooled to room temperature.

3.5 Solid State Fermentation

Dried and milled sample of orange peel with particle size of 0.05µm were dispensed into 250ml Erlenmeyer flask as described by Torado *et al.* (2011); Amenaghawon *et al.* (2017) and mixed with dissolved, cultured and autoclaved Aspergillus niger as it was also used by Dienye *et al.*(2018) in deionized water in the ratio of weight in grams of the substrate to twice the volume of digester (Aspergillus niger in deionized water) without any additional nutrients. The contents were thoroughly mixed and centrifuged at 3,500 rpm for 30minutes at room temperature to enhance proper separation of peels and solution. The supernatants were collected by decanting it out of the centrifuge tubes and transferred in to a round bottom flask for keeping.

3.6 Extraction of Water from the Crude Extract

Water was extracted from the crude extract by the use of thermostatic water cabinet model HH-W600.

The crude extract (VOPE) was put inside a 250ml capacity beaker and weighed in an electronic digital weighing balance.

The extract was placed on the thermostatic water cabinet in order to extract the water in

it by heating it to a temperature of 90^0C. The crude extract (VOPE) is a monohydrate crystals from cold aqueous solution which loses its water of crystallization in a dry air or when heated at about 40-50^0C (this was observed during the experiment). The following is the summary of the extraction of the water content from the crude extract (VOPE).

W_{t1} = Initial weight of the crude extract (VOPE) = 1 litre = 1000g
Wt_2=Weight after 3hrs = 120g
Wt_3=After heating for 4hrs, 30 mins, = 78g
Wt_4=After heating for 7hrs, 30mins = 36g
Wt_5=After heating for 9hrs, 30mins = 18g
Wt_6=After heating for 11hrs = 8g
Wt_7=After heating for 12hrs, 30mins = 8g
The heating was stopped after heating for 12hrs, 30mins as constant 8g/litre of the crude extract (VOPE) was maintained. Anhydrous crude extract (VOPE) was obtained for keep.

3.7 Safety and Storage

It was observed during the laboratory experiments that storage of diluted citric acid is not advisable due to the presence of Aspergillus niger organism which can still be grown in the liquid extract, therefore it is recommended to extract water from the liquid extract VOPE etchant to enable it to be stored for so many years and it is very safe in this condition.

3.8 Determination of citric acid in the crude extract of (VOPE) by volumetric titration method

The concentration of citric acid in weight percent (wt%) in the solution of crude extract of (VOPE) was determined using volumetric titration method. The IUPAC name is 2-oxidopopane-1,2,3-tricarbodylic acid. The citric acid titration method is user-friendly, inexpensive, water soluble and crystalline solid carboxylic acid, using solid citric acid and its solution in water, is safer and more convenient (David, 2014).

Some other authors determined citric acid by volumetric titration method Chen *et al.* (2018), Saha*et al.* (2015), LiszKowska*et al.* (2015), Gupta *et al.* (2014), Kelebk*et al.* (2009), Tran and Farid (2004) and Chen *et al.* (2003).

3.9 Apparatus used

Top loading digital balance, sufficient volume of 0.1M Nant solution, and sufficient 8g of crude extract (VOPE). Sufficient volume of phenolphthalein indicator in a small labelled dropper bottle, 123ml Erlenmeyer flasks, 10ml of automatic pipet manufactured by: Lab world, 100ml conical flasks, distilled water in a polymer small bottle, water basin made of ceramic installed for laboratory purpose.

3.10 Preparation

Due to the appearance amber colour of the crude extract (VOPE) which is too deep and not distinct colourless of citric acid in its isolated state and this may affect the titration experiment, therefore, 0.1g of crude extract were dissolved in 1ml of distilled water and then add 9ml of water to make up of 10ml of extract, as reported by David, (2014).

3.11 Procedure

10ml of extract was titrated against 0.1M sodium hydroxide (NaOH) solution. Volumetric titration procedures and methods of titration of David, (2014) was employed in this study.

3.12 Experimental Design

The effect of etchant at certain concentration in percent (%) of aqueous solution of extract (citric acid as a major component) on mild steel and time of etching in (minutes) was studied, by means of a two level factorial design (the 2^2Factorial Design).

In this design, only two factors A and B are used, each run at two levels. A denotes reactant concentration of etchant of extract (citric acid) at low (1.5%) and at high (2.5%) and B is etching time at low (1 minute) and at high (2minutes).

3.13 Factorial Design using 2^2

The 2^2 factorial design in a standard order matrix are presented in Table 2.

Table 2: Factorial design in a standard order matrix.

Factor		Treatment
A	B	Combination
–	–	A low, B low
+	–	A high, B low
–	+	A low, B high

3.14 Level of factors

Table 3 presents the level of the factors used in studying the effect of crude extract (VOPE) as etchant and time of etching of mild steel.

Table 3: Level of factors used.

	Factor	Factor
Level	A	B
	Etchant (%)	Etching Time (Min.)
Low (-)	1.5	1
High (+)	2.5	2

3.15 Estimation of main effects and interaction effects

The estimate of main effect A and B and interactions effect AB are presented in Table 4.

3.16 Estimation of factor effects

The estimate of factor A and B in order to validate the main effects and interaction effects are presented in Table 4. In this design, the metallographic experiment is run for three times which is the number of replicates.

Let y represent (data value) the average number of grains at 100x/mm^2 counted per view of microstructure.

y_{11} = 1st experiment and the 1st value recorded

y_{12} = 1st experiment and the 2nd value recorded

y_{12} = 1st experiment and the 3rd value recorded

This is continued until 3 x 5 matrix replicate y is obtained as thus:

$$\begin{pmatrix} y_{11} & y_{12} & y_{13} \\ y_{21} & y_{22} & y_{23} \\ y_{31} & y_{32} & y_{33} \\ y_{41} & y_{42} & y_{43} \\ y_{51} & y_{52} & y_{53} \end{pmatrix} \begin{Bmatrix} y_1 \\ y_2 \\ y_3. \\ y_4 \\ y_5 \end{Bmatrix} = \begin{matrix} \bar{y}_1 \\ \bar{y}_2 \\ \bar{y}_3 \\ \bar{y}_4 \\ \bar{y}_5 \end{matrix}$$

Let $y_1.$, $y_2.$, $y_3.$, $y_4.$and$y_5.$ represent the total number of grains at 100x/mm^2 in each run.

$\bar{y}_1$, $\bar{y}_2$, $\bar{y}_3$…… $\bar{y}_5$ represent average number of grains at 100x/mm^2 in each run.

Table 4: Estimation of main effect A and B and interaction AB

Treatment Combination	Effect of factors 1	A	B	AB
(1)	+	–	–	+
a	+	+	–	–
b	+	–	+	–

Table 5: The estimation of factor effects with n replicates.

Run	Factor A	Factor B	Treatment Combination	Replicate Number of grains At 100x/mm^2 I	II	III	Total Number of grains at 100x/mm^2	Average Number of grains at 100x/mm^2
1	Control		Nil	y_{11}	y_{12}	y_{13}	$y_{1.}$	y_1
2	_	_	A low, B low	y_{21}	y_{22}	y_{23}	$y_{2.}$	y_2
3.	+	_	A high, B low	y_{31}	y_{32}	y_{33}	$y_{3.}$	y_3
4.	_	+	A low, B high	y_{41}	y_{42}	y_{43}	$y_{4.}$	y_4
5.	+	+	A high, B high	y_{51}	y_{52}	y_{53}	$y_{5.}$	y_5

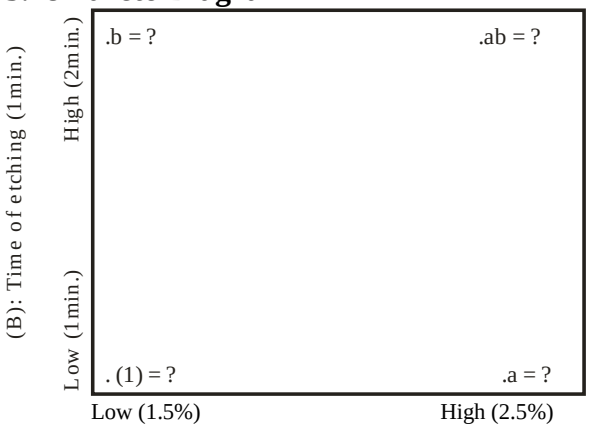
Low (1.5%) High (2.5%) (A): concentration (%) of extract

3.17 Coded Treatment Combination of the two factors A and B

Based on the formulated and experimental design of the estimated factors effect in table 5 above, in order to be easy for us to summarize the result obtained from experimental design in table 5 above by Pareto diagram, we therefore coded treatment combination of the two factors A and B as thus:

.a = A at high level, B at low level
.b = Both A and B at high level
. (1) = Both A and B at low level
.b = A at low level, B at high level.

3.18 Pareto Diagram



(A): concentration (%) of etchant

Figure: Pareto diagram of 2^2 experimental design

3.19 Metallography

Micro-structure examination was first carried out on the standard specimen AMS H_3 produced by metallurgical services, Betchworth, Surrey-England. Grinding of the standard sample was carried out using paper grit of sic of different grades ranges from 220-800 grit. The polishing of sample by the use of emery clothe with alumina and water were carried out in a rotating polishing machine disc.

The polished samples were etched by 1.5% of crude extract VOPE and for 1min and 2.5% for 2minutes according to the experimental design use in this study. The etched standard sample was examined using optical reflected microscope, and the number of grains at100x/mm$_2$ per view of microstructure were counted.

4.0 RESULTS AND DISCUSSION

4.1 Determination of citric acid in a crude extract VOPE by titration method Observation

It was observed that an amber colour of crude extract VOPE changed to red colour which persists for two minutes. Citric acid contained in the crude of extract VOPE was confirmed.

From the observation and inference of the test, it validates the presence of citric acid

in the extract VOP, although, other acid or compounds may be present in the extract as earlier reported in the literature

Table 6: Titre value of 0.1M Na0H against citric acid contained in extract

Trial	Titrated Na0H Volume (ml)
1.	4.67
2.	4.66
3.	4.67 →
Average Titre value	4.67

Chemical reaction of citric acid and NaOH solu. Equation of reaction.

$C_6H_8O_{7(aq)} + 3NaOH_{(aq)} = C_6H_5Na_{3(aq)} + H_2O$ (l)

From balancing eqn, above,

1mole of citric acid = 3 moles of Na0H solu.

:. Amount of citric acid (moles) = 3 x amount of Na0H (moles)

(i) Amount of known reagent 0.1MNa0H (moles)

= volume of Na0H at titre point x moles oh Na0H used for titration

= 4.67ml x 0.1 = 0.467mol Na0H

(ii) Amount of unknown reagent citric acid (moles)

(iii) Mass in grams of citric acid/litre of extract VOPE

= density of citric acid x titre

Density of anhydrous citric acid is 1.665 (Anders *et al.*, 2014; Apelblat, = 3 x amount of Na0H (moles)

= 1.401mol citric acid

2014;Kesha*et al.*, 2012;Kanniah*et al.*, 2012; Telxeira*et al.*, 2012)

= 1.665 x 4.67 = 7.776

= 7.8g of citric acid/litre of extract

= 8g/litre citric acid of extract VOPE which the same with 8g/litre of anhydrous extract.

(w) Weight percent (wt %) of citric acid/litre of extract obtained in extraction of H_2O above.

$$= \frac{\text{density of citric acid x titreX 100\%}}{\text{10ml of extract VOPE}}$$

$$= \frac{1.665x4.67 \text{ x } 4.67 \text{ X } 100\%}{10} = 77.76 = 77.76\%$$

citric acid/litre of extract VOPE

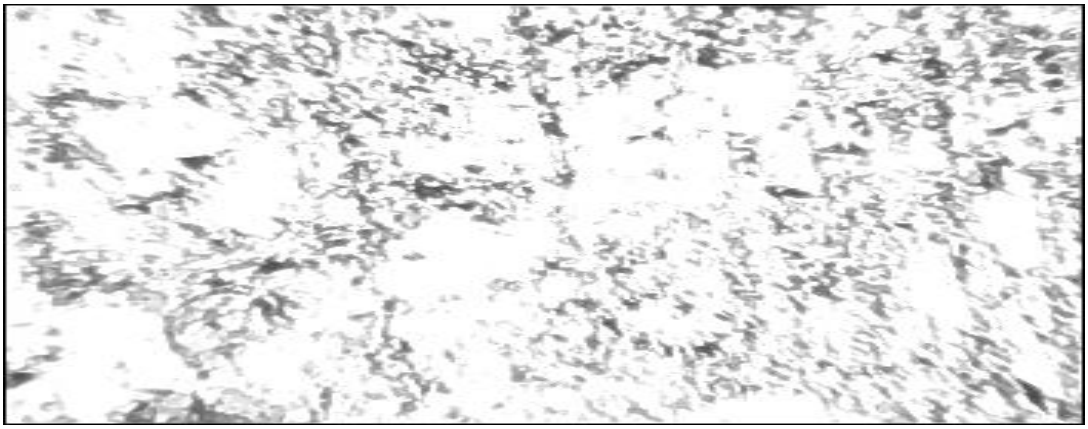
This confirmed that the extract VOPE contained 77.8% of citric acid/litre of extract VOPE

Approximately 8g of citric acid/litre of extract was obtained by volumetric titration test which is the same value of 8g of citric acid obtained in the end when water is being extracted from diluted 1litre of extract obtained from solid state fermentation (SSF), by this, we deduced the concentration of citric acid in g/litre obtained when water is extracted after (SSF) is equal to the concentration of citric acid in g/litre obtained by the volumetric titration method.

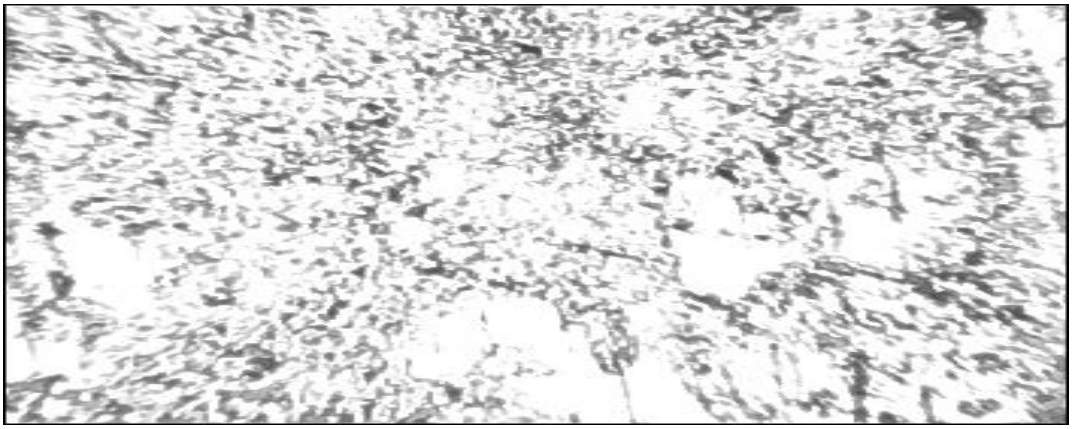
Table 7: Summary of the results of concentration in moles of citric acid against Na0H solution

Trial	**Titrated Na0H Volume (ml)**	**Na0H amount (mol)**	**Citric acid amount (mol)**
1	4.67	0.467	1.401
2.	4.66	0.466	1.398
3	4.67	0.467	1.401
Average values	4.67	0.467	1.40

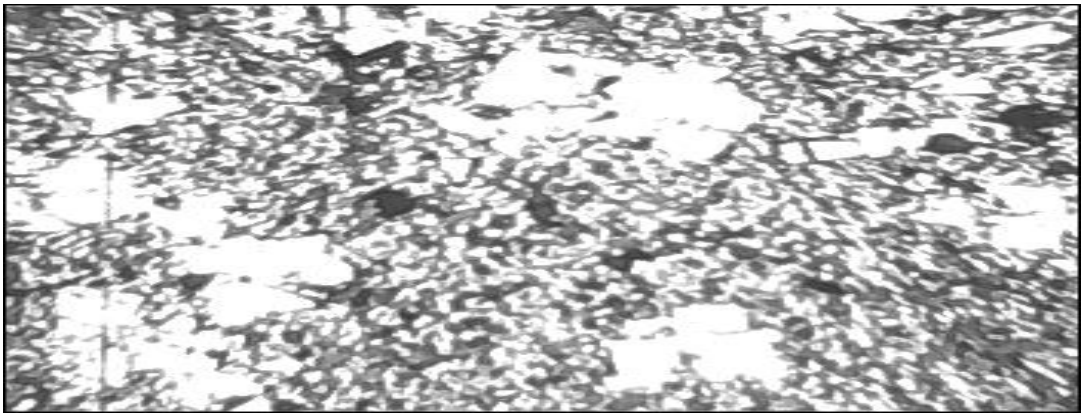
4.2 Microstructures of AMS H_3 revealed by Nital solution and VOPE etchant



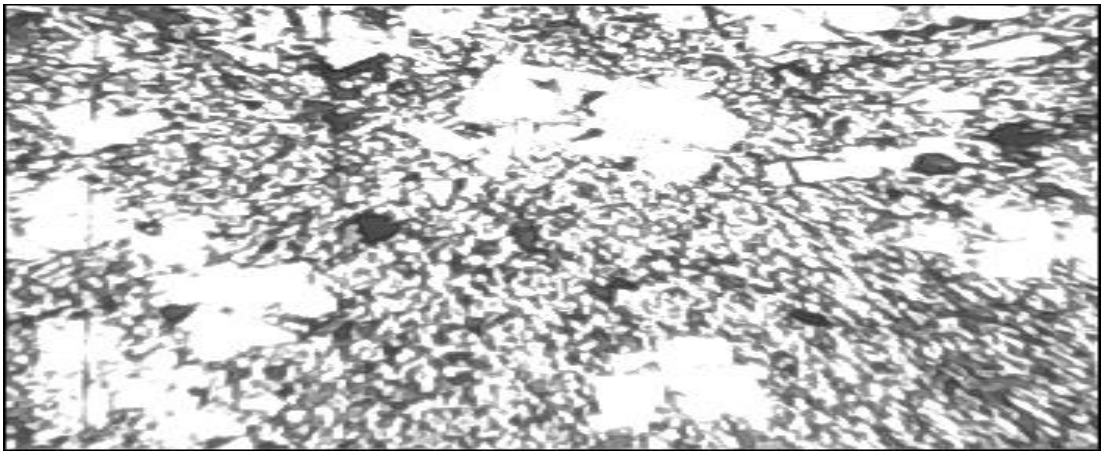
ASM H_3Standard sample etched in 2mol HNo3 + 100mol Ethanol (Nital solution) under 100X for 5 minutes,(run 1).



ASM H_3Standard sample etched in 2mol HNo3 + 100mol Ethanol (Nital solution), under 100X for 5 minutes, (run 2).

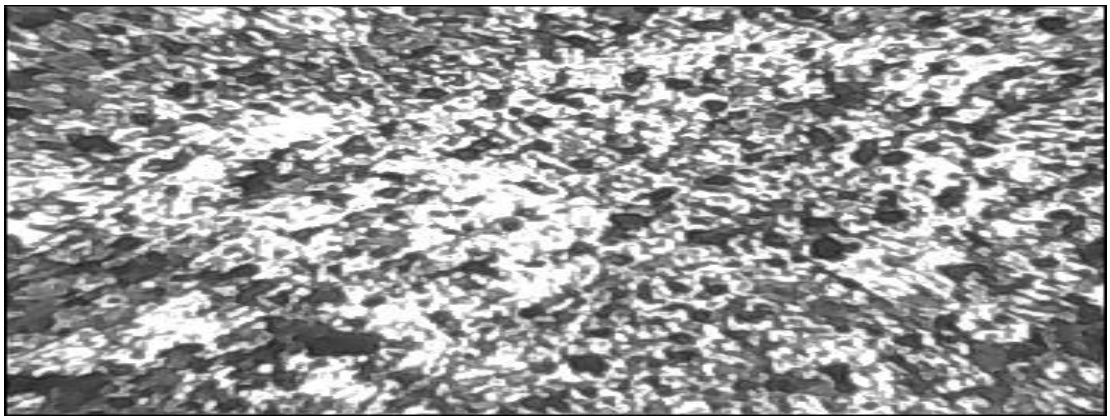


ASM H_3Standard sample etched in 2mol HNo3 + 100mol Ethanol (Nital solution), under 100X for 5 minutes, (run 3)

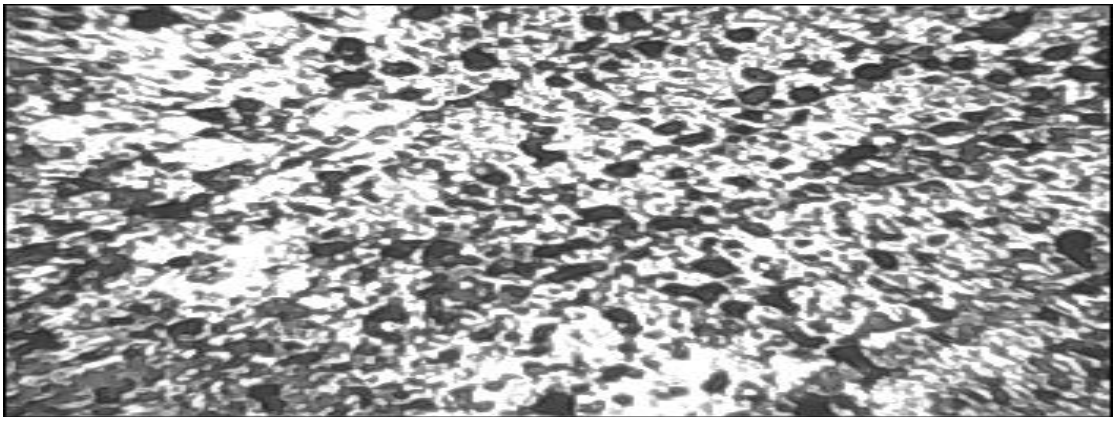


A high, B low (A 2.5, B 1min) for replicate II, ASM H_3etched in (VOPE solution) Screened through Centrifuge after culture, 100X

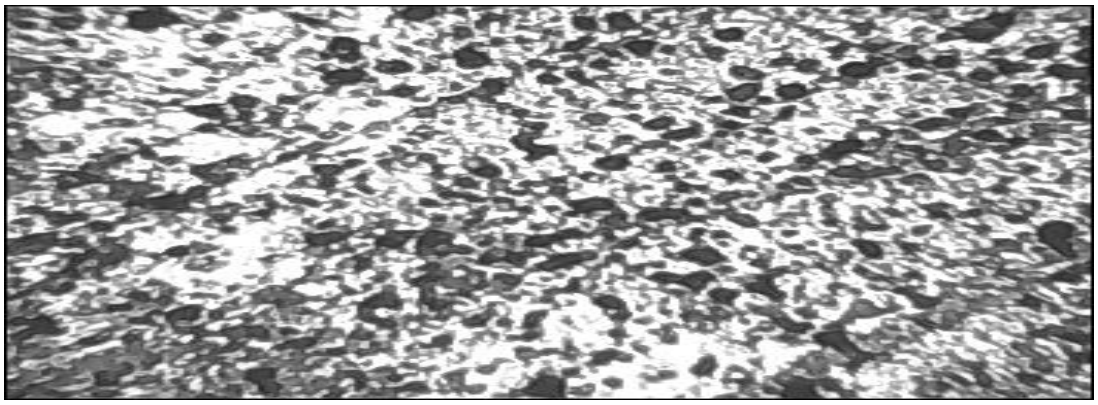
A high, B low (A 2.5, B 1min) for replicate III, ASM H_3etched in (VOPE solution) Screened through Centrifuge after culture, 100X



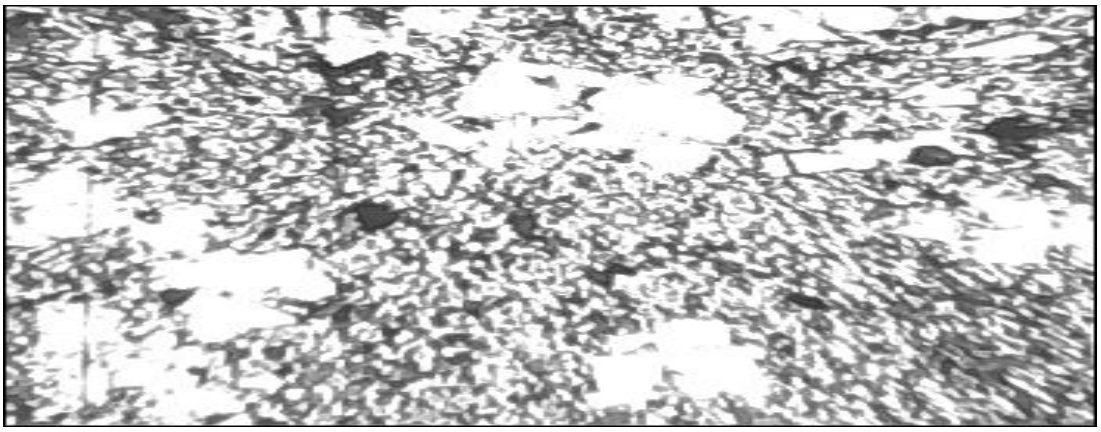
A high, B high (A 2.5, B 2min) for replicate I, ASM H_3etched in (VOPE solution) Screened through Centrifuge after culture, 100X



A *high, B high (A 2.5, B 2min) for replicate II, ASM H₃etched in (VOPE solution) Screened through Centrifuge after culture, 100X*



A high, B high (A 2.5, B 2min) for replicate III, ASM H₃etched in (VOPE solution) Screened through Centrifuge after culture, 100X



A high, B low (A 2.5, B 1min) for replicate I, ASM H₃etched in (VOPE solution) Screened through Centrifuge after culture, 100X

Thus, 8g of $C_6H_8O_{7(aq)}$ after H_2O extraction yields 8g of $C_6H_8O_{7(aq)}$ by the titration method.

The titration test also confirmed that citric acid $C_6H_8O_{7(aq)}$ is the major acid or compound present in the crude extract.

VOPE having revealing 77.76% by weight percent (wt %) concentration of citric acid per litre of crude extract Microstructure reveals that it is steel that has undergone homogenization heat treatment. Specimens were heated to a high austenitic temperature of about 1000^0C for at least 2hrs and then air cooled.

