Inhibitive Efficiency of Some Cellulosic materials as Corrosion Inhibitors for Mild Steel in petroleum Industry

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Abstract

Green inhibitors plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency. This article gives a vivid account of natural products which are used as corrosion inhibitors for various metal and alloys in aggressive media. The purpose of this study aimed to assess some of highly efficient environmentfriendly corrosion inhibitors for corrosion protection of steel in different environments. The novel corrosion inhibitor is based on the investigation of function groups of the extract of crushed adsorbent materials which are responsible for the inhibition of corrosion. The second part of this study will include studying of some factors affecting on inhibition corrosion process such as pH, inhibitor dose, concentration of medium, temperature of solution, as well as the contact time in (acidic) medium at 25°C.

Keywords: Corrosion, corrosion inhibitors, natural inhibitors, green inhibitors, Plant extracts.

1. Introduction

Corrosion is an unavoidable but a controllable process. Due to the issues of toxicity of substances like chromate inhibitors, there is an increasing interest in exploration and utilization of eco-friendly inhibitors, which are known as green inhibitors **(Devarayan*et al.,* 2012).**Metals are the permanent important materials used in structural and decorative applications. Corrosion of metals has a significant impact on the development of a country, which can be compared to any natural disasters like earthquake, flood, etc.

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For example; the direct metallic corrosion cost in the US was estimated as approximately \$276 billion on an annual basis, which is several times greater than the normalized loss incurred due to the natural disasters (\$17 billion per annum). It was also suggested that about 25-30% of the annual corrosion costs could be saved by means of optimum corrosion management practices (**Devarayan*et al.,* 2012 and Koch *et al*., 2002**). Corrosion of metallic surfaces can be controlled or reduced by the addition of chemical compounds to the abrade. This form of corrosion control is called *inhibition* and the compounds added are known as *corrosion inhibitors.* These inhibitors will reduce the rate of either anodic oxidation, cathodic reduction, or both.

Several different methods can be employed to slow or prevent corrosion of metallic structures. The most commonly used methods are protective coatings on metals using organic molecules, plastics, polymers; and cathodic and/or anodic protection using organic or inorganic inhibitors. The initial report of corrosion inhibition by organic inhibitors is attributed to (**Speller *et al.,* 1927**) who examined the corrosion inhibition of scaled water pipes in HCl. Since then, many organic and inorganic compounds that are added to the corrosive fluids have been investigated for this purpose. The inhibitors themselves form a protective film on the surface of the metal. It has been postulated that the inhibitors are adsorbed onto the metal surface either by physical (electrostatic) adsorption or chemisorptions. Physical adsorption is the result of electrostatic forces between the organic ions and the electrically charged metal surface. Chemisorptions is the transfer, or sharing, of the inhibitor molecule's charge to the metal surface, forming a coordinate-type bond (**Trabanelli*et al.*,1970**) .

Water hyacinth *(Eichhorniacrassipes)*

Earlier, inourlab. at Suez Oil Processing Company(**SOPC**) had been used the adsorption technique by using EichhorniaCrassipes to remove the petroleum oils and their products from oily wastewater drained to the sea, in addition, several parameters affecting on the adsorption process were studied, such as; concentration of oils, concentration and surface area of adsorbent, contact time, pH and temperature. Recently, another investigated studies to the adsorptive efficiency of the cellulosic surface with lignin of this adsorbent were done through the adsorption treatment of water for Pb, Cd, Fe and Zn removal by Using EichhorniaCrassipes, whereas the favorable factors affecting on their adsorption such as metal concentration, dosage of adsorbent, pH of solution, contact time, and temperature were investigated too (**Nabila*et al.,* 2011 a&b).**

Rice Straw

Rice Strawisalignocellulosesmaterialproducedas a byproduct fromagriculturalcrop production.Its mainly composedofcellulose,hemicelluloses,lignin,nitrogenous compounds,and ash. The exactcompositionofstrawvarieswiththetypeandvarietyof straw.The growing,harvesting, andcollectionconditionscanalsoaffectthemake-up of the straw.

Generally speaking, straw containsabout35to50%cellulose, 15 to 30% hemicelluloses, 20 to 30% lignin, and lesser amounts of ash and other components. (**Brijwani, K** *et al.,***2011**)

Cellulose

Cellulose constitutes the most abundant, renewable polymer resource available today worldwide. It has been estimated that by photosynthesis, 10^{11}-10^{12} tons are synthesized annually in a rather pure form, e.g., in the seed hairs of the cotton plant, but mostly are combined with lignin and other polysaccharides (So-called hemicelluloses) in the cell wall of woody plants (**Klemm, D***et al.***, 1998 andBrijwani, K** *et al.,***2011**).

Lignin

 Lignin is derived from the Latin word for wood (lignum). *De Candolle* firstly introduced this term in 1819. (Cellulose was named by *Anselme Payer* in 1838). In 1897, *Peter Klason* studied the composition of lignosulfonates and put forward the idea that lignin was chemically related to coniferyl alcohol. In 1907, *Klason* proposed that lignin is a macromolecular substance.
After ten year (1917) *Klason* further purposed that coniferyl alcohol units are joined together by ether linkages (**Boerstel, H***et al.***, 2001**).

2. Materials and Methods

EichorniaCrassipes plant was collected from Ismailia Lake and stored in polyethylene bags, the sugar cane bagass and rise straw were collected from the fields .Then transported to the laboratory within the limited time. The samples plant were collected from its place in a clean plastic bag and was cut, washed with tap water followed by deionized water, and washed with dilute nitric acid to remove any metals traces, then it was washed too by deionized water, dried at 70 ℃ for 8 hours, ground by a mortar and stored in a plastic bag.
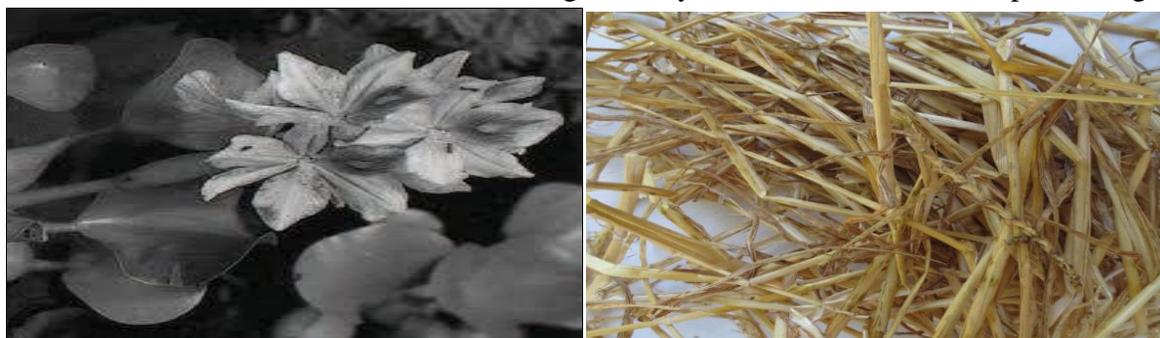
Figure (1) water hyacinthFigure (2) Rice straw

Steel samples preparation

The samples which pretreated prior to the experiment by grinding with emery paper (grade 600, 800, 1000 and 1200) then cleaned with double distilled water, degreased with acetone and dried. The rectangular specimens with dimension 2.5cm× 2.0cm× 0.25cm were used in weight loss experiments.

Table (1): Chemical compositions of Mild steel

Element	Fe	C	Si	Mn	P	Cr	Ni	Al	Cu
Wt%	99.30%	0.076%	0.026%	0.129%	0.012%	0.050%	0.050%	0.023%	0.135%

Weight loss experiments were performed at 308K (except for temperature effect) for 3h (except for immersion time effect) by immersing the mild steel in acid solution (100ml) with various amounts of inhibitors, in addition to the blank sample without additive inhibitor. After the elapsed time, the specimens were taken out, washed, dried and weighed accurately. All the tests were conducted in 1M HCL. All the experiments were performed in triplicate and average values were reported. The inhibitor efficiency (E %) and surface coverage (θ) was determined by using the following equation:

$$\theta = \frac{w` - w}{w`}$$

$$E(\%) = \frac{w` - w}{w`} \times 100$$

Where w` and w are the weight loss value in presence and absence of inhibitor, respectively. The corrosion rate (CR) of mild steel was calculated using the relation:

CR (mm year^{-1}) $=\frac{87.6w*}{ATD}$ where w* is the corrosion weight loss of mild steel (mg), A the area of the coupon, t the exposure time (h) and D is the density of mild steel (g cm^{-3}) (**Ambrish,S***et al.***2010**).

Inhibitor Preparation

Dried water hyacinth leaves were soaked in solvent (Methanol) and refluxed in soxhlet for 5h. The solution was filtered and concentrated to 100ml.This concentrated solution was used to prepare solution of different concentrations (**Ambrish,S***et al.***,2010**).

Identification of the Components by GC

The samples were determined by gas chromatograph using a 60:80 Carbopack B: 5% Carbowax 20 M glass column. The injector was operated at 200°C. The flame ionization detector (FID) was kept at 200°C. Nitrogen gas was used as carrier gas at a flow rate of 30 ml/min. The temperature was programmed at 120°C for 1.4 min, from 120°C to 240°C at 30°C/ min, then held 5 min at 240°C.

Table (2): composition of water hyacinth by using GC

Component	Composition %
Cellulose	18
Hemicelluloses	28
Lignin	7
Other	46

Table (3): Composition of rice straw by using GC

Component	Composition%
Cellulose	43-49
Hemicelluloses	23-28
Lignin	12-16
Ash	15-20
Silica	9-14

3. Results and Discussion

of cellulosic material as corrosion inhibitor

Effect of pH on inhibitor efficiency

The pH of solution has been identified as the most important governing of corrosion inhibitor from the extract of water hyacinth on mild steel. The pH range 1-14, created and maintained by universal buffer solutions at room temperature $25^{o}C$, and the other factors that affecting on inhibitor efficiency (contact time, inhibitor concentration, solution volume) are constant. The obtained data indicate that as the pH is increasedthe corrosion inhibitor efficiency of cellulosic materials on the studied mild steel increases until pH9 then it is observed a little decrease. The inhibition efficiency may be interpreted based on the surface charge of the inhibitor and on the type of exiting metal ion species. When the pH increase, the effect of H^{+} ions competition decrease and the positive charge will be associated with OH^{-} and become neutral at certain pH range. Then at higher pH range the ions might result in lower the efficiency since the OH^{-} take place on the surface of the metal So the efficiency decrease. In the stronger acidic media the inhibition value decreased due to the effect of

competition of H^+ and M^{2+} on the negatively charged sites of the inhibitor surface sites (polymeric hydroxyl groups on the adsorption sites). The H^+ ions are much larger than ions of steel, so the corrosion inhibition% of metal ions is decreased.

Table (4): Effect of pH on inhibitor efficiency of water hyacinth inhibitor

pH	Weight loss (mg cm^{-2})	Inhibition efficiency/E(%)	Corrosion rate CR (mmyear^{-1})
1	0.080	18	0.02
2	0.073	20.5	0.019
3	0.064	21	0.015
4	0.05	23	0.01
5	0.043	25	0.009
6	0.0038	29	0.008
7	0.0026	74	0.0005
8	0.002	85	0.0004
9	0.0008	89	0.0002
10	0.0017	85	0.0004
11	0.0024	74	0.0006
12	0.0035	50	0.0008
13	0.005	35	0.0011
14	0.006	30	0.0013

Table (5): Effect of pH on inhibition efficiency of rice straw

pH	Weight loss (mg cm^{-2})	Inhibition efficiency E(%)	Corrosion rate (mmyear^{-1}) CR$\times10^3$
1	0.071	20	19
2	0.065	27	16
3	0.060	33	14
4	0.057	38	8
5	0.051	40	7
6	0.015	46	6
7	0.0039	55	0.7
8	0.0028	76	0.4
9	0.0005	92	0.2
10	0.002	88	0.4
11	0.0039	65	0.7
12	0.0041	52	0.8
13	0.0048	39	1
14	0.0055	33	1.1

Effect of inhibitor dose on corrosion

The effect of inhibitor dose on corrosion of mild steel was investigated in the relation to the amount of inhibitorwhere the other parameters (temp., pH, solution volume) were fixed. The illustrated data indicate that the corrosion inhibition % of metal ions increases with increasing the dose of inhibitor until the dose reach to 15ml, then the efficiency get decrease. That is clearly due to the affinity of ground plants surface area, associated with increasing the number of available adsorption(inhibition) sites upon increasing the amount of adsorbent(inhibitor).Therefore this results in an increase of inhibition efficiency until the adsorption sites get saturated then the efficiency of the inhibitor give constant value or get little decrease. The decrease in adsorption density can be

attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process.

Table (6): Effect of Inhibitor Dose on Inhibitor Efficiency of water hyacinth

Inhibitor dose	Weight loss (mg cm^{-2})	Inhibition efficiencyE (%)	Corrosion rate CR (mmyear^{-1})
0 ml	1.81	--	0.4
5 ml	0.382	37	0.08
10 ml	0.308	48	0.006
15 ml	0.235	67	0.005
20 ml	0.329	45	0.007

Table (7): Effect of inhibitor dose on inhibition efficiency of rice straw

Inhibitor dose	Weight loss (mg cm^{-2})	Inhibition efficiency E (%)	Corrosion rate (mmyear^{-1}) CR×10^2
0 ml	1.81	--	40
5 ml	0.37	79	4
10 ml	0.22	85	0.5
15 ml	0.2	91	0.3
20 ml	0.26	81	0.4

Effect of temperature on inhibitor efficiency

The effect of temperature of metal solutions on corrosion inhibition %of steelwasinvestigated at different temperatures in the range 308-338K while keeping the other parameters such as pH, solution volume, dosage of inhibitor, and metal concentration fixed.

The data obtained indicate that the efficiency of the inhibitor show decrease with increasing the temperatureof metal solution. Such effect may be due to the increase of dissolution process (desorption)of mild steel and partial desorption of the inhibitor from the

metal surface as the temperature increased. Also, as the temperature increases the attraction forces (polar attraction and Wander Vales forces) between the metal molecules and the adsorbent (inhibitor)' surface sites are loosened. Therefore, the rate of adsorption is decreased.

Table (8): Effect of temperature on inhibitor efficiency of water hyacinth

Temperature	Weight loss (mg cm^{-2})	Inhibition efficiencyE(%)	Corrosion rate CR (mmyear^{-1})
308 K	0.0008	87	0.0001
318 K	0.0016	84	0.00032
328 K	0.0027	66	0.00036
338 K	0.0045	39	0.001

Table (9): Effect of temperature on inhibition efficiency of rice straw

Temperature	Weight loss (mg cm^{-2})	Inhibition efficiency E (%)	Corrosion rate (mmyear^{-1}) CR$\times 10^4$
308 K	0.0008	91	1
318 K	0.002	89	2
328 K	0.0026	77	2.4
338 K	0.003	50	9

Effect of contact time on inhibitor efficiency

From the obtained data, it is quite clear that the corrosion inhibition% took place with an initially rapid rate. The effect of contact time was studied where the other conditions were constant.

So by increasing the contact time the efficiency of the inhibitor show decreasing. This is due to the fact that the surface area of the mild steel is completely covered at first rate. A further increase in contact time led to slight decrease in the covering inhibitor. So the efficiency show decrease in its value (adsorption decrease with increasing the contact time

and attend equilibrium at available time according to the initial concentration of inhibitor).These result due to the fact that the surface area of steel is completely covered at a fast rate.

Table (10): Effect of contact time on inhibitor efficiency of water hyacinth

Contact time	Weight loss (mg cm^{-2})	Inhibition efficiencyE(%)	Corrosion rate CR (mmyear^{-1})
48 h	0.0026	68	0.0005
24 h	0.0011	74	0.0002
3 h	0.0008	87	0.0001

Table (11): Effect of contact time on inhibition efficiency of rice straw

Contact time	Weight loss (mg cm^{-2})	Inhibition efficiencyE(%)	Corrosion rate (mmyear^{-1}) CR$\times10^4$
48 h	0.0015	69	2.7
24 h	0.001	82	1.9
3 h	0.0008	91	1

Effect of medium concentration on inhibitor efficiency

From the experimental work it will be shown that as the concentration of the medium increase, the efficiency of the inhibitor decrease. The decrease in inhibition efficiency can be attributed to the fact that as the conc. of HCl increases (corrosive media parameter) the acid medium is being more strong so the rate of inhibition decreased due to the effect of competition of H$^+$ and M^{2+} on the negatively charged sites on the metal and the inhibitor surface sites (polymeric hydroxyl groups on the adsorption sites on the surface of inhibitor). The H$^+$ ions are much larger than ions of steel, so the corrosion inhibition% of metal ions is decreased

Table (12): Effect of medium concentration on inhibitor efficiency of water hyacinth

Medium concentration	Weight loss (mg cm^{-2})	Inhibition efficiencyE(%)	Corrosion rate CR(mmyear^{-1})
0.5 M	0.0039	45	0.0008
1 M	0.0008	21	0.0015
2 M	0.009	19	0.002

Table (13): Effect of medium concentration on inhibition efficiency of rice straw

Medium concentration	Weight loss (mg cm^{-2})	Inhibition efficiencyE(%)	Corrosion rate (mmyear^{-1}) CR $\times 10^4$
0.5 M	0.0009	50	1
1 M	0.001	42	19
2 M	0.006	27	90

4. Conclusion

The corrosion is an important issue that faces the industry all over the world. So many researches have been studied to reduce the effect of corrosion by manufacturing inhibitor or natural product that can be used as corrosion inhibitor. Features of the natural inhibitors are non-toxicity, inexpensive and renewable. One of the most important examples of natural plants which can be used as corrosion inhibitors in Egypt are water hyacinth and rice straw. The water hyacinth is water floated plants that spread on the Nile River and the reason of many issues in the agriculture and irrigation fields, carrying disease and treating the aquatic life. So the government collect the water hyacinth and burn it which cause environment pollution although it can be used in useful ways. The rise straw was waste of agriculture fields with low cost and use in animal feeding.

In this study the sample plants will be investigated as corrosion inhibitor for mild steel which can be used in petroleum industry. The collected plants dried and crashed then

reflux it in soxhlet extractor with solvent as methanol then the extract will be concentrated to 100ml and make some experiments on it by changing in temperature, pH, inhibitor concentration, contact time, acid medium concentration(corrosive media) with samples of mild steel which known their weights and dimensions to know the best conditions that show the best inhibition efficiency % by using the weight loss method and the corrosion rate by using corrosion erosion method

The present study on the extract (100ml) showed maximum inhibition efficiency of 89 %. The inhibition efficiency % on metal surface was greater in rice straw than water hyacinth. And the corrosion rate showed minimum value of 0.003 mm year $^{-1}$ which it lower in rice straw than water hyacinth as the percentage of cellulose in the sample because of the hydrogen bond which make a film that covered the metal surface and protect it from corrosion . This protective film depended on (pH, inhibitor dose, temperature, contact time and medium concentration)

At weight loss method as the inhibition efficiency increases with increasing the pH value of the solution until pH 9 then give slight decreasing. Also, as the temperature increases the inhibition efficiency % decreases whereas the effect of the corrosive media on the inhibition efficiency showed similar behavior towards inhibition efficiency % of inhibitors

At corrosion erosion method as corrosion rate decrease with increasing the pH value of solution until pH 9 then the corrosion rate give slight increasing. Also as the temperature increase the corrosion rate increase whereas the effect of the corrosive media on the corrosion rate showed similar behavior

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الملخص باللغة العربية

فاعلية التثبيط لبعض المواد السليلوزية كمثبطات لتآكل الفولاذ الطري في صناعة البترول

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التحكم فى التآكل هو عنصر أساسي لتطوير العمليات الصناعيه طويله الامد. بما في ذلك قضايا مثل اختيار وتطوير مواد مقاومة للتآكل، والطلاء ومثبطات صديقة للبيئة.المثبطات الخضراء تصبح ذات أهمية كمصدر مقبول بيئيا ومتاحة وقابلة للتجديد وهي مصادر غنية بالمجموعات الوظيفيه التي لديها كفاءه تثبيط عاليه جدا. وهذه الرساله تعطى بعض الامثله من المنتجات الطبيعية التي تستخدم كمثبطات لتآكل الحديد الطرى المستخدم فى صناعه البترول. على غرار التصنيف العام لل"مثبطات" فأن "المثبطات الخضراء" يمكن أيضا أن تصنف إلى فئتين، مثبطات الخضراء وهي العضوية وغير العضوية. لتقييم أداء كفاءه المثبط فقد أجريت العديد من الاختبارات التي تشمل قياس التآكل من خلال الأساليب المعروفة فقدان الوزن، اختبار معدل التآكل .. لتحديد العوامل المؤثره على كفاءه(ورد النيل و قش للارز) كمثبطات للتآكل الحديد الطرى والظروف المناسبه للحصول على اعلى كفاءه لمثبط التآكل مع تغيير بعض العوامل مثل:

١. الاس الهيدروجينى
٢. تركيز الوسط الحامضى
٣. تركيز المثبط
٤. الوقت المعرض له الصلب لبيئه التآكل
٥. درجات الحراره

ومن هذه الدراسه نستنتج ان كلما زادت نسبه السيليلوز فى النبات زادت كفاءته كمثبط للتآكل نظرا لقوه الرابطه الهيدروجينيه بين جزيئات السيليلوز فتعمل كطبقه عازله للحديد الطرى من الوسط المحيط وانه يمكن تحويل بعض النباتات عديمه المنفعه الاقتصاديه ومسببه للتلوث البيئى وتؤثر بالسلب على الثروه السمكيه كمثبطات لتآكل الحديد الطرى ذات كفاءه عاليه دون استخدام مواد مكلفه او مضره للبيئه.