

CORROSION INHIBITION OF STAINLESS STEEL(314L) USING MOLASSES

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ABSTRACT

The inhibition effect of molasses of varying concentrations (0.2g/L, 0.3g/L, 0.4g/L, 0.5g/L) on the corrosion of austenitic stainless steel (type 316L) in 0.5M tetraoxosulphate(vi) acid (H_2SO_4), Brine (6% NaCl), seawater (3% NaCl) and freshwater media was studied at room temperature. The corrosion rates of the steel were determined using the weight loss method for a period of fifty six days. The solution of the molasses inhibited the corrosion of the stainless steel samples to an extent depending on the concentration of the molasses and the type of medium. The results obtained showed that the higher the concentration of the molasses, the higher the inhibition efficiency (the lower the corrosion rate). The lowest corrosion rates were observed in freshwater medium while H_2SO_4 acid medium showed the highest corrosion rates. The inhibition is attributed to the physical adsorption of the inhibitor (molasses) on the surface of the stainless steel.

KEYWORDS: Inhibition, Molasses, Weight loss, Corrosion rate, Austenitic stainless steel, physical adsorption.

1.0 INTRODUCTION

Corrosion of engineering materials especially metals as a major industrial problem has posed a serious concern to engineers, scientists and other researchers who are committed to the study of corrosion and its control. Metals are exposed to the action of acids, bases and brine solutions in different ways and for many reasons. Therefore, the corrosion rates can be controlled or minimized by means of corrosion inhibitors¹.

1.1 Molasses as a corrosion Inhibitor

Inhibitors are known for their specificity of action when added or present in any given corrosive environment. An inhibitor is a substance which when added in small concentrations to an environment decreases the corrosion rate². They are commonly added in small amounts either continuously or intermittently to acids, cooling waters and other environments to minimize or control serious corrosion menace.

Most of the well known inhibitors are natural products of plant origin e.g. molasses, alkaloids, tannins, pigments and amino acids. These inhibitors are known for their efficient characteristics which include non-expensive, ecologically friendly and non-toxic to the environment⁽³⁻⁷⁾.

Molasses is a black viscous by-product of the processing of sugar⁽⁴⁾. Molasses contains sucrose, reduced sugars, salts (organic and inorganic), colloidal materials, vitamins, amino acids and waxes. The corrosion inhibition action of molasses and other natural plant inhibitors include the following mechanism:

- Adsorbing themselves on the metallic surfaces hence protecting the metallic surfaces by forming a thin film (passivation).
- Increasing the anodic or cathodic polarization behaviours (Tafel slopes).
- Increasing the electrical resistance of the metallic surface
- Reducing the movement or diffusion of ions to the metallic surface.

1.2 Austenitic Stainless Steel

Stainless steel generally denotes a large family of steel containing at least 11.5% chromium⁽⁸⁾. This amount of chromium prevents the formation of rust in unpolluted atmospheres, and it is from this characteristic that the popular designation “stainless” is derived. Stainless steel is corrosion resistant but not resistant to all corroding media (corrodants). Being corrosion resistant is due to a thin transparent film of chromium oxide that forms on the surface⁽⁹⁾. It will withstand oxidizing agents such as nitric acids but is attacked by reducing agents, e.g. hydrochloric acid (HCl), halogen salts such as sodium chloride (NaCl).

According to metallurgical structure, stainless steel is divided into three groups namely; austenitic (FCC) stainless steel, ferritic (BCC) stainless steel and martensitic (FCC or tetragonal) stainless steel⁶. The austenitic stainless steel contains 18% chromium and 8% Nickel, hence is known as 18-8 stainless steel. As a group, austenitic stainless steel is non-magnetic, resistant to atmospheric corrosion, more ductile than the ferritic and martensitic stainless steels and can only be hardened by cold working.

1.3 Objectives of the work

- To determine the inhibition efficiency of molasses on the corrosion of austenitic stainless steel in acidic, salty (brine and seawater) and freshwater environments
- To show that stainless steel is not always corrosion resistant in all environments but can corrode when subjected to severe environments.

2.0 MATERIALS AND METHODS

2.1 Samples preparation

The austenitic stainless steel sample (type 316L) used for this investigation was obtained from Nigerian Foundry, Lagos. It was obtained in sheet of thickness, 0.5cm and cut into coupons of dimension, 5cm X 1.5cm. a hole of 0.35cm was drilled on each coupon through which a twine was passed to aid suspension and total immersion in the media.

The chemical composition of the steel sample is shown in Table 1.

Table 1: Chemical Composition of the Austenitic Stainless Steel (Type 316L)

Element	C	Cr	Ni	Mn	Si	P	S
Wt.(%)	0.08	18.04	8.34	2.00	1.00	0.05	0.03

2.2 Environmental and Inhibitor preparations

Four different environments were used for the investigation. They are standard solutions of

- Brine (6% NaCl solution)
- 0.5M H₂SO₄ acid
- Seawater (3% NaCl solution)
- Freshwater

The brine and H₂SO₄ acid solutions were prepared in the chemistry laboratory of chemistry department, Federal University of Technology, Owerri, Nigeria. The seawater used in this study was obtained from Abonema high sea creek, Port-Harcourt while the freshwater was collected from the local otamiri river in Owerri, Imo State. The chemical analyses of the water samples were performed at SAAT laboratory, Federal university of technology, Owerri.

Table 2: Chemical Analyses of Water samples

Ions	Ca ²⁺	Mg ²⁺	Fe ²⁺	Na ⁺	CO ₂	Cl ⁻	O ₂ ⁻	SO ₄ ²⁻	HCO ₃	NO ₃ ⁻
Seawater	7.10	3.12	0.29	4.70	0.31	54.36	0.55	2.99	5.23	0.001
Freshwater	1.38	3.34	0.01	1.50	4.25	14.47	5.50	0.40	42.12	0.006

2.3 Experimental Set up and Monitoring

The initial weights of the coupons were taken to the nearest 0.001g on a digital electronic weighing machine (OHAUS Adventurer), degreased and dried in acetone (analar grade).

In each of the environment, five different experiments were setup using the varying concentrations of the molasses including a control (without molasses). The sample coupons were totally immersed in a plastic bowls containing each of the prepared corrosive medium.

The weight loss of each coupon was determined at intervals of seven days for a total of fifty-six days. Thus, the weight loss within the immersion period was determined as the difference between the initial weight prior to immersion and the final weight after immersion, and the corresponding corrosion rate calculated.

3.0 EXPERIMENTAL RESULTS

3.1 Determination of Corrosion Rates

The corrosion rates were calculated using weight loss measurement obtained over the period of the investigation. The following relationship was used for the calculation⁽¹⁰⁾:

$$Cr = \frac{534}{D.A.T}$$

Where; Cr = Corrosion rate in mils penetration per year (mpy)

W = Weight loss (g)

D = Density of the metal = 8.4g/cm³

A = Area of the specimen = 6.68 cm²

T = Time of exposure (days)

3.2 Calculation of Inhibition Efficiency

The percentage inhibitor efficiency was determined for all the environments at the 56th day (last day) of the experiment. It was calculated by⁽⁵⁾:

$$I\% = \frac{[W_0 - W_1]}{W_0} 100$$

Where; I% = percentage Inhibitor efficiency

W₀ = Weight loss without inhibitor

W₁ = Weight loss with inhibitor

The results obtained are shown in Tables 3 -6 and presented in Figures 1 –5 with the corresponding variables.

Table 3: Weight loss, Corrosion rate (Cr) and % Inhibitor efficiency (%) of Austenitic stainless steel exposed to 0.5M H₂SO₄

Medium/coupon No.	14 th day		28 th day		42 nd day		56 th day		70 th day		%I
	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	
S ₁	40.00	27.20	50.00	17.00	70.00	15.86	80.00	13.60	100.00	13.60	-
S ₂	20.00	13.60	30.00	10.20	40.00	9.10	45.00	7.65	50.00	6.80	27.80
S ₃	15.00	10.20	20.00	6.80	30.00	6.80	35.00	5.95	40.00	5.44	33.30
S ₄	10.00	6.80	10.00	3.40	15.00	3.34	15.00	2.55	15.00	2.04	45.60
S ₅	5.00	3.40	10.00	3.40	10.00	2.27	10.00	1.70	12.00	1.63	56.70

Legend:

- S₁ = 0.5M H₂SO₄ without molasses (Control)
 S₂ = 0.5M H₂SO₄ with 0.2g/L concentration of molasses
 S₃ = 0.5M H₂SO₄ with 0.3g/L concentration of molasses
 S₄ = 0.5M H₂SO₄ with 0.4g/L concentration of molasses
 S₅ = 0.5M H₂SO₄ with 0.5g/L concentration of molasses

Table 4: Weight loss, Corrosion rate (Cr) and % Inhibitor efficiency (%) of Austenitic stainless steel exposed to Brine

Medium/coupon No.	14 th day		28 th day		42 nd day		56 th day		70 th day		
	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	%
B ₁	30.00	20.39	40.00	13.60	60.00	13.60	70.00	11.90	80.00	10.88	-
B ₂	20.00	13.60	25.00	8.50	30.00	6.80	40.00	6.80	45.00	6.12	28.60
B ₃	15.00	10.20	20.00	6.80	25.00	5.67	25.00	4.25	30.00	4.08	35.70
B ₄	8.00	5.44	10.00	3.40	12.00	2.72	15.00	2.55	18.00	2.45	50.00
B ₅	4.00	2.72	5.00	1.70	5.00	1.13	6.00	1.02	10.00	1.36	57.10

Legend:

- B₁ = Brine without molasses (Control)
 B₂ = Brine with 0.2g/L concentration of molasses
 B₃ = Brine with 0.3g/L concentration of molasses
 B₄ = Brine with 0.4g/L concentration of molasses
 B₅ = Brine with 0.5g/L concentration of molasses

Table 5: Weight loss, Corrosion rate (Cr) and % Inhibitor efficiency (%) of Austenitic stainless steel exposed to seawater

Medium/coupon No.	14 th day		28 th day		42 nd day		56 th day		70 th day		
	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	%
W ₁	25.00	17.00	30.00	10.20	40.00	9.06	45.00	7.65	50.00	6.80	-
W ₂	15.00	10.20	20.00	6.80	25.00	5.67	25.00	4.25	30.00	4.08	33.30
W ₃	10.00	6.80	10.00	3.40	15.00	3.40	15.00	2.55	18.00	2.45	44.40
W ₄	5.00	3.40	5.00	1.70	7.00	1.59	10.00	1.70	10.00	1.36	55.60
W ₅	5.00	3.40	5.00	1.70	5.00	1.13	8.00	1.19	8.00	1.09	66.70

Legend:

- W₁ = Seawater without molasses (Control)
 W₂ = Seawater with 0.2g/L concentration of molasses
 W₃ = Seawater with 0.3g/L concentration of molasses
 W₄ = Seawater with 0.4g/L concentration of molasses
 W₅ = Seawater with 0.5g/L concentration of molasses

Table 6: Weight loss, Corrosion rate (Cr) and % Inhibitor efficiency (%) of Austenitic stainless steel exposed to Freshwater

Medium/coupon No.	14 th day		28 th day		42 nd day		56 th day		70 th day		
Freshwater	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	Weight loss (mg)	Cr X 10 ⁻³ (mpy)	%I
F ₁	15.00	10.20	20.00	6.80	25.00	5.67	30.00	5.10	30.00	4.08	-
F ₂	10.00	6.80	10.00	3.40	12.00	2.72	15.00	2.55	18.00	2.45	33.30
F ₃	8.00	5.44	10.00	3.40	10.00	2.27	12.00	2.04	15.00	2.04	53.30
F ₄	5.00	3.40	5.00	1.70	8.00	1.81	10.00	1.70	10.00	1.36	66.67
F ₅	2.00	1.36	4.00	1.36	5.00	1.13	5.00	0.85	5.00	0.68	83.33

Legend:

- F₁ = Freshwater without molasses (Control)
- F₂ = Freshwater with 0.2g/L concentration of molasses
- F₃ = Freshwater with 0.3g/L concentration of molasses
- F₄ = Freshwater with 0.4g/L concentration of molasses
- F₅ = Freshwater with 0.5g/L concentration of molasses

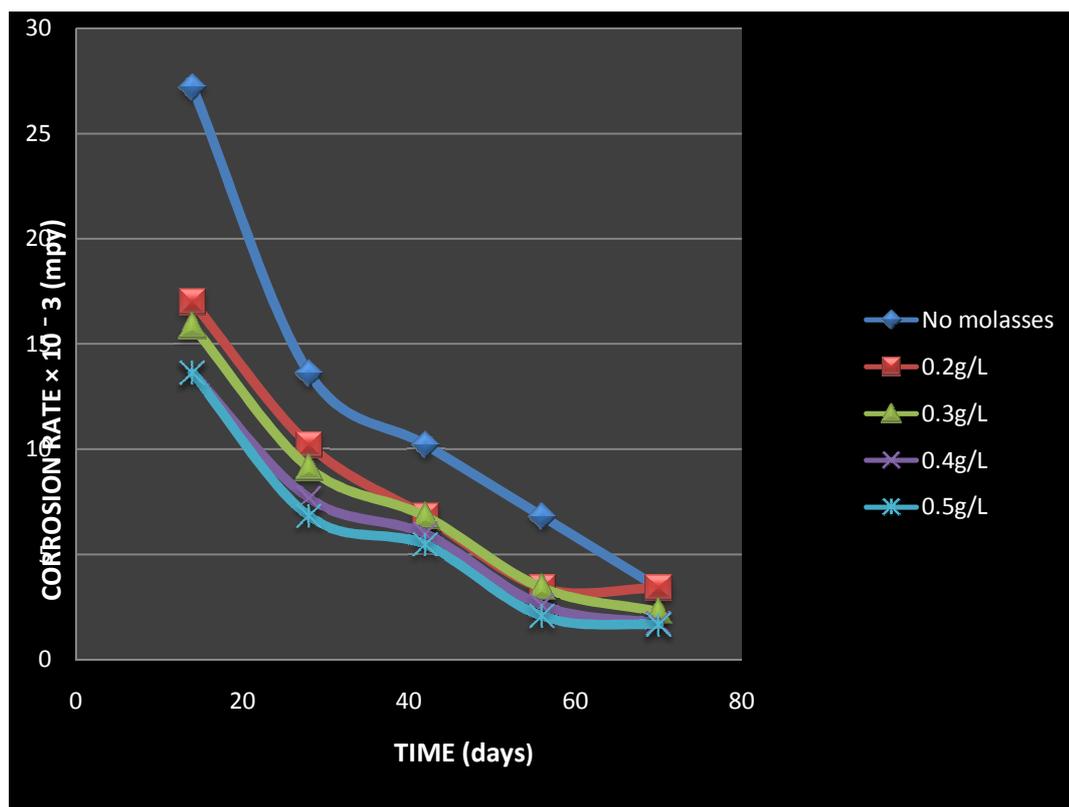


Fig 1. CORROSION RATE (CR) × 10⁻³(mpy) Vs EXPOSURE TIME (DAYS) OF STEEL EXPOSED TO H₂SO₄

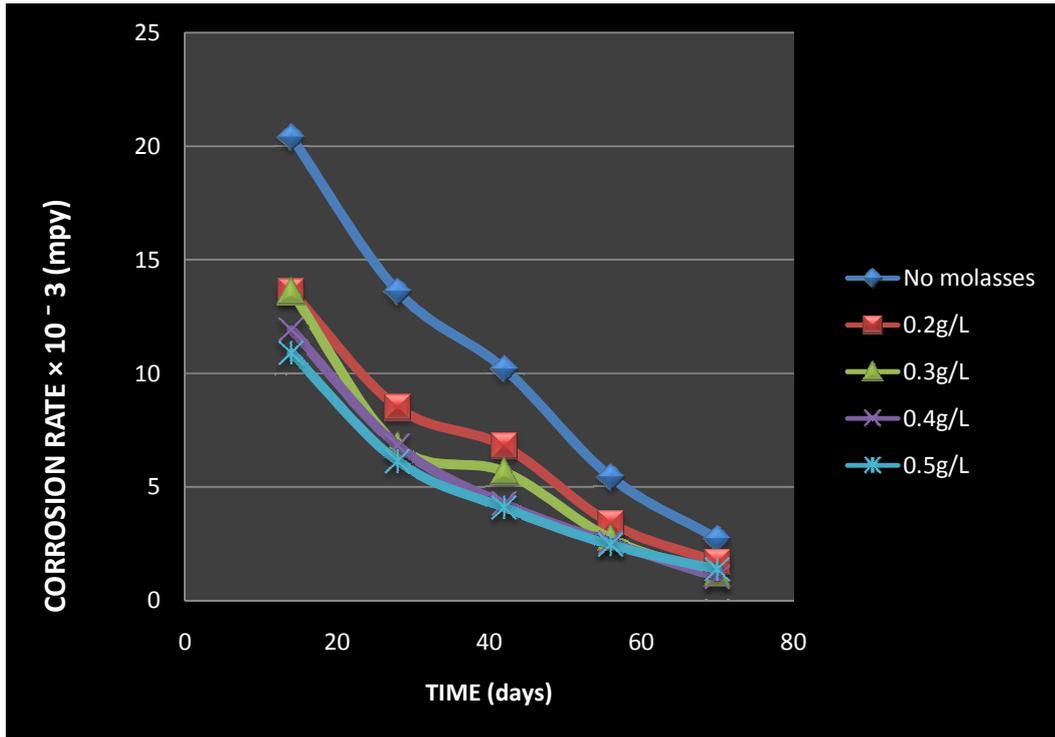


Fig 2. CORROSION RATE (CR) $\times 10^{-3}$ (mpy) Vs EXPOSURE TIME (DAYS) OF STEEL EXPOSED TO BRINE

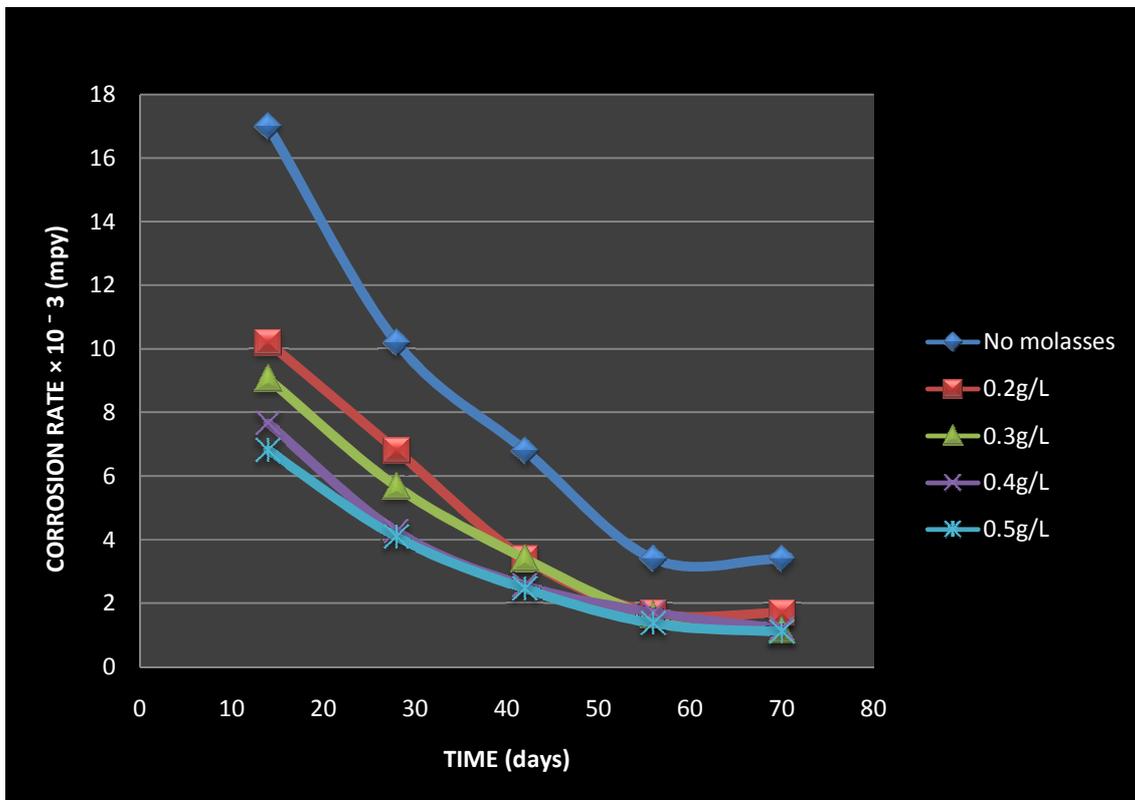


Fig 3. CORROSION RATE (CR) $\times 10^{-3}$ (mpy) Vs EXPOSURE TIME (DAYS) OF STEEL EXPOSED TO SEAWATER

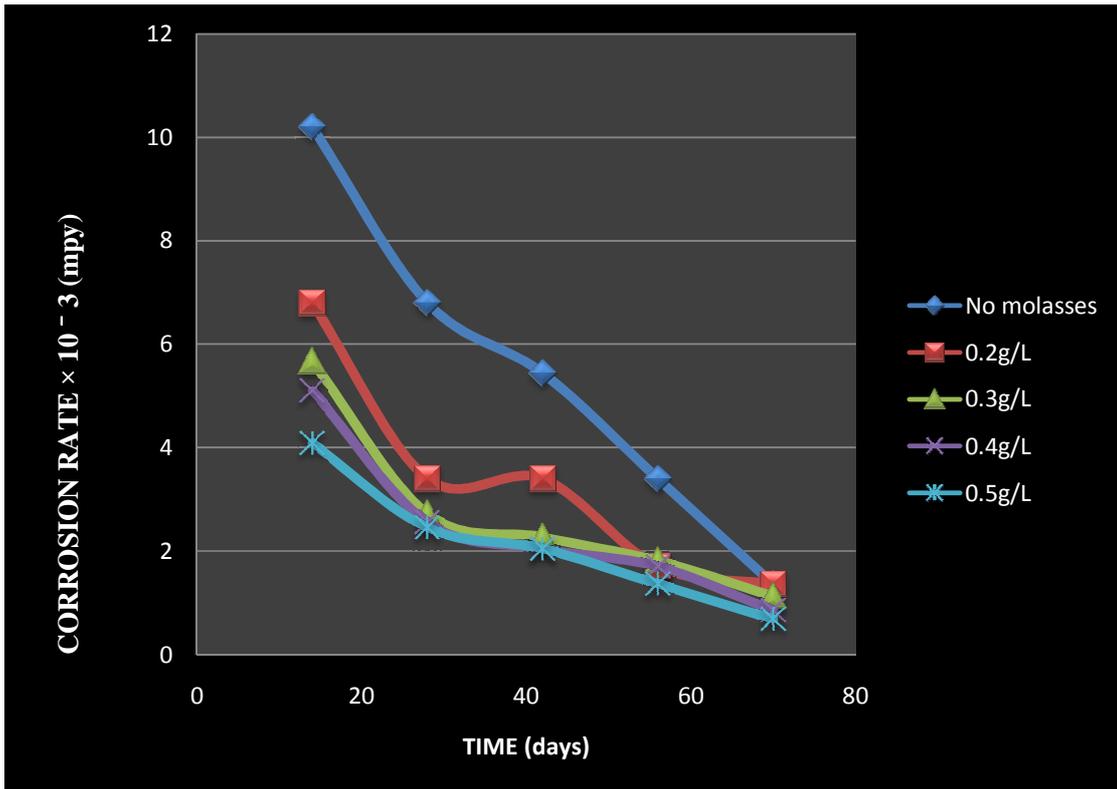


Fig 4. CORROSION RATE (CR) $\times 10^{-3}$ (mpy) Vs EXPOSURE TIME (DAYS) OF STEEL EXPOSED TO FRESHWATER

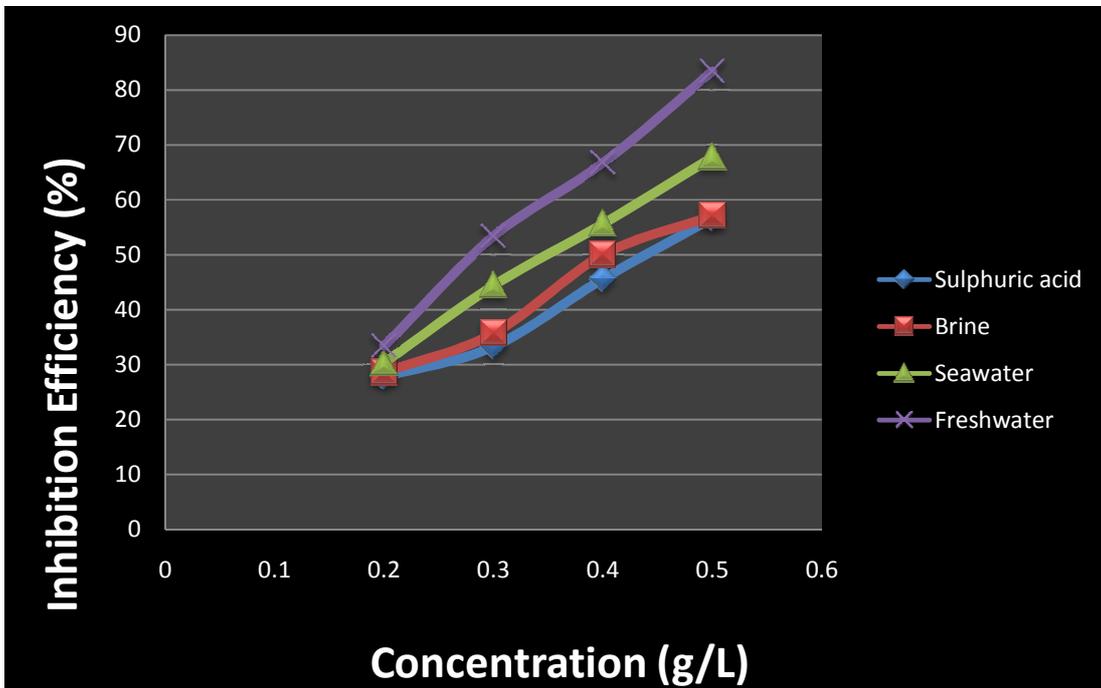


Fig 5. % INHIBITION EFFICIENCY Vs CONCENTRATION (g/L)

4.0 DISCUSSION OF RESULTS

4.1 weight Loss

Tables 3 -6 show the values of weight loss of the steel sample with time for all the media. From the results obtained and presented in the tables, it was observed that the weight loss increases with the time of exposure.

