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Hydrotropic Extraction of Lignin from Vegetation Mass

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ABSTRACT: Dried leaf vegetation is a source of lignin, a valuable chemical entity. The challenges involved in the available lignin extraction processes are the use of chemicals, high temperature, and pressures. The current work has contributed in optimizing the extraction of lignin from dried leaf vegetation using the hydrotrope, a green solvent at low temperature and pressure. The current process involved studying, extraction of lignin at hydrotrope (NaXS) concentration from 10%-30 % w/w, extraction temperatures from 333 K to 383 K using 2.5 % w/w – 15 % w/w of dried leaves. The optimum parameters for lignin extraction were 30 % w/v of hydrotrope NaXS, 373 K extraction temperature, 12.5 % w/w leaf loading concentration. The estimated diffusion co-efficient of the process was loading 4.8 x 10^{-12} m. s^{-2}, and the activation energy was 52.9 KJ.mol^{-1}. The obtained lignin was chemically and physically of standard quality confirmed by its UV-absorption spectrum, infrared spectroscopy, gas chromatography-mass spectroscopy, differential scanning calorimetry, X-ray diffraction study, scanning electron microscopy, gel permeation chromatography. The characteristic properties of the extracted lignin were free-flowing and amorphous nature, dark brown color with a molecular weight of 4509 g.mol^{-1}. The developed process in the present research is green, devoid of using any organic solvent, thereby proving to be an excellent replacement to the traditional de-lignification processes.

Keywords: Aqueous Extraction, Polymer Extraction, Dried Leaves Processing, De-Lignification, Green Extraction

I. INTRODUCTION

About 23.3 million hectares of land in India is deciduous plantation due to its tropical and sub-tropical climate. In the forest area or agricultural land, the soil microbes decompose the fallen foliage from these trees and eventually fortify the soil. In urban towns, most of the land is concrete. The disposal of the foliage through burning is banned under the environment protection act as it affects the environment. The dried leaves contain (18-22 % w/w) lignin, (34- 40 % w/w) cellulose, (20- 22 % w/w) hemi cellulose and other compounds [1]. The lignin is a cell wall structure that is a non-cellulosic aromatic 3-D component made up of guaiacyl- syringyl, polyphenols units. The bond between the lignin and cellulose is strong and difficult to break, it hinders the effective utilization of the biomass by biological treatments [2]. Lignin is raw material useful in various applications like in the making of starting materials, composites, binders, coatings, surfactants, phenols, wood products, preservation, polyurethane foams, coal substitute, adhesive, animal feed, pesticide, cleaner [3].
The extraction of lignin from the cell wall structure leads to the weakening of the plant cell wall, which assists the extraction of natural active constituents from lingo-cellulosic networks of plant material. The recent works have emphasized finding a suitable and sustainable process to monetize the abundant biomass [4–8].
Fernandez-Bolanos *et al.,* [5] have reviewed various methods of delignification, including alkali and acid treatments, organic solvents, and ionic liquid. Subhedar & Gogate [8] have studied the effect of ultrasound treatment which produced 18 % delignification of paperusing 1.75 N NaOH solutions made 40.2 % delignification at 80°C for 6 h. They found that combining 1 N NaOH solution with 100W ultrasonication produced 80 % delignification in 1.16 h [8]. Nagula and Pandit [7] achieved 50- 75 % de-lignification of Napier grass in 6 h by combining ultrasound with enzyme laccase.
Moniruzzaman has reported an improved rate of enzyme-assisted extraction of lignin by pre-treatment of the wood with ionic liquid. Their study revealed that the solvents, including ethanol and acetone, enable 90 % w/w de-lignification of breech wood sawdust and have replaced sulphuric acid by combining the solvents with acetic acid, oxalic acid, or phosphoric acid [6]. Ansari & Gaikar [4] have reported the hydrotropic extraction of good quality lignin from baggase without affecting cellulose structure.
Depending on the method and chemicals used for delignification, the structure of lignin is affected. Further, the cellulose polymer linked to the lignin varies, and the lignin acquires its specific name accordingly [5–10].
Hydrotropes are readily available green solvents and help enhance the solubility of various compounds [11-12]. Hydrotropes are non-volatile, possess no fire hazards, and show good recovery. They are selective in extraction, giving higher separation factors. Unlike conventional surfactants, hydrotropes show no

emulsification losses. Several organic salts with anionic or cationic groups are very soluble in water. In an aqueous solution, the hydrotrope salts create the '*salting in*' effect on the non-electrolytes, known as "*hydrotropism*" [13].

There are reports on hydrotropic extraction of various natural components. Sharma & Gaikar [14] have reported the extraction of reserpine from *Rauwolfia vomitoria* roots. Further, Dandekar & Gaikar [15] report the extraction of curcuminoids from turmeric rhizomes. These results showcase the advantages of using hydrotropes to obtain the product without high temperature, harmful solvent.

Thus, to monetize voluminous bio-waste and obtain lignin by the green, sustainable method, the current research focuses on optimizing lignin extraction and its characterization.

II. METHODS AND MATