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Crustacean Shell based Corrosion Resistant Surface Coating.

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(Accredited by NBA, NAAC with 'A' Grade & ISO 9001:2008 Certified Institution)

A Mini Project Report submitted in partial fulfillment for the award of the degree of

BACHELOR OF TECHNOLOGY

in

CHEMICAL ENGINEERING

Submitted by

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CERTIFICATE

This is to certify that the report entitled Crustacean Shell based Corrosion Resistant Surface Coating. submitted byA.V.Sai Kumar, B.Rohith, B.Naveen, G.Tarun Kumar, P.Srikar Chakravarthi bearing Regd. No. 20341A0802, 20341A0806, 20341A0808, 20341A0813, 21345A0803 have been carried out in partial fulfilment of the requirement for the award of degree of Bachelor of Technology in Chemical Engineering of JNTUGV, Vizianagram is a record of Bonafide work carried out by them under my guidance & supervision of Dr. Suryanarayana Dash. The results embodied in this report have not been submitted to any other University or Institute.

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ABSTRACT :

Corrosion has been a major field of research for many years. As more and more metals are being used for industrial and commercial product, prevention of corrosion has become a key consideration. There are numerous researches on this topic, where most of them focuses on developing a solution using complex methodologies and coating materials made out of chemicals, this report aims to synthesize a coating material which can prevent corrosion without involving any complex procedure and raw materials. Along with prevention of corrosion this report also focuses on waste management of crustacean waste, sea-food processing generates a huge amount of waste which are considered as bio pollutants. This report is intended to reduce the solid waste by developing a solution that will recycle the waste and produce valuable product. A coating material was made using crab shell powder as an additive and alkyd resin as a binder to protect a mild steel substrate. The resulting coating material was applied onto the mild steel substrate by spraying. The coated metal's corrosion resistance was investigated by keeping the metal sample in a salt solution. The metal sample were visually inspected for any signs of corrosion. The resistance of samples were also determined by weighing. The results from the test shows that the metal sample coated with the crab shell coating has good corrosion resistance.

Keywords: Corrosion; Surface coating; Crab shell; Crustacean waste;

Table of Contents

Chapter No.				Content	Page No.
1				Introduction	678
	1.1			Corrosion and its prevention methods	678
	1.2			Properties of crab shells and its production	678
	1.3			Spray coating and coating sample	679
2				Literature Review	679
3				Materials and methods	680
	3.0			Materials	680
		3.0.1		Coating sample	680
			3.0.1.1	Binders	680
			3.0.1.2	Solvents	681
			3.0.1.3	Additive	681
		3.0.2		Metal sample	681
	3.1			Methods	681
		3.1.1		Coating synthesis	681
		3.1.2		Application of coating	682
	3.2			Testing	682
4				Result and Discussion	683
	4.0			Result	683
		4.0.1		Weight loss determination	683
		4.0.2		Corrosion rate	683
		4.0.3		Loss percentage	685
		4.0.4		Visual inspection	686
5				Conclusion	686
	5.0			Conclusion	686
6				Reference	686

List of Figures

Fig. No.	Figure Captions	Page No.
Fig. 1	State-wise estimates of marine crab landings during 2007-2020	679
Fig. 2	Alkyd resin	680
Fig. 3	Structure of alkyd resin	680
Fig. 4	Microscopic images of crab shell powder	681
Fig. 5	Mild steel sample	681
Fig. 6	Synthesis of coating sample.	682
Fig. 7	Application of coating sample on metal surface.	682
Fig. 8	Graphical representation of weight loss after 12hrs.	684
Fig. 9	Graphical representation of weight loss after 10 days.	685
Fig.10	Area of corrosion	686

List of Tables

Table No.	Table Captions	Page No.
Table 1	Global cost of corrosion by region by sector	678
Table 2	State-wise trend in overall crab landings of India during 2007- 2020	679
Table 3	Composition of paint	680
Table 4	Coating compositions	682
Table 5	Weights of coated metal sample.	682
Table 6	Reduction in weight after 24hrs	683
Table 7	Reduction in weight after 10 days	683
Table 8	Weight loss after 12hrs	684
Table 9	Weight loss after 10 days	685
Table 10	Percentage of weight loss after 12hrs.	685
Table 11	Percentage of weight loss after 10 days.	686

CHAPTER-1

INTRODUCTION :

1.0. Introduction

1.1. Corrosion and its prevention methods:

Corrosion is a chemical reaction between metal and its surrounding which results in formation of metal oxides and destroys the metal, reducing its structural strength. Studies have shown that over the past 5 decades the cost of corrosion has reached 3.4% of global GDP which is 74,314 billion US $. And 1446 billion US $ were from industrial sector. India spent 4.2% of its GDP (20.3 billion US $) [1].
To prevent corrosion numerous methods have been developed over the years, which includes electroplating, cathodic protection, sacrificial method, barrier protection and many more [2]. However, barrier protection is the easiest method of protecting metal substrates from corrosion by providing a physical barrier between metal and its environment[2,3].Various coating materials based on organic compounds, metals are applied to the metal surface for protection[3].

Economic Regions	Agriculture CoC USD billion	Industry CoC USD billion	Services CoC USD billion	Total CoC USD billion	Total GDP USD billion	CoC % GDP
United states	2	303.2	146	451.3	16720	2.70%
India	17.7	20.3	32.3	70.3	1670	4.20%
European region	3.5	401	297	701.5	18331	3.80%
Arab world	13.3	34.2	92.6	140.1	2789	5.00%
China	56.2	192.5	146.2	394.9	9330	4.20%
Russia	5.4	37.2	41.9	84.5	2113	4.00%
Japan	0.6	45.9	5.1	51.6	5002	1.00%
Four Asian Tiger	1.5	29.9	27.3	58.6	2302	2.50%
Rest of the world	52.4	382.5	117.6	552.5	16057	3.40%
Global	152.7	1446.7	960.0	2505.4	74314	3.40%

Table.1. Global cost of corrosion by region by sector [1].

1.2. Properties of crab shells and its production:

Crabs are decapod crustaceans,which have an exoskeleton. The exoskeleton is made up of calcium carbonate, proteins, and chitins[4,5]. the crab shell have low water absorption and has good thermal stability, the structure of the shell contains chitins and protein which provides it mechanical properties like strength and plastic nature [6].
India accounted for 1.61 million tonnes of crabs from 1975-2020 which is 9.6% of global production, where Tamil nadu, Gujarat, Andhra pradesh being the top three producers. Andhra pradesh with a coastal length of 974 kms produced 76795955tonnes of crabs [7].along with this high production, the waste production is also high, about 50-70% of crab's weight is waste where shell makes up most of it. Crab shell consists of 50–70% calcium ,15–30% chitin and 15-23% protein [8].

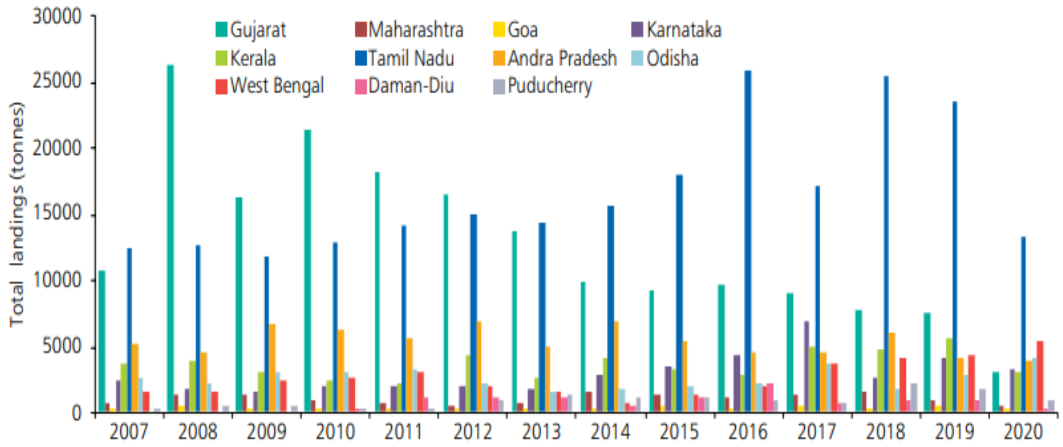

Fig.1.0. State-wise estimates of marine crab landings during 2007-2020 [7]

States	Coastal length (km)	Coastal districts	Total (t)	Rank	Percentage	Overall trend
Tamil Nadu	1076	13	233164001	1	33.31	Decreasing
Gujarat	1600	15	179602878	2	25.66	almost steady
Andhra Pradesh	974	9	76795955	3	11.00	Decreasing
Kerala	590	9	51622213	4	7.37	Increasing
Karnataka	300	3	41839864	5	6.00	Increasing
Odisha	480	6	36941425	6	5.28	Increasing
West Bengal	158	4	36762107	7	5.25	Decreasing
Maharashtra	720	7	15153865	8	2.16	Increasing
Puducherry	45	4	12953456	9	1.85	Increasing
Daman & Diu	21	2	10496116	10	1.50	Decreasing
Goa	104	2	4681290	11	0.67	Increasing

Table 2. State-wise trend in overall crab landings of India during 2007- 2020 [7].

1.3. Spray coating and coating sample:

Spray coating is a process of application of coating material onto a surface, it is one of the most widely used process in painting. Spray coating provides an even layer of coating liquid by atomizing the coating liquid[9].

The coating sample for spray coating has a composition similar to conventional paint, it consists of four components which are 35% of binder, 25% pigments, 40-50% solvent and 2% additives. The paint should have low viscosity, to reduce the viscosity a suitable solvent is used [10].

CHAPTER-2

REVIEW OF LITERATURE :

2.0.

Reviewing reports have provided a detailed overview of various studies carried out on paints, coatings, and coating materials by various authors.

F.S. da Silva et al, conducted cold gas spray studies using copper coating materials under conditions of gas velocity:500 mm/s, distance 40 mm, nitrogen gas temperature 400 °C, pressure 30 bar, corrosion test: Electrochemical impedance spectroscopy of metals:120h,for copper coating:1100h, frequency: It is from 100 kHz to 5 mHz, and the results show that the substrate potential tends to stabilize at around -0.70 V. For copper plating, the EOCP value remained around -0.2 V.

AA2024-T3 aluminum alloy was used as the base material for the sol-gel coating material and coated by dip coating. This study provides results as Li

coatings may be considered as a potential hexavalent chromium-free system for unpainted parts in the aircraft industry. It was published by R. delormo et al.

A.S. Gnedenkov et al, coated Pulsed bipolar mode in a silicate-fluoride (SiF) electrolyte on MA8 magnesium alloy (wt.%: 1.5 to 2.5 Mn; 0.15 to 0.35Ce; Mg - balance) by using plasma electrolytic oxidation coating method, these increases the corrosion resistance of the base PEO-coating by 4 times.

S. Luangkularb et al, coated teflon by spray coating and different pressures, spray orientations, nozzle sizes to determine the factors that affect the thickness and formations of coating. Their report concludes that the material consumption and dry film thickness depends on the spray settings like spray time, nozzle size, air pressure. They were successful in making a geometric model for the relationship between material consumption and dry film thickness.

Bocchetta et al experimented on biomedical titanium oxide by applying a passive layer to improve corrosion resistance of the Ti-6Al-4V alloy for biomedical use. A layer of oxide was developed by passivation. The corrosion resistance of the alloy and the layer was determined as Non coated metal: 121.58 nA/cm^2 Coated metal :494.5 nA/cm^2

These reports helps to understand and define corrosion and contributes in development of various methods and coatings to prevent corrosion in different sectors, where most of them focuses on developing coating materials based on chemicals and alloying which may sometimes turn out to be a complicated procedure and economically non-viable.