H₂SO₄ acid medium exhibited the highest weight losses (as shown in Table 3), while the lowest weight loss was observed in the freshwater environment (Table 6). The weight loss observed in the steel samples was due to the presence of the aggressive molecular species (ions) contained in the test media^(10,11,12,13). These ions are SO₄²⁻ (from H₂SO₄), Cl⁻ (from brine and seawater) and OH⁻ (from freshwater). The SO₄²⁻ ion is the most aggressive and therefore attacks the stainless steel strongly.

Generally, the control experiments (i.e.those media without molasses) recorded higher weight losses more than those media with different concentrations of the inhibitor (molasses).

4.2 Corrosion Rate

The corrosion rates of the steel samples were shown in Tables 3 – 6 and presented in Figures 1 -4. From the plots, corrosion rates decrease sharply with increase in exposure time in all the media. The highest corrosion rate was observed in H₂SO₄ medium due to the presence of the aggressive SO₄²⁻ ions followed by brine and seawater media containing Cl⁻ ions while the freshwater medium which contains OH⁻ ions recorded the least corrosion rates.

The higher the concentration of the molasses, the lower the corrosion rate of the steel sample. Molasses is an organic inhibitor, hence adsorption type inhibitor. It adsorbs on the metal surface and depresses both metal dissolution and reduction reactions⁽¹⁴⁾. Therefore, this blocking effect is due to the blanketing of the metal surface which in turn reduces the active sites on the metal surface upon which anodic and cathodic reactions could occur.

4.3 Inhibition Efficiency

Figure 5 shows the variation of inhibition efficiency (I %) with concentration of molasses (g/L). It was observed from the graph that the inhibition efficiency increases with increase in the concentration of the molasses. Thus, the higher the concentration of the molasses, the lower the corrosion rates. The inhibition (decrease in corrosion rate) is attributed to the physical adsorption of the molasses. Consequently, adsorption of the molasses was proposed as the reaction mechanism for the inhibition. However, further work is on-going on the investigation of this reaction mechanism.

5.0 CONCLUSION

Based on the results obtained, the following conclusions can be made:

- (1) Molasses could best serve as a corrosion inhibitor in freshwater, seawater, brine and H₂SO₄ solutions and performing optimally at 0.5g/L concentration.
- (2) Molasses inhibited the corrosion reaction through the mechanism of physical adsorption on the metal (steel) surface.
 - (3) The inhibition efficiency (I %) of molasses increases with increase in the concentration of the inhibitor.
 - (4) Austenitic stainless steel is naturally resistant to corrosion to a measurable extent due to its nickel and chromium contents.

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