Table8: Average number of grains at 100x/mm^2 counted per view of microstructure

Run	Factor A	Factor B	Treatment Combination	Replicate Number of grains At 100x/mm^2 I	II	III	Total Number of grains at 100x/mm^2	Average Number of grains at 100x/mm^2
1	Control		O	61	83	85	229	76
2	_	_	A low, B low	43	35	24	102	34
3.	+	_	A high, B low	75	73	63	211	70
4.	_	+	A low, B high	17	20	20	57	19
5.	+	+	A high, B high	103	98	100	301	100

They were then reheated to a lower temperature of 900^{0}C and cooled and reheated again to 650^{0}C and air cooled. Then finally they were tempered in a Furnace at a very low temperature of 300^{0}C. Microstructure reveals austenite (white) and martensite (dark)

4.3 Average number of grains at 100 x /mm^2 counted

The experiment is replicated three times, which presents the average numbers of grains at 100 x/mm^2 in a microstructure of ASM H_3 mild steel standard sample.

4.4 Pareto Diagram

Pareto Diagram, in Figure 2 .below was used to summarize the result of 2^2 factorial experiment

Pareto Diagram

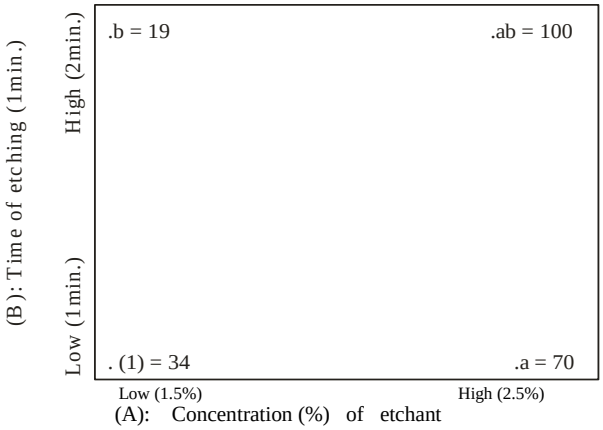


Figure 2:Pareto diagram of data 2^2 factorial experiment on number of grains at 100x/mm^2 counted per view of microstructure of a standard sample AMS of mild steel

Pareto Diagram in Figure 2 below used to summarize the result of a 2^2 factorial experiment performed in table 8 .above in a graphical manner

From the Pareto diagram, the effect of factor A is positive: increasing concentration of etchant extract from low (1.5%) to high (2.5%) increases the yield. More surface morphology of the substrate (mild steel etched) revealed the best microstructures with the highest quality and quantity of an average number of grains at 100x/mm^2 per view of microstructure. The effect of factor B is also positive: increasing the etching time from (1 minute) to (2 minutes) increases the yield. From microstructures revealed in this work, the best microstructure with the highest number of grains at 100x/mm^2 per view of microstructure was produced by (2.5%) concentration of etchant crude extract VOPE with (2 minutes) etching time. The treatment combination (.ab) at high (.1) concentration at (2.5%) etchant of crude extract and etched for (2 minutes) produced the best metallography with highest number of grains at 100x/mm^2 per view of microstructure which is 100 number of grains. The result obtained in this work reveals that: the control standard sample etched, using conventional etchant of mild steel Nital solution gives a good yield of microstructures with 76 average numbers of grains at 100x/mm^2 per view of microstructure.

Despite that an existing etchant of mild steel Nital solution gives a good performance, it is established that from Factorial data that result obtained in this work revealed that: a newly produced and developed etchant of crude extract VOPE gives a better metallographical performance on mild steel.

5.0 CONCLUSIONS

Having carried out research on the effect of VOPE etchant in metallography of mild steel, the following conclusions are drawn: citric acid is the major organic acid or compound present in Valencia orange peel extracts (VOPE) used in this research work. The mass in grams of anhydrous solid crude extract citric acid / litre of liquid extract VOPE is approximately 8g. The concentration of citric acid in weight percent (%)/ litre of extract VOPE is 78%. The microstructure produced by the organic etchant VOPE gives more clarity and revelation of austenite (white) and martensite (dark) with the highest average number of grains at $100x/mm^2$ per view of microstructure compared to the existing etchant of Nital solution.

Finally, the designed parameters recommended in etching of mild steel using Valencia orange peel extracts (VOPE) organic etchant is (2.5%) concentration and 2 minutes time of etching.

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