These reports haven't considered the possibilities of using sea food waste as an ingredient to make a corrosion resistant coating that will help in reducing the solid waste pollution and produce a valuable product.

CHAPTER-3

MATERIALS AND METHODS :

3.0. Materials:

3.0.1. Coating sample:

For synthesis of coating solution we require an additive, binder, and a solvent. The coating sample were prepared with different concentrations. The synthesized sample is heterogenous mixture of binder, additive, and solvent with low viscosity and the additive was evenly dispersed in the binder. The general composition of paint are given in Table.3. [10]

Table.3. Composition of paint.

Composition	Percentage	Example
Binder	± 35 %	Alkyd resin, Epoxy resin, Acrylic resin
Pigment	25 %	Titanium dioxide, Zinc Oxide, Yellow Dyes, Red 170
Solvent	40-50 %	White spirit, ethanol,
Additives	± 2 %	Dryer; anti-skin product;anti-sag product; moistener

3.0.1.1. Binder:

Binder in used combine all components of paint. Binder is responsible for adhesion of paint onto the surface and the formation of film [10].

The binder that has been used in this report is Alkyd resin provided by Vinay Chemicals and Synthetics. Alkyd resin is most commonly used resin for spray coating as its has properties like low viscosity and quick drying [10].

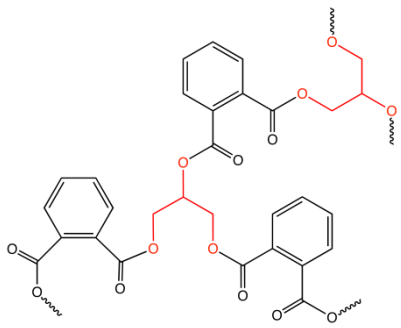

Fig.2. Alkyd resin. **Fig.3. Structure of alkyd resin(Source).**

3.0.1.2. Solvent:

Solvent is used to dilute the paint and gives good handling properties like flow-ability, quick drying, and makes the paint easy to apply.
For this report Toulene was used as a solvent from Fisher Scientific.
Properties of toulene:
Formula: $C_6H_5CH_3$
Boiling point: 110.6 °C
Density: 867 kg/m³
Molar mass: 92.14 g/mol
Melting point: -95 °C

3.0.1.3. Additive:

Additives are used to improve technical properties of the paint. For this report Crab shells are used as an additive.
Crabs (Portunus sanguinolentus [7]) were collected from local market. The shells were removed and cleaned with distilled water. Shells were dried under sun for 24hrs. Then the shells were powdered in a attrition mill (Equipment provided by institute laboratory). The powdered shells were inspected under a microscope to analyse the uniformity of the powder (Shown in Fig. .) . The result showed that the powder had large particles.

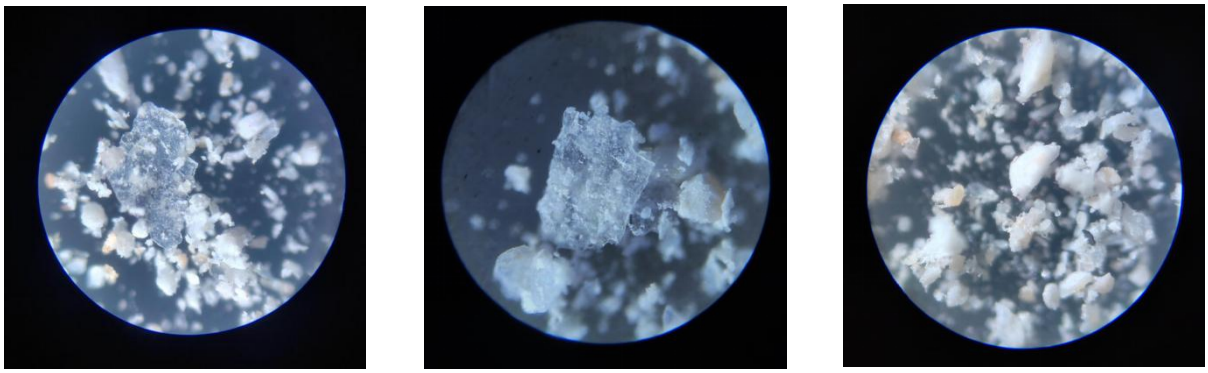

Fig.4. Microscopic images of crab shell powder.

The powder was then sieved using a B.S.S 200 mesh, the particles passing through the mesh were used which had diameter less than 75 microns.

3.0.2. Metal substrate:

Scrap mild steel pieces (5cm x 5cm x 0.3cm) were acquired from workshop in the institute. The pieces were cleaned and polished using a sand paper to remove any traces of corrosion. The pieces were weighed.

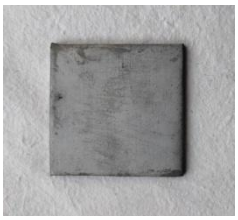

Fig.5. Mild steel sample.

3.1. Synthesis:

3.1.1. Coating sample preparation:

Once the appropriate amounts of raw materials were acquired they are thoroughly mixed in a beaker using a mechanical stirrer at room temperature.
The sample formed was then mixed with solvent, the amount of the solvent depends on the desired consistency the solvent added until the viscosity of the sample reaches the point where it is easier to apply.The table. . shows the weights of components taken.The mixing process in shown in the flow sheet (Fig.3.5.)

Table 4. Coating sample compositions.

	Sample 1 (gms)	Sample 2 (gms)	Sample 3 (gms)
Resin	60	30	40
Additive	40	70	60

Fig.6. Synthesis of coating sample.

3.1.2. Application of coating sample:

The metal samples were coated with the coating material samples mentioned in Table 1.4, using spray coating. The samples were coated with a single layer of the coating sample evenly.
The three coating samples were coated onto three metal pieces using an air spray gun. The coated metal was dried under sun.

Fig.7. Application of coating sample on metal surface.

3.2. Testing procedure:

3.2.1. Salt solution test:

After application of the coating the metal samples were tested using salt test method.
Salt solution : 5% NaCl solution.
Temperature : Room temperature (20-31°C)
The samples were kept in 300 ml of 5% NaCl solution for 24 hrs. The initial weights of the sample (mentioned in Table.).

	Wt % of crab shell	Weight of the sample (gms)
Sample 1	40	59
Sample 2	70	62
Sample 3	60	65

Table.5. Weights of coated metal sample.

CHAPTER-4

RESULTS & DISCUSSION

4.0. Result:

4.0.1. Weight loss determination:

a) After 24hrs.

The samples after 24hrs were weighed to analyse the amount of coating degraded in the salt solution. The reduction of weight is tabulated in table. The weight were taken every hour for 12hrs. and a final weight was taken at end of 24hrs.

Table.6. Reduction in weight after 24hrs

	Initial Weight of the sample	**Final Weight of the sample**	**gms. of weight lost**
Metal sample 1	59	56.8	2.2
Metal sample 2	62	61.87	0.12
Metal sample 3	65	64.67	0.32

b) After 10 days.

Similar to the 24hrs test the samples were subjected to immersion test for 10 days and the weight samples were taken every 24hrs.

Table.7. Reduction in weight after 10 days

	Initial Weight of the sample	**Final Weight of the sample**	**Weight loss after 24hrs.**
Metal sample 1	59	56.8	2.2
Metal sample 2	62	61.87	0.12
Metal sample 3	65	64.67	0.32

4.0.2. Corrosion rate:

After 24hrs.

A graph has been plotted between loss of material (gms) and time (hrs) to produce the corrosion rate curve.

Table.8. Weight loss after 12hrs.

Time (mins)	Sample 1 weight loss	Sample 2 weight loss	Sample 3 weight loss
0	59	62	65
60	58.98	62	64.99
120	58.98	62	64.98
180	58.98	61.99	64.98
240	58.98	61.99	64.97
300	58.98	61.99	64.97
360	58.97	61.99	64.96
420	58.87	61.98	64.96
480	58.75	61.98	64.95
540	58.72	61.98	64.95
600	58.68	61.98	64.94
660	58.63	61.98	64.93
720	58.42	61.98	64.92

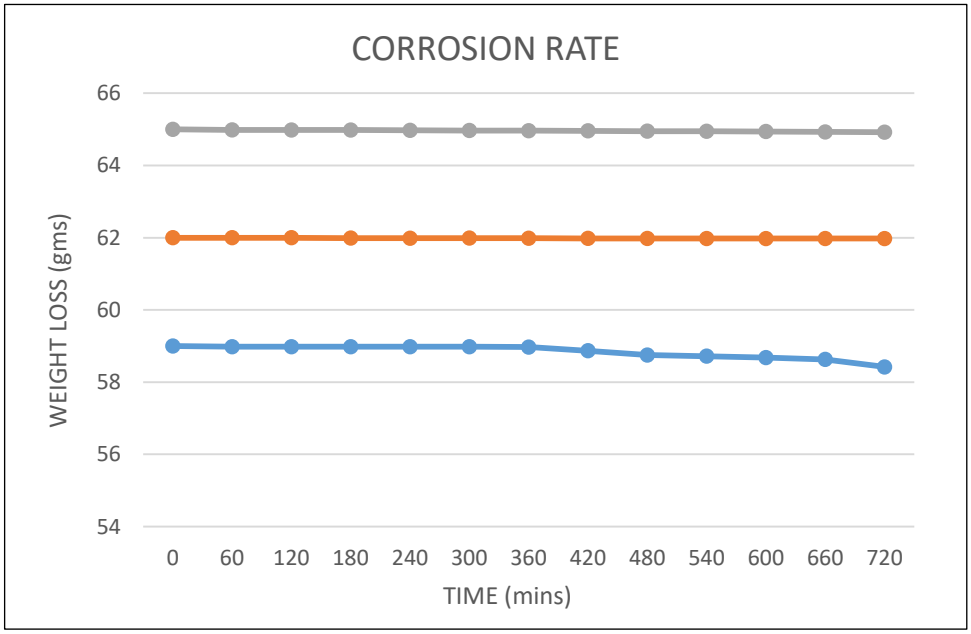

Fig. 8. Graphical representation of weight loss after 12hrs.

After 10 days

The test was carried out for 10 days and the observations were recorded every 24hrs. The data collected has been plotted on a graph to develop a corrosion rate curve.

Table.9. Weight loss after 10 days.

Time (hrs)	Sample 1	Sample 2	Sample 3
0	59	62	65
24	56.81	61.87	64.68
48	55.78	61.74	64.52
72	53.48	61.57	64.38
96	52.63	61.50	63.67
120	49.56	61.37	63.38
144	46.84	61.28	63.21
168	42.65	61.11	62.63
192	42.32	60.84	62.37
216	39.29	60.73	62.27
240	39.15	60.38	62.13

