

Chemical analysis of agro-pollutant coir pith- a byproduct of coir industry

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Abstract— Coir pith is a byproduct of coir industry. It is dumped as an agricultural waste for a long period of time. Usually it is disposed by burning which may release lot of carbon into atmosphere causing air pollution. Coir waste has a high lignin and cellulose content. its carbon nitrogen ratio is around 100:1. Because of the high lignin content Left to itself, coir waste takes decades to decompose. Thus it is leached out during course of time due to rain in to water resources causing water pollution. Enhanced microbial activity due to climatic effects eventually degrades the pith. Coir pith is recalcitrant and accumulates in the environment forming hillocks posing environmental pollution in the areas close to coir fiber extraction units. In this study, 4 samples of coir pith at different stages as a function of time were selected and the chemical contents were compared for the degradation studies. It was observed that the raw coir pith contained higher chemical contents. Therefore, coir pith can be treated with the help of microbes in the raw stage itself and can be used as the raw material for plant growth in an eco-friendly way.

Keywords— Cellulose, Coir pith, Electrical conductivity, Lignin, pH, Total dissolved solids.

I. INTRODUCTION

Coir pith is a Lignocellulosic substrate, usually dark brown in color, light weight corky dust that decomposes very slowly in soil as it contains 30%-35% of Lignin; particle size varies from 100-300 microns similar to peat moss. It is porous structured and the pores are responsible for allowing good aeration around the roots of plants and retain water content in the pores for rewetting when dry. Chemical analysis reveals that coir pith contains three major constituent: cellulose, hemicellulose and lignin. The fungi species has the ability to slowly degrade lignin and is capable of detoxifying phenolic compounds and also produce enzymes (Paramanandham et al., 2014).

Coir waste is a spongy material that binds the coir fiber in the husk . In the process of extraction of coir fiber from husk, generally about one third of it is obtained as fibre and two third of it is obtained as coir waste. Coir waste is used as a soil conditioner, surface mulch, rooting medium, highly compressible and desiccant. Coir waste absorbs water in the range of 400-600% its weight and releases it into the soil very slowly. Composted coir waste is an excellent organic manure and is used as an eco friendly peat moss substitute. This is effective against saline and alkaline condition of soil(Savithri and Hamed Khan, 2004).

1.1 Effects of coir pith on the environment

The coir industry is one of the major agro-based industries and it requires a large amount of water and consequently generates an equally large quantity of waste water, which contains lignin, cellulose, soluble tannin like phenolic compounds. The effluent generated from the coir industry is acidic, also contains toxic substances(Vinodhini et al., 2006).

Coir pith is a biomass residue generated during the extraction of coir fiber from coconut husk and is a byproduct of the coir manufacturing industry. It is a ligno-cellulosic material forming about 70%of the coconut husk. Normally, coir pith is dumped as agricultural waste and become accumulated as a waste product in the form of heaps of coarse and fine dust. These agricultural wastes have traditionally been disposed of by burning, which resulted in various environmental problems, including carbon deposits as well as the warming of the atmosphere. During the rainy season , the tannins and phenols of the coir pith leached out into the soil and the irrigation canals, thereby making agricultural lands unproductive . Moreover, the water pollution caused by such leaching is harmful to the aquatic and soil biological life(Antara et al., 2015).

Coir pith degrades very slowly and it remains in the soil for a very long period of time, however due to the natural climatic effect of repeated washing in the rains, leading to enhanced microbial activity which eventually degrades the pith. Coir pith is recalcitrant and accumulates in the environment forming hillocks posing environmental pollution in the areas close to coir fiber extraction units.

Coir industries and fiber extraction units contribute considerably to the problems of environmental pollution, both land and water pollution. During monsoon rains leaching of tannins and salts from the hillocks of coir pith leads to ground water pollution and may be magnified up the food chain to levels that are harmful for wild life and possibly for humans because most of these pollutants are extremely difficult to remove by waste treatment methods. Therefore, biodegradation of coir pith is essential to control the pollution caused by accumulation (Warrier and Moudil., 1947). Even though coir pith is a problematic waste, it is a potential wealth that can be converted into valuable organic manure by microbial degradation.

Here, an attempt to study the physical and chemical properties such as pH, Electrical conductivity, Total dissolved solids, Lignin content (Acid soluble and Acid insoluble), Cellulose content (Alpha, Beta, Gamma) of coir pith of different ages (1, 7, 14, 21 days old) at different stages was made.

II. MATERIAL AND METHOD

2.1 Collection of coir pith

The coir pith was collected from the industrial area TANCI, Krishnagiri, Tamilnadu.

2.2 Estimation of basic parameters

The basic parameters such as pH, Electrical conductivity, Total Dissolved Solids were determined for all the samples using pH meter, conductivity meter and the results were tabulated.

2.3 Estimation of chemical contents

The sample was hydrolyzed similar to the standard methods (Scandinavian Pulp, Paper and Board Testing Committee CM 71:09, Technical Association of the Pulp and Paper Industry T 249 cm-00), for the estimation of the high lignin content in precipitated lignin samples cause prolonged filtering time. After hydrolysis, the sample was filtered, the acid-insoluble residue was determined gravimetrically (Technical Association of the Pulp and Paper Industry T 222 om-02), and the acid-soluble lignin was determined spectrophotometrically (Technical Association of the Pulp and Paper Industry UM 250).

Samples were extracted consecutively with 17.5% and 9.45% sodium hydroxide solution. The soluble fraction, consisting of beta and gamma celluloses was determined by oxidation with potassium dichromate, and the alpha-cellulose, as an insoluble fraction by T 203 cm-99 method using titration.

2.4 Lignin content

2.4.1 Test material preparation

- A test portion of (100 ± 10) mg to the nearest 0.1 mg was weighed and added into a glass beaker with a volume of at least 150 ml.
- The oven-dry weight of the test portion that is a portion of the sample material was weighed to determine the dry matter content by drying at 105°C until constant weight was achieved (The International Organization for Standardization 638) and recorded in grams.

2.4.2 Acid-Insoluble Residue (AIR)

- 10 ml of 72 % sulphuric acid with a pipette was added to the test material in the beaker and stirred with a glass rod until the test material began to dissolve.
- The beaker was placed in a $(30 \pm 0.5)^{\circ}\text{C}$ water bath for 1 h, 28 ml of water was added and stirred occasionally.
- The beaker was covered with aluminium foil and placed in an autoclave at $(120 \pm 5)^{\circ}\text{C}$ for 1 h and then allowed to cool to approximately 80°C .
- The content of the beaker was filtered while hot through a single or double pre-weighed glass fiber filter and was transferred to a separate beaker (this filtrate was used for the determination of acid soluble lignin).
- The retained residue was washed with hot water (check with pH-indicator paper) while the filter with residue was removed from the filter container carefully and allowed to dry overnight at 105°C , cooled down in exsiccator and weight increase was determined (i.e. the acid-insoluble residue).

2.4.3 Acid-Soluble Lignin (ASL)

- 10 ml of 72 % sulphuric acid was added with a pipette to the beaker with test material and the contents were stirred with a glass rod until the test material began to dissolve.
- 28 ml of water was added then the beaker was heated and to approximately 80 °C, and was filtered while still hot.
- The content of acid-soluble lignin in the filtrate was determined spectrophotometry at 205 nm. The filtrate was diluted until the absorption was in the range of 0.2–0.7 AU.

Calculation

Acid-insoluble residue (AIR)

$$AIR = \frac{m}{M} * 1000 \quad (1)$$

Where,

m = the weight increase (i.e. the residue after drying), in g

M = Oven-dry weight of sample (i.e. as 100% dry matter) before acid hydrolysis/suspension, in g

Acid-soluble lignin (ASL):

$$ASL = \frac{A * D * V}{a * b * M} * 1000 \quad (2)$$

Where,

A = Absorption at 205 nm

D = Dilution factor

V = Volume of the filtrate, in l (here: 0,029 l)

a = Extinction coefficient of lignin, in g/l cm (here: 110 g/l cm, according to TAPPI UM 250)

b = cuvette path length, in cm (here: 1 cm)

M = Weight of sample (as 100% dry matter) before acid hydrolysis/suspension, in g

Total lignin content:

$$\text{Total lignin content} = \text{AIR} + \text{ASL} \quad (3)$$

2.5 Cellulose contents

2.5.1 Reagents

Sodium hydroxide solution: 17.5% Sodium Hydroxide by weight, 5.21±0.005N, carbonate free. A concentrated (about 50%) Sodium Hydroxide solution was prepared and left to stand until the suspended carbonates was settled. Then decant clear solution was diluted with Carbon-dioxide-free (recently boiled) distilled water, and the normality was adjusted to 0.005N.

Potassium dichromate solution, 0.5N: 24.52 g of Potassium dichromate solution was added in water and diluted to 1000 M

Sulfuric acid: concentrated Sulfuric acid, 96 to 98%, specific gravity 1.84.

Sulfuric acid 3N: 83.5 ml of concentrated Sulfuric acid was added to an excess of water and diluted to 1000 ml.

Ferrous ammonium sulfate solution, 0.1N: 40.5 g of ferrous ammonium sulfate was added in water then 10 ml of concentrated Sulfuric acid was added and diluted to 1000 ml. The solution was not stable and the exact normality was thus determined daily by titration with 0.100N potassium dichromate standard solution.

Phenanthroline – ferrous sulfate: 1.5 g of 1, 10-phenanthroline monohydrate and 0.7 g of Ferrous sulfate was added to 100 ml of water. The indicator solution was also available commercially as Ferroin.

2.5.2 Preparation of filtrate

- The test specimen (1.5g±0.1g) was placed in a 300 ml tall-form beaker and 75 ml of 17.5% Sodium Hydroxide reagent was added, and adjusted previously to 25±0.2 °C. The time at which the reagent added was noted.
- The pulp within the apparatus was stirred until it completely gets dispersed. The air was avoided from drawing into the pulp suspension. During stirring, air was not allowed into the pulp suspension.
- When the pulp gets dispersed, the stirrer was raised and then adhered pulp fibers were removed with a pointed glass rod. The stirrer was rinsed with 25 ml of 17.5% Sodium Hydroxide reagent, added to the beaker, so that exactly 100 ml of the reagent have been added to the pulp. The pulp suspension was stirred with a rod and placed in a bath at 25± 0.2°C.
- After a period of 30 minutes from the first addition of the Sodium Hydroxide reagent, 100 ml of distilled water at 25±0.2°C was added to the pulp suspension and stirred thoroughly with a rod.
- The beaker was left in the bath for another period of 30 minutes so that the total extraction time would be 60 ± 5 minutes.
- At the end of the 60minutes period, the pulp suspension was stirred with a rod and transferred to a filtering funnel. The first 10 to 20 ml of the filtrate was discarded and about 100 ml of the filtrate was collected in a clean and dry filtration flask.

2.5.3 Alpha-cellulose determination

- 25 ml of the filtrate and 10 ml of (0.5 N) potassium dichromate solution was pipetted out into a 250 ml flask.
- 50 ml of concentrated Sulfuric acid was added while swirling the flask and allowed to remain hot for 15 minutes, then 50 ml of water was added and cooled to room temperature.
- 2 to 4 drops of the ferroin indicator was added and titrated with (0.1 N) ferrous ammonium sulfate solution to a purple color.
- Blank titration was made by substituting the pulp filtrate with 12.5 ml of 17.5% Sodium Hydroxide and 12.5 ml of water.

2.5.4 Beta- and gamma-cellulose determination

- 50 ml of the pulp filtrate was pipetted out into a 100 ml graduated cylinder having a ground glass stopper. 50 ml of 3 N Sulfuric Acid was added and mixed thoroughly by inverting.
- The cylinder was heated by submerging in a hot water bath at about 70⁰-90⁰C for few minutes to coagulate the beta-cellulose. Then the precipitate was allowed to settle for several hours, preferably overnight and filtered to obtain a clear solution.
- 50 ml of the clear solution and 10 ml of 0.5 N potassium dichromate solution was pipetted out into a 300ml flask and 90 ml of concentrated Sulfuric acid was added cautiously. The solution was allowed to remain hot for 15 mins and titration was carried out until purple color is achieved.
- Blank titration was made by substituting the pulp solution with 12.5 ml of 17.5% Sodium Hydroxide, 12.5 ml of water and 25 ml of 3 N Sulfuric Acid. (T 203 cm-99)

Calculation

Calculate the alpha-cellulose content in pulp:

$$\alpha \text{ Cellulose } \% = 100 - \frac{6.85(V2 - V1) * N * 20}{A * w} \quad (4)$$

Where,

V1 = titration of the pulp filtrate, ml

V2 = blank titration, ml

N = exact normality of the ferrous ammonium sulfate solution

A = volume of the pulp filtrate used in the oxidation, ml

W = oven-dry weight of pulp specimen, g

- Calculate the beta-cellulose content in pulp:

$$\beta \text{ Cellulose } \% = \frac{6.85(V4-V3)*N*20}{25*w} \tag{5}$$

Where,

V3 = titration of the solution after precipitation of beta-cellulose, ml

V4 = blank titration, ml

- Calculate the beta-cellulose content in pulp:

$$\gamma \text{ Cellulose } \% = 100 - (\alpha \text{ Cellulose } \% + \beta \text{ Cellulose } \%) \tag{6}$$

III. RESULTS AND DISCUSSION

pH is a numeric scale used to specify the acidity or basicity of an aqueous solution. It is roughly the negative of the logarithm to base 10 of the molar concentration, measured in units of moles per liter, of hydrogen ions. The pH values of coir pith filtrate of different ages are in table 1.

**TABLE 1
PH OF VARIOUS AGES OF COIR PITH**

Samples	Fresh	Partially fresh	Partially old	Old
1 Day	6.04	6.88	6.91	7.17
7 Days	6.08	7.22	7.09	7.21
14 Days	6.21	7.43	7.16	7.24
21 Days	6.23	7.67	7.29	7.31

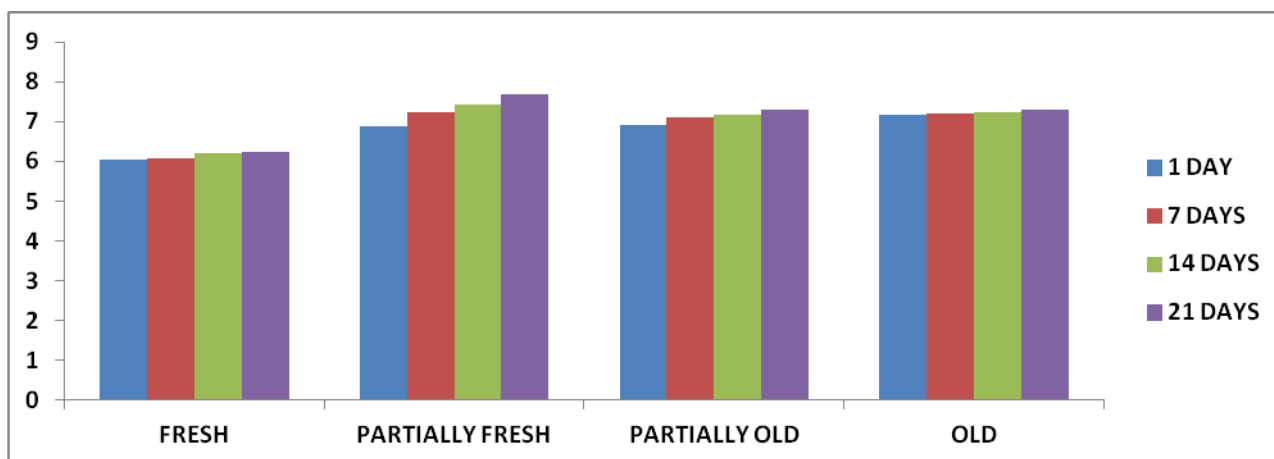


FIG. 1: GRAPH SHOWING DIFFERENT AGES OF COIR PITH AND ITS pH VALUE AT DIFFERENT STAGE

It has been found (Fig.1) that the sample which is 21 days old has high pH while for others it is less in all the four stages. The pH values differed as a function of time (Priya et al., 2016) and the filtrate was found to decrease in the acidic range slowly of pH in all the four stages.

Electrical conductivity is the measure of a material’s ability to accommodate the transport of an electric charge. It is usually expressed in Siemens per meter. Table 2 shows the results of analysis of samples on their conductivity.

TABLE 2
ELECTRICAL CONDUCTIVITY OF VARIOUS AGES OF COIR PITH

Samples	Fresh	Partially fresh	Partially old	Old
1 Day	939	339	307	270
7 Days	932	321	300	254
14 Days	926	305	274	231
21 Days	922	300	254	219

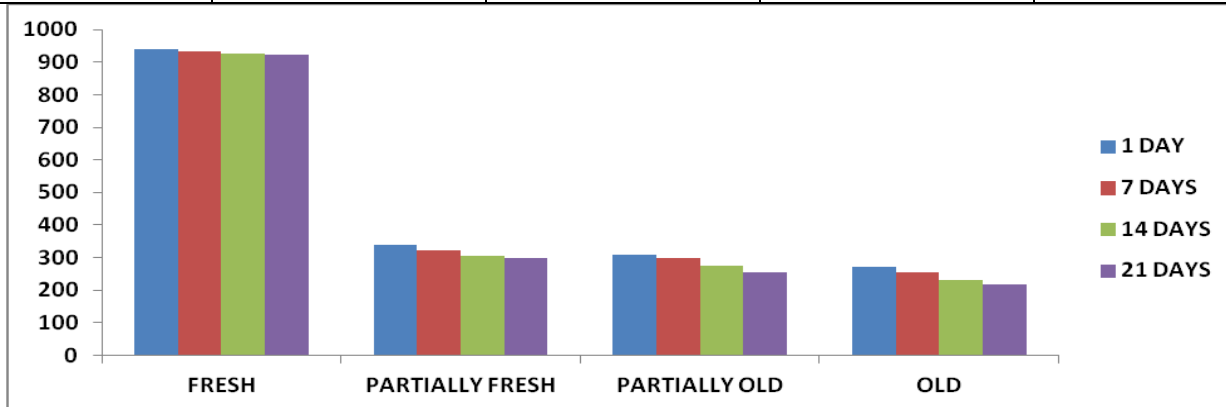


FIG. 2: GRAPH SHOWING DIFFERENT AGES OF COIR PITH AND ITS CONDUCTIVITY

The higher conductivity changes the chelating properties of water bodies and produces an imbalance of free metal availability (Ajitha et al., 2015). The EC was observed (Fig.2) to reduce rapidly in the start from the fresh sample to the partially fresh sample but reduces slowly and later, proving that the natural degradation by microbes which had been used as its substrate. It was found that the microbial activity was high in the beginning but decreases further indicating the reduction in substrate content. This is in accordance with the results obtained by Priya et al (2016).

Total dissolved solids is a measure of the combined content of all inorganic salts(principally calcium, magnesium, potassium, sodium, chlorides, bicarbonates and sulfates) and a small amount of organic substances contained in a liquid in molecular, ionized or micro-granular suspended form. Table 3 shows the amount of total dissolved solids present in the samples.

TABLE 3
TOTAL DISSOLVED SOLIDS PRESENT IN DIFFERENT AGES OF COIR PITH

Samples	Fresh	Partially fresh	Partially old	Old
1 Day	619	221	202	153
7 Days	615	217	185	147
14 Days	609	209	169	129
21 Days	608	204	151	106

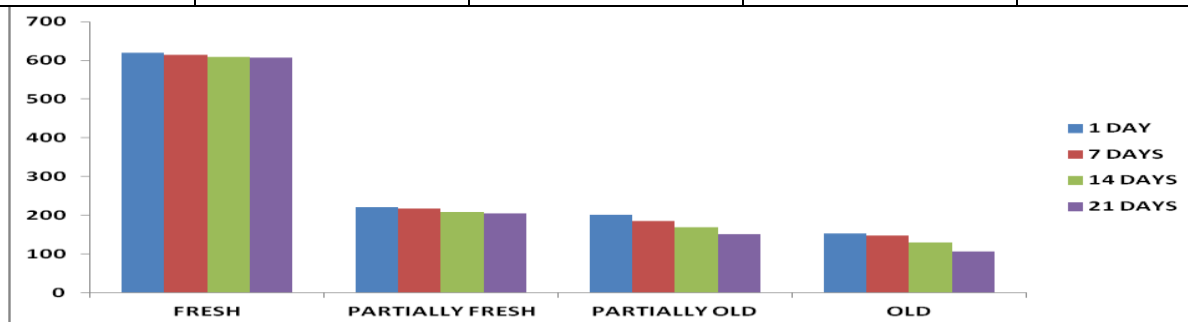


FIG. 3: GRAPH SHOWING AGES OF COIR PITH AT DIFFERENT STAGES VERSUS ITS TOTAL DISSOLVED SOLID CONTENT

The TDS was observed (Fig.3) to be very high in the fresh sample which can be never used for any purpose, as it was getting older. The large amount of TDS was due to the presence of both organic and inorganic salts (Rojith and Bright Singh, 2013). TDS was recorded to have reduced values since most of the sample was used by the microbes as substrate. The result is in par with Priya et al (2016).

Cellulose is an abundant renewable carbon source on earth. It is an important structural component of many plants, also present in some algae and bacteria. The cellulose is of three types; alpha, beta, gamma cellulose. The percentage of the three types of cellulose in the samples after analysis is given in the Tables 4(a) and 4(b).

TABLE 4: (A)
CELLULOSE CONTENT OF FRESH AND PARTIALLY FRESH COIR PITH

Samples	Fresh			Partially fresh		
	α cellulose	β cellulose	γ cellulose	α cellulose	β cellulose	Γ cellulose
1 Day	83.91	0.50	15.59	90.12	-1.11	10.99
7 Days	82.12	0.47	17.41	88.55	-1.04	12.49
14 Days	81.36	0.42	18.22	82.31	-1.06	18.75
21 Days	78.32	0.39	21.29	81.98	-0.88	18.90

TABLE 4: (B)
CELLULOSE CONTENT OF PARTIALLY OLD AND OLD COIR PITH

Samples	Partially old			Old		
	α cellulose	β cellulose	Γ cellulose	α cellulose	β cellulose	Γ cellulose
1 Day	91.12	-0.90	9.78	95.51	0.15	4.34
7 Days	91.07	-0.74	9.67	90.28	0.04	9.68
14 Days	85.21	-0.58	15.37	84.21	0.01	15.778
21 Days	74.33	-0.51	26.18	76.91	0.009	23.0805

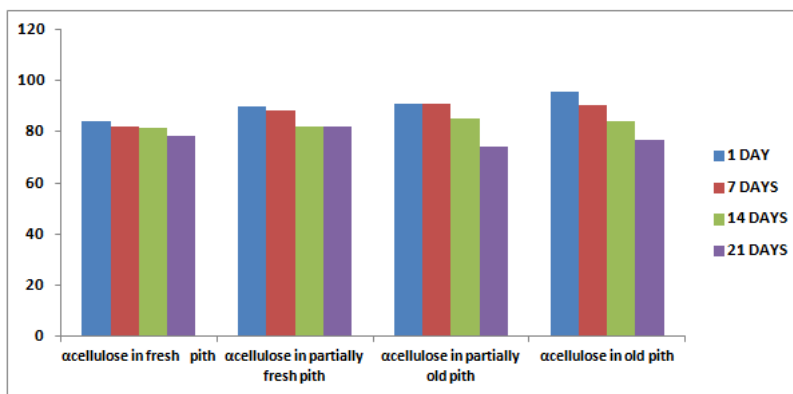


FIG. 4(A): GRAPH SHOWING DIFFERENT AGES OF COIR PITH VERSUS ITS A CELLULOSE CONTENT AT DIFFERENT STAGES

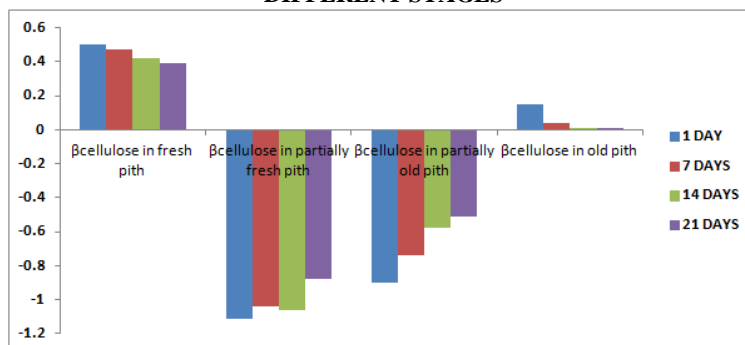


FIG. 4(B): GRAPH SHOWING DIFFERENT AGES OF COIR PITH VERSUS ITS B CELLULOSE CONTENT AT DIFFERENT STAGES

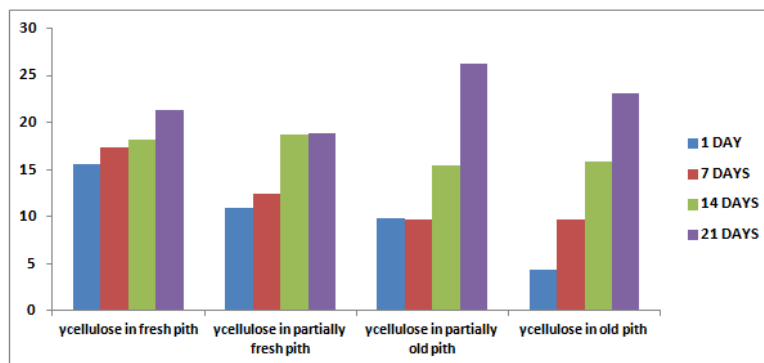


FIG. 4(C): GRAPH SHOWING DIFFERENT AGES OF COIR PITH VERSUS ITS CELLULOSE CONTENT AT DIFFERENT STAGES

The presence of cellulose and lignin is highly responsible for carbon fixation in soil and since it takes long time for the pith to degrade these polymers cause soil pollution and also water pollution if they are leached due to rain. It was found that the cellulose content was lower in old sample as the microbes performed decomposition. The result is similar to the work carried out by Priya et al (2016).

Lignin is an organic substance binding the cells, fibers and vessels of plants. They are particularly important in the formation of cell walls because they lend rigidity and do not rot easily. It is also a renewable carbon source. Based on their solubility lignin may be of 2 types; acid soluble and acid insoluble. The results are shown in Tables 5(a) and 5(b).

**TABLE 5 (A)
LIGNIN CONTENT OF FRESH AND PARTIALLY FRESH COIR PITH**

Samples	Fresh			Partially fresh		
	Acid soluble lignin	Acid insoluble lignin	Total lignin content	Acid soluble lignin	Acid insoluble lignin	Total lignin content
1 Day	1.49	413.04	414.53	1.41	326.53	327.94
7 Days	1.48	411.98	413.46	1.40	322.09	323.49
14 Days	1.45	409.64	411.09	1.39	321.55	322.94
21 Days	1.44	407.98	409.42	1.38	320.12	321.50

**TABLE 5 (B)
LIGNIN CONTENT OF PARTIALLY OLD AND OLD COIR PITH**

Samples	Partially old			Old		
	Acid soluble lignin	Acid insoluble lignin	Total lignin content	Acid soluble lignin	Acid insoluble lignin	Total lignin content
1 Day	1.38	192.98	194.36	1.33	86.95	88.28
7 Days	1.34	190.12	191.46	1.31	84.23	85.54
14 Days	1.32	184.51	185.83	1.28	80.64	81.92
21 Days	1.28	180.65	181.93	1.22	74.09	75.31

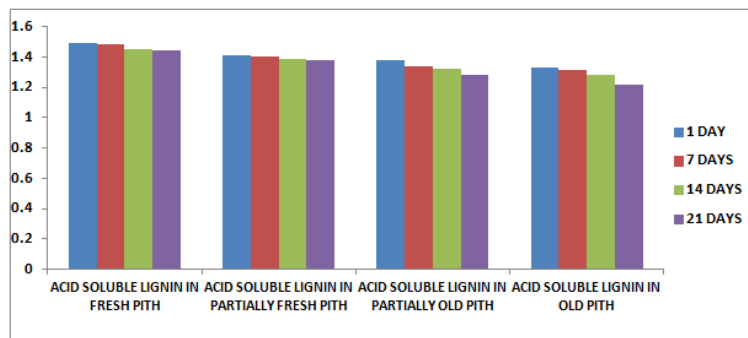


FIG. 5(A): GRAPH SHOWING DIFFERENT AGES OF COIR PITH VERSUS ITS ACID SOLUBLE LIGNIN

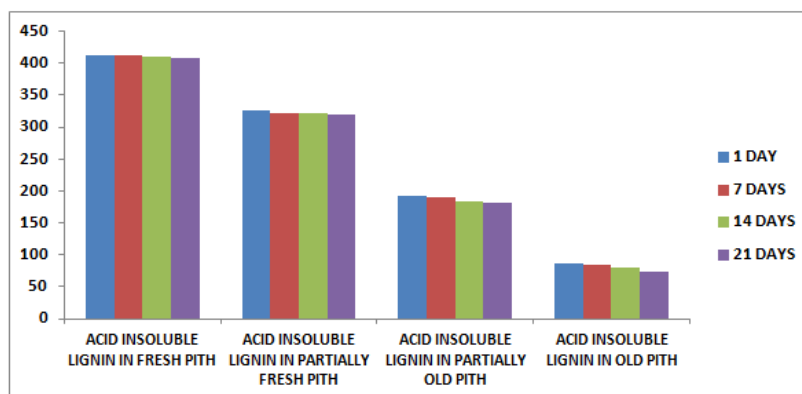


FIG. 5(B): GRAPH SHOWING DIFFERENT AGES OF COIR PITH VERSUS ITS ACID INSOLUBLE LIGNIN

Among the collected samples, the total lignin content was observed to be higher in the raw coir pith samples (Priya et al., 2016). It was found that the decomposition was faster in the 21 days old sample followed by 14 days, 7 days, 1 day which implies that decomposition occurred.

IV. CONCLUSION

Coir pith which is an industrial byproduct can be utilized as a raw material for various processes which in turn should be decomposed completely. When the coir is accumulated for a long period, it will end up in causing environmental pollution. Polyphenolics exudation from the coir may affect Nitrogen release by forming complexes with proteins, which stops decomposition. In this study, four samples of coir pith at different stages as a function of time were selected and the chemical contents were compared for the degradation studies. It was observed that the natural degradation occurred rapidly at the start and the raw coir pith contained higher chemical contents. Coir pith can be treated with the help of microbes in the raw stage itself and can be used as the raw material for plant growth medium in an eco-friendly way.

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REFERENCES

- [1] V. Ajitha, S. Rajathy, G.Rojith, and R. Syamkumar, "Physico-Chemical Characterization of Coir Pith Black Liquor and Coir Pith Effluent", *Int. Res. J. Env. Sci.*, Vol. 4(2), pp. 46-49, February 2015.
- [2] S. Antara, B. Ranjan, D. Anupam, S. Susmita, K. C. Ashis, K. B. Arun, and M. Debashis, "Successful biodegradation of coir pith waste using novcom composting method: A case study from Vaniampara rubber estate, India", *J.Pharma.Sci. Innov.*, vol. 4(1), pp. 72-77, February 2015.
- [3] J. Paramanandham, P. Ronald Ross, K. S. Abhiramy, and M. Muthulingam, "Studies on the Moisture Retention Capacity of Coir Pith, as a Function of Time", *Int. J.ChemTech Res.*, vol. 6(12), pp. 5049-5042, October 2014.
- [4] V. Priya, M. C. Sambath Kumar, and N. Balasubramanya, "Evaluation of Chemical Parameters of Agro – Pollutant – Coir Industrial Residue", *Int. J. Sci. Re.*, vol. 5(3), pp.1719-1722, March 2016.
- [5] G. Rojith, and I. S. Bright Singh, "Hydrogen Peroxide Pretreatment Efficiency Comparison And Characterisation of Lignin Recovered From Coir Pith Black Liquor", *J. Environ. Res. Develop.*, vol. 7(4), pp. 1333-1339, April 2013.
- [6] G. Savithri and S. Hamed Khan, "Industrial application of Coir Waste", *Plant Physiology*, Vol. 23(8), pp. 13-30, 2004.
- [7] TAPPI T 222 Om-02, Acid-insoluble lignin in wood and pulp, in: 2002-2003 TAPPI Test methods, 2002, Tappi press Atlanta, GA, USA.
- [8] TAPPI UM 250, Acid-insoluble lignin in wood and pulp in: 1991 TAPPI useful methods, 1991, Tappi, Atlanta GA, USA.
- [9] S. Vinodhini, S.N. Padmadevi, and S. Padma, "Biodegradation of lignocellulosic coir pith by using fungal forms", *Asian J. Microbial.Biotech.Env.Sci.*, vol. 8(3), pp. 499-502, July 2006.
- [10] N.S. Warriar, and K. L. Moudil, "Retting of coconut husk", *J.Scient.Ind.Res.*, Vol. 6, pp. 114-116, 1947.