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CHARACTERIZATION AND EXTRACTION OF TANNIN FROM ARECA NUT WASTE AND USING IT AS RUST DEACTIVATOR

KIRANKUMAR RATHOD[1], M SHIVAPRASAD[2], RAJSHEKHAR[3]

[1]Assistant Professor, Department of Chemical Engineering, SDM college of Engineering and Technology, Karnataka, India, Email: kiri.rathod@gmail.com

[2]Student, Department of Chemical Engineering, SDM college of Engineering and Technology, Karnataka, India, Email: smatalainni@gmail.com.

[3]Student, Department of Chemical Engineering, SDM college of Engineering & Technology, Karnataka, India, Email: natikarrajshekhar1@gmail.com.

ABSTRACT

The type of extraction plays a vital role in leaching process. The percentage of extraction depends on various parameters like feed to solvent ratio, contact time, different solvents combinations, temperature and solubility. In our project "Characterization and extraction of tannin from areca nut waste and using it as a rust deactivator" was conducted to study some of above mentioned parameters. The tannin extracted from areca nut waste is used for formulation of rust deactivator.

The first part, involves the extraction of tannin for different feed to solvent ratios and at different contact time. In the second part, tannins extracted from areca nut is characterized by using UV-VIS Spectroscopy and FTIR spectroscopy. The last part, involves the formulation of rust deactivator and testing their rust deactivating effects on mild steel.

Keywords: *Deactivator, extraction, leaching, spectroscopy, tannin.*

1. INTRODUCTION

Areca nut is one of popular traditional herbal medicine used in Thailand. The activities of areca seeds are anthelmintic, antifungal, antibacterial, anti-inflammatory, antioxidant, insecticide, and lavicidal. The areca seed extract could inhibit enzyme elastase, act as parasympathomimetic on muscarinic receptor and at high dose on nicotinic receptor, increase smooth muscle tone, dilate blood vessel, decreased blood pressure and increase secretion (saliva and sweat).
The seed contains 50-60% sugars, 15% lipid (glyceride of lauric, myristic and oleic acid), 15% condensed tannins (phlobatannin, catechin), polyphenolics and 0.2-0.5% alkaloids (arecoline, arecaidine, guvacine and guvacoline).

1.1. PRODUCTS

1.1.1. Tannin or dyestuff

Long before the nature and properties of tannins were determined, the tannins in areca nut were being used for dyeing clothes, as adhesives in plywood manufacture, and for tanning standard for home use in South East Asia and the Pacific Ocean countries. The tannins are obtained as a byproduct in preparing immature betel nuts for chewing.

1.1.2. Fibre

The husk fibres are predominantly composed of cellulose with varying proportions of hemi-cellulose, lignin, pectin and protopectin. Based on various tests, it has been proposed that the husk fibres could be used in making such items as thick boards, fluffy cushions and non-woven fabrics. Trial experiments have shown that satisfactory yield and quality of brown wrapping paper could be prepared from blends of areca nut and bamboo or banana pseudo stem pulp.

1.1.3. Timber

Areca nut stem forms a useful building material in the villages, and it is widely used throughout South East Asia for a variety of construction purposes. The timber can also be used in making a variety of utility articles such as rulers, shelves and waste paper baskets. Nails made from areca stem are widely used in the furniture industry.

1.1.4. Lipids

The nut contains 8-12% fat that has characteristics comparable with hydrogenated coconut oil. It contains both saturated and unsaturated fatty acids. Areca nut fat can be extracted by using hexane as a solvent, and the fat can be made edible by refining it with an alkali. Simple blending of areca nut fat with butter fat followed by inter-esterification gives good products, acceptable in confectioneries.

1.1.5. Alcohol

Inoculated with Saccharomyces cerevisiae, the leaves of areca nut can be used as a fermentation stimulant in industrial alcohol production.

1.1.5. Poison

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The areca nut decoction as well as arecoline and its salts have been found to be effective on various helminthes infections such as those caused by Taenia spp.

1.1.6. Medicine

Areca nut is used against anemia, fits, leucoderma, leprosy, obesity and worms. In combination with otheringredients, it is also a purgative and an ointment for nasal ulcers. Kernels of green and mature fruits are chewed as an astringent and stimulant, often with the leaves or fruit of betel pepper (Piper betel) and lime.

1.1.7. Other products

Areca nut husk can be a good source of furfural. Possibilities of producing activated carbon from the husks have been investigated, and yields of 25-28% have been recorded.

2. BACKGROUND

2.1. BOTANICAL BACKGROUND OF ARECA NUTS

Areca nut is an erect, unbranched palm reaching heights of 12-30 m, depending upon the environmental conditions. The stem, marked with scars of fallen leaves in a regular annulated form, becomes visible only when the palm is about 3 years old. Girth depends on genetic variation and soil conditions.

Areca nut starts flowering from 3-4 years after planting. December-March is the main flowering season and harvesting period from June to July to get tender nuts and November-March for ripe nuts. The nuts are harvested at 45-50 days' interval in 3 pickings.

2.2. CONSTITUENTS OF ARECA NUTS

Four alkaloids have been conclusively identified in biochemical studies, arecoline, arecaidine, guvacine&guvacoline, of which arecoline is the main agent.

Four alkaloids were isolated from areca nuts. Arecoline ($C_8H_{13}NO_2$), a colorless, volatile, and oily, nicotine-like principle, identical with Bombalon's (1885) arekane. Arecaine ($C_7H_{11}NO_2+H_2O$) probably a betaine-like body, physiologically inert, forms permanent, colorless crystals, insoluble in ether, chloroform, and benzol, almost insoluble in absolute alcohol, but dissolving with ease in diluted alcohol and water. Arecaïdine ($C_7H_{11}NO_2+H_2O$), an isomer of arecaine and non-poisonous. A fourth alkaloid, discovered by Jahns, and called guvacine ($C_6H_9NO_2$), is the lower homologue of arecaidine, and non-poisonous.

2.2.1. CHEMICAL CONSTITUENTS OF ARECA NUTS

- Moisture content: 10-12%.
- Ash content at 85˚C: 4-6%.
- Tannin content: 50-60%.
- Specific gravity @ 20˚C: 1.54 g/cc.
- Bulk Density: 0.71 g/ml.
- Solubility in water: 800 g/liter.
- Viscosity mPa.s @ 30˚C -400g/l solution: 20 pass.

2.2.2. PHYSICAL AND CHEMICAL PROPERTIES:

- Reddish brown color.
- High tannin content.
- Excellent tanning properties.
- Uniform quality.
- Not dusty powerful astringent.
- Easily soluble in cold water.

2.3. TANNIN

Tannins (polyphenols) are produced via condensation of simple phenolics that are secondary metabolites and are widespread in the plant kingdom. Tannins do not constitute a unified chemical group, but have a variety of molecular structures. They are generally divided into hydrolysable (galloyl and hexahydroxydiphenoyl esters and their derivatives) and condensed proanthocyanidins (polymers of avan-3-ols). Tannins are biologically active compounds and may have beneficial or adverse nutritional effects. Tannins form insoluble complexes with digestive enzymes and dietary proteins. Some methods commonly employedin tannin analysis suffer from lack of specificity, as they do not distinguish polyphenols of nutritional concern from other low molecular weight phenols that also occur naturally in these products. All tannins have several common properties amongst them[2]:

- Are miscible with water in any ratio.
- Are insoluble in organic liquids such as: chloroform, ether, gasoline etc.
- Are polyvalent phenols derivatives.
- Are amorphous substances, very sensitive to oxidation and reduction in the presence of enzymes.
- Are hygroscopic and give birth to polydisperse colloidal solutions.

2.3.1. CLASSIFICATION OF TANNIN

The tannins are broadly classified into two groups based on the complexity of their chemical structures.[4]

Hydrolysable tannins are basically derived from simple phenolic acids like gallic acid or ellagic acid and when heated they give away pyrogallol.

On the other hand, condensed tannins, also known as non-hydrolysable tannins, do not split easily and hence it is difficult to analyze these.

Condensed tannins are basically flavonoid dyes formed through bio-synthesis of flavins and catechins. When these non-hydrolysable tannins are heated up in acids they synthesize to yield a red insoluble substance known as tannin reds or phlobaphenes.

2.3.2. PHYSICAL PROPERTIES

- SYNONYMS: tannin, tannins, "natural tannin", "gallotannic acid", gallotannin, glycerite
- FORMULA: $C_{76}H_{52}O_{46}$.
- COLOUR: Yellowish brown to Reddish brown.
- TASTE: Puckering taste.
- STATE: Non crystalline, powder or amorphous solid.

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- SOLUBILITY: Soluble in water, alcohol, dilute alkalis, glycerols and acetone.
- MOLECULAR WEIGHT: 1701.28 g/ mol.
- MELTING RANGE (°C): 198 - 218 decomposes.
- pH (1% solution): 5 approx.
- TOXICITY:Moderate.

2.3.3. CHEMICAL PROPERTIES

Precipitation: Tannins have ability to precipitate solutions ofGelatins, Alkaloids, Glycosides, Heavy metals, Protein.

Anti-oxidizing properties: It is because of accumulation of OH group on small size nucleus, these agents have oxidative nature.

Astringent: Tannins have property to react with protein of mucos membrane and cause precipitation.

Carcinogenicity: Prolong use of tannin containing plant material is hazardous because it causes cancer. Habitual use *Areca Catechu* can cause oral and esophageal cancer.

Reaction with salts:

Hydrozable tannin + ferric salt = blue black precipitates

Condensed tannin + ferric salt = brownish green precipitates

Reaction with potassium ferricyanide and ammonia:

Tannins + potassium ferricyanide/ammonia = Deep Red colour formation.

2.3.4. CORROSION INHIBITION:

Tannins are incompatible with alkalis, gelatin, heavy metals, iron, lime water, metallic salts, strong oxidizing agents and zinc sulphate, since they form complexes and precipitate in aqueous solution[2]. This turns advantageous as this can give rise to a passivation layer on reaction with the metal.

A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rates of a material, typically a metal or an alloy [3]. A common mechanism involves formation of a passivation layer, which prevents access of the corrosive substance to the metal. Mimosa tannins reduce both the cathodic and anodic processes, thus categorizing the tannins as mixed type inhibitors. The general fact remains that all tannins exhibit a decrease in efficiency with an increase in pH.

Tannins have been called rust converters since their presence converts active rust into compounds that are more stable and corrosion resistant, viz. Ferric tannate (major product), Ferric vivianate and Ferric phosphate complexes. Displacement of pre-adsorbed water molecules by adsorbing inhibitor molecules is the fundamental step of inhibition. One tannin molecule replaces four water molecules in the process of adsorption. Tannins can interact in three ways with the Fe ions. First, the tannins can complex with Fe2+ ions to form ferrous tannates, which are readily oxidised into ferric tannates in the presence of oxygen. Second, the tannins can react directly with Fe^{3+} ions to form ferric tannates[3]. And finally, due to the reducing capability of tannins, the Fe^{3+} oxides can be reduced to Fe_{2+} ions that can complex with tannins to form ferrous-tannates. The ferrous-tannates are then converted to ferric-tannates (blue-black in colour) when in contact with oxygen.

3. METHOD

3.1. LEACHING (liquid-solid extraction)

Leaching is the removal of a soluble fraction, in the form of a solution, from an insoluble, permeable solid phase with it is associated [2].