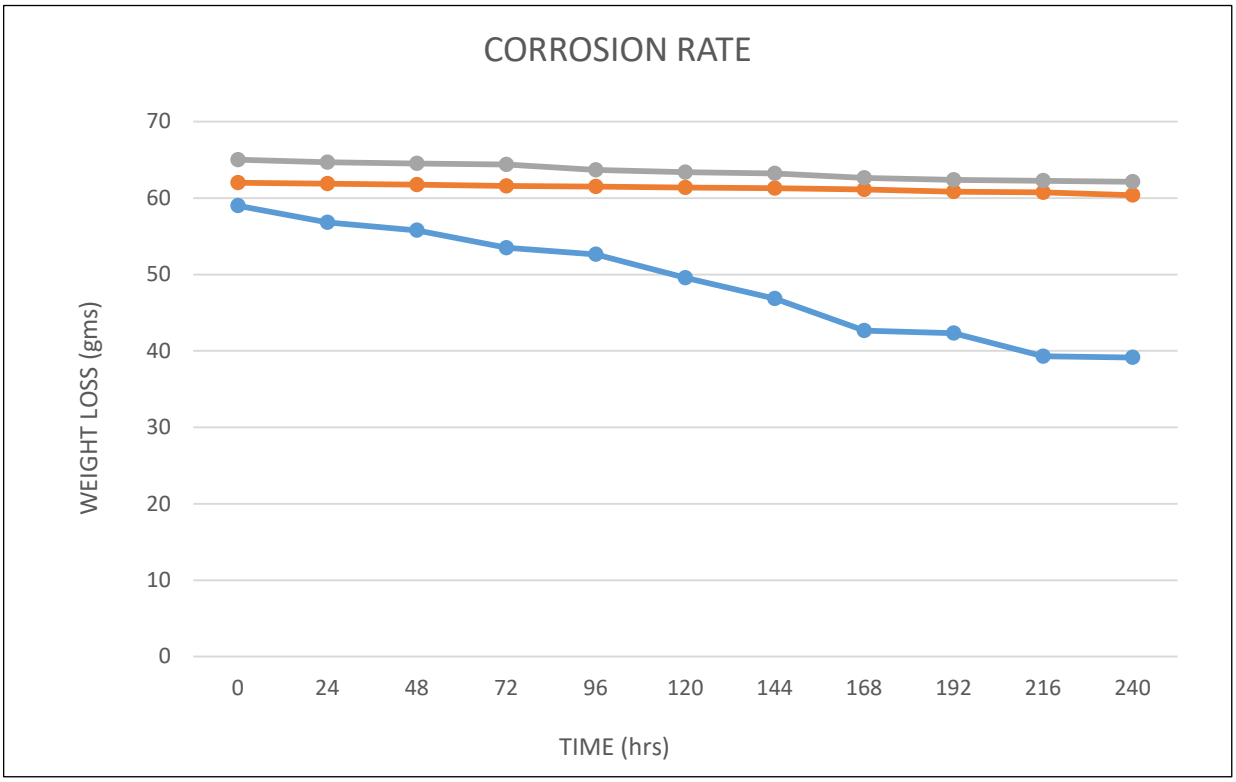

Fig. 9. Graphical representation of weight loss after 10 days.

4.0.3. Loss percentage:

a) After 24hrs.

The percentage of weight lost after the first 24hrs of the testing was determined. This wasn't enough to evaluate the rate of corrosion.

Table.10. Percentage of weight loss after 24hrs.

	Initial Weight	Weight loss after 24hrs.	%loss of weight
Sample 1	59	56.8	3.71
Sample 2	62	61.87	0.2
Sample 3	65	64.67	0.5

b) After 10 days

To get a better idea on the rate of corrosion and to evaluate which of the three samples have better resistance towards corrosion the test was carried out for 10 days.

Table.11. Percentage of weight loss after 10 days.

	Initial Weight	Weight loss after 24hrs.	%loss of weight

Sample 1	59	39.15	33.6
Sample 2	62	60.38	2.61
Sample 3	65	62.13	4.41

4.0.4. Visual inspection:

Visual inspection revealed that the places where the metal wasn't fully coated the corrosion was significant.

Fig.10. Area of corrosion.

CHAPTER-5

CONCLUSION :

5.0. Conclusion

Upon conducting test and analyzing the result it has been found that the coating provides some extent of protection, where one of the sample lost 2.19 grams whereas sample 2 and sample 2 lost 0.126 grams, 0.325 grams, of coating respectively, the sample which lost highest weight had more traces of corrosion whereas other samples had few spots of corrosion. The report revealed that level of resistance depends on the various aspects, the method of coating, coating thickness, solid dispersion in the binder and many more, and are factors that affect the resistance of the coating. However this report focuses on one method (spray coating) and limited concentration of the coating, and for limited time. The review establishes that the samples are capable of providing protection towards corrosion, but there is room for development as the other aspects has to be explored.
This report attempts to develop a product that is easy to produce and provides comparable protection without significant compromises. Along with that this report explores the possibilities of synthesizing coating using sea food waste to reduce the impact of such waste on the environment.

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