The separation usually involves selective dissolution, with or without diffusion, but in the extreme case of simple washing it consists merely of the displacement (with some mixing) of one interstitial liquid by another with which it is miscible. The soluble constituent may be solid or liquid; and it may be incorporated within, chemically combined with, absorbed upon, or held mechanically in the pore structure of the insoluble material. The insoluble solid may be massive and porous; more often it is particulates and the particles may be openly porous, cellular with selectively permeable cell walls, or surface activated.

3.2. TECHNIQUE FOR SOLVENT EXTRACTION

Solvent extraction may be made use of analytically for concentrating or rejecting a particular substance, or for the separation of mixtures. The extraction may be accomplished by the following two limiting processes.

3.2.1. Batch extraction

Batch extraction is the simplest and most widely used method. This method is used where a large distribution ratio for the desired separation is readily available. In this method, the solute is extracted from one layer by distributing it with a second immiscible layer until partition equilibrium has been attained. The two layers may be shaken in a separatoryfunnel. The layers are then allowed to settle out and the layer containing the desired constituent is removed.

3.2.2. Continuous extraction

Continuous extraction method is applicable when the distribution ratio is low. This method makes use of continuous flow of immiscible solvent through the solution to be extracted. Although partition equilibrium may not be achieved during the time of contact, solute is being removed continuously with the spent extraction solvent. If the extracting solvent is volatile, it is recycled by distillation and condensation and is dispersed in the aqueous phase with the help of a sintered glass disc or any other suitable device.

3.3. UV VISIBLE SPECTROSCOPY

The tannin concentration of the sample was measured using UV-Visible Spectroscopy. The diagram of the components of a typical spectrometer is shown in the following diagram. The functioning of this instrument is

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relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by aprism or diffraction grating[1]. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared[4]. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $\mathbf{I_0}$. The intensity of the sample beam is defined as **I**. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm. If the sample compound does not absorb light of of a given wavelength, I = I0. However, if the sample compound absorbs light then I is less than I0, and this difference may be plotted on a graph versus wavelength, as shown on the right. Absorption may be presented as transmittance (T = I/I0) or absorbance (A= log I0/I). If no absorption has occurred, T = 1.0 and A= 0. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λmax.

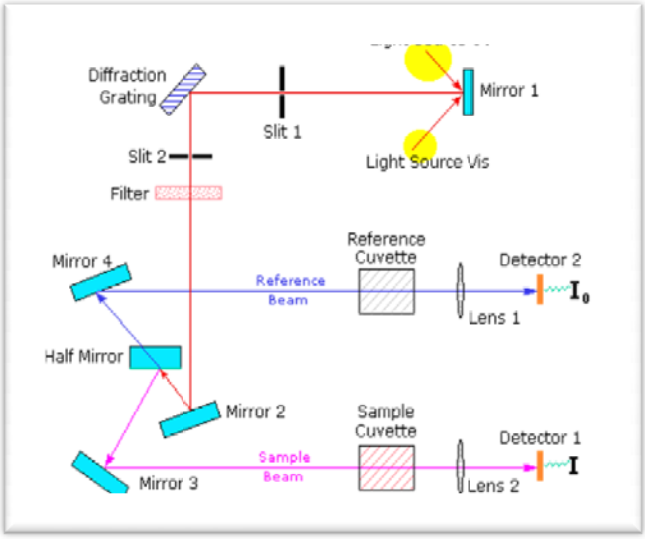

Figure 1: flow diagram uv absorption spectroscopy

Different compounds may have very different absorption maxima and absorbance. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are ater, ethanol, hexane and cyclohexane. Solvents having double or triple bonds, or heavy atoms (e.g. S, Br & I) are generally avoided. Because the absorbance of a sample will be proportional to its molar concentration in the sample cuvette, a corrected absorption value known as the molar absorptivity is used when comparing the spectra of different compounds.

4. EXPERIMENTATION

4.1. RAW MATERIAL

The raw material is the waste slurry from areca nut industry which is produced during manufacturing or processing of areca nut. This waste is disposed from hot water treatment of areca nuts which is rich in tannin. Raw material is collected from the Areca nut industry, Kundapur, Karnatak.

4.1.1 DRYING

The raw material is in form of slurry, therefore we are drying it in a laboratory scale rotary dryer to reduce or minimize the liquid moisture content of the material it is handle by bringing it into direct contact with a heated gas. This gas stream can either be moving toward the discharge end from the feed end (known as co-current flow), or toward the feed end from the discharge end (known as counter-current flow). The temperature maintained in the rotary drier is 90°C.

OBSERVATIONS

(i) Weight of raw sample taken to drier = 100 gms.
(ii) Weight of dried raw sample = 38.9 gms.

4.2. IDENTIFICATION:

Apparatus: Measuring cylinder, Test tubes, Pipette.

Chemicals Used: 1:1 Ferric chloride solution, Bromine water.

Ferric chloride test: Bluish black colour indicates the presence of the hydrolysable tannins.

Bromine test:No change in color is the identification of saturation in hydrolysable tannins.

4.3. EXTRACTION

- Step 1: Add dried raw sample and solvent (acetone) and vary the Feed:Solvent ratio from 1:20 to 1:30.
- Step 2: Stir the solution in beaker by varying the time from 45 min to 75 min.
- Step 3: Filter the solution with filter paper.
- Step 4: Take the residue and repeat the steps 1-3, two times for high yield.
- Step 5: Take the filtrate in rotary drier for tannin powder.
- Step 6: Take the extracted tannin for tannin identification test

4.4. RUST DEACTIVATOR

Mild steel (containing Carbon, 0.16%, Magnesium 0.53%, Silicon 0.16% and Iron 99.25%) specimen is used. Mild-steel panels approximately 7.0 cm x 15.0 cm and 2.5 mm

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thick which had been mechanically wire-brushed and abraded with aluminium oxide paper down to visual brightness and free of any residual rust were used as exposure panels and a steel panel without any coating was included as a control.

The panels were subjected to the salt spray for 24 hours, after which they were removed from the chamber. Uniform rust formation was allowed to take place over the surface. As mentioned earlier, tannin was tested as a rust deactivator by two different methods. The first method is by using mild steel plates that have been rusted by 3% sodium chloride. A solution containing 5% phosphoric acid, 10% tannin aqueous, 0.25% isopropanol was applied on two rusted plates and left for 1 day and a week at room temperature. Any changes that happened on these plates were observed after 1 day and a week.

(b) Rust deactivator.

The second method was done by applying the solution that containing 5% phosphoric acid, 10% tannin aqueous and 0.25% isopropanol on two different plates. These plates were then left for 1 day to dry before rusted it by 3% sodium chloride and left for 1 day. The changes were observed after 1 day and a week. Half of the plates were brushed using sandpaper to discover the affection of the solution on those plates.

5. ANALYSIS

5.1. FTIR ANALYSIS

The tannin extract was examined in order to better compare the fraction resulting from with those resulted from standard tannin. For the standard tannin, that must contain components able to mask certain absorption bands, a spectra deconvolution was imposed. The IR-spectra of the standard tannin and of the tannin extract contain bands that can be assigned to the ellagic acid, the main constituent.

The ketonic group valence vibration C=O is located at 1694 cm-1 in the pure tannin extract spectra, and at 1710 cm-1 for the standard tannin spectra (probably due to the participation in other bonds). The ≡C-H group vibrations C-H are centred at 2990 cm-1 for the tannin extract and at 2928 cm-1 for the standard tannin. The symmetrical and asymmetrical C-O valence vibration appears at 1366 cm-1 and at 1056 cm-1 respectively for the tannin extract and at 1322cm^{-1} and 1083 cm-1respectively, for the standard tannin. The vibrations assigned to aromatic rings are located between 1617 cm-1 and 1451 cm-1.

Both characteristic absorption peaks of the tannin extract and standard tannin can be observed in the FTIR spectrum of the industrial waste of areca nut tannin extract indicating that tannin is mainly present in the dried raw sample.

5.2. ESTIMATION OF TANNIN

5.2.1. PREPARATION OF STANDARD SOLUTIONS AND BLANK SOLUTIONS

1st Dilution: Weigh 100gms of both the raw sample and the standard tannic acid, take it in two separate 100ml volumetric flask and dilute it upto the mark and shake them thoroughly.

2nd Dilution: Take 1ml solution from each volumetric flask of 1st dilution in two 100ml volumetric flask seperately and again dilute it upto mark and shake them thoroughly.

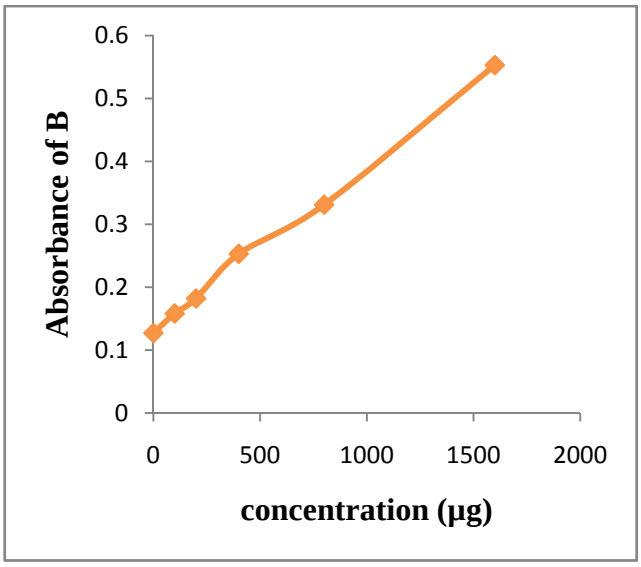
Take 5, 10 and 15 ml of given solution of raw sample solution in different 20 ml test tubes. Add 1ml of 1:1 ferric chloride solution to each of the test tubes and dilute it upto 20 ml and shake them thoroughly. Prepare blank solution in 20 ml test tube by taking 1 ml 1:1 ferric chloride solution and dilute it upto 20 ml. Blank solution is used in order to account for the absorbance light by water and ferric chloride.

Take 0.1, 0.2, 0.4, 0.8 and 1.6 ml of given solution of standard tannic acid sample solution in different 10 ml test tubes. Add 1ml of 1:1 ferric chloride solution to each of the test tubes and dilute it upto 10 ml and shake them thoroughly. Prepare blank solution in 10 ml test tube by taking 1 ml 1:1 ferric chloride solution and dilute it upto 10 ml.

5.2.2. ESTIMATION

Plot a graph of concentration of standard tannic acid versus absorbance of standard tannic acid solutions at 560nm and obtain a standard curve. This standard curve is known as calibration curve. Calculate the slope of the calibration curve and calculate the quantity of tannic acid in the raw sample.

$$Amount\ of\ Tannin = \frac{\text{Absorbance of A}}{\text{Slope X dilution fator}}$$



Slope 0.0003

7. RESULTS AND DISCUSSION

7.1. DISCUSSION

Variation of % Recovery of Tannin V/s F/S ratio

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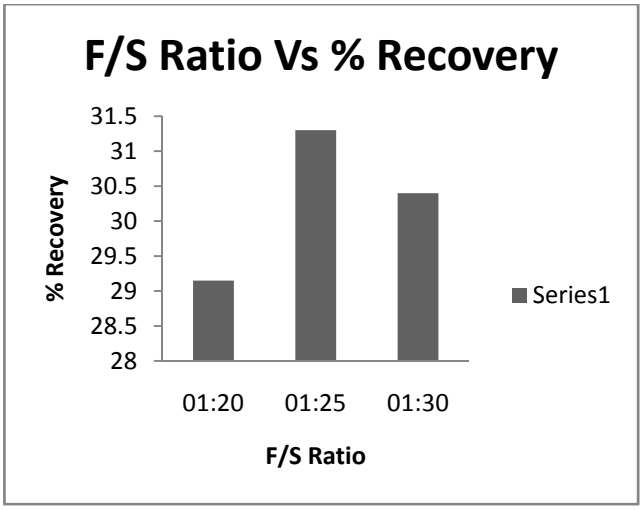
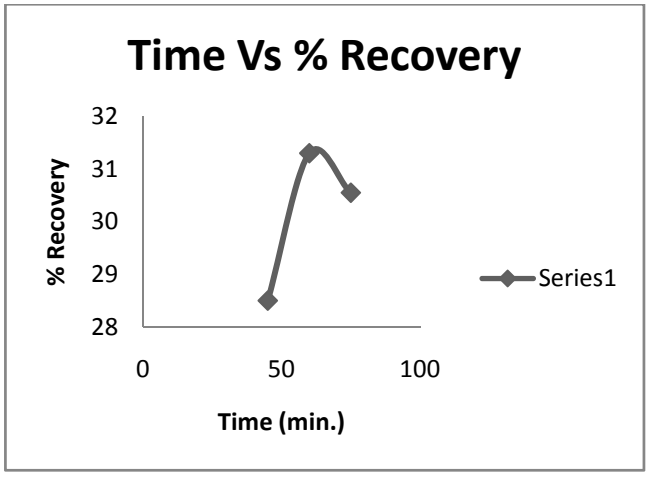


Above plot shows that maximum recovery is obtained at 1:25 ratio. The effect of solvent concentration to achieve maximum degree of tannin extraction was studied by varying the solvent concentration between 20ml to 30 ml and it was found that the optimum solvent concentration for maximum tannin extraction is 30 ml.

7.3.1. Variation of % Recovery of Tannin V/s Time



Plot shows that maximum recovery is obtained at 60 minutes of contact time. The effect of time to achieve maximum degree of tannin extraction was studied by varying the time period between 45 min to 75 min and it was found that the optimum time period for maximum tannin extraction is 60 minutes.

7.3.2. Effect of Rust Deactivator

It can be seen from fig that the plate covered with tannin formulation showed less blackspots after one week compared to the plate surface after one day treated. The rust was cleared without indelible marks when it was cleaned with sandpaper. Again, this indicates that rusting process has been deactivated due to the presence of tannin formulation where it acts as a shield to the plate.

Figure 2: plate applied with tannin formulation after one week.

8. CONCLUSIONS

The aim of this study was to determine the amount of total tannin from dried raw sample Results indicated the possibility on changing feed:solvent ratio and time process that resulted approximated 30% of tannins from raw sample.

Tannins had shown a considerable anticorrosive property as a rust converter. Tannins based rust converter was not able to achieve a good corrosion protection in aggressive environments for long periods of exposure. It could only be used for temporary corrosion protection. The anticorrosive property of extracted tannins indicated that it could be developed for future use in the various corrosion protection areas.

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BIOGRAPHIES

Mr. Kirankumar Rathod, working as Assistant Professor in Department of Chemical Engineering, SDM College of Engineering & Technology, Dharwad, Karnataka, India. Since 2010, he has 6 international journal publications.

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	**Mr. M Shivaprasad**, is pursuing his Bachelor of engineering degree in Department of Chemical Engineering, SDM College of Engineering & Technology, Dharwad, Karnataka, India.
	**Mr. Rajshekhar,** is pursuing his Bachelor of engineering degree in Department of Chemical Engineering, SDM College of Engineering & Technology, Dharwad, Karnataka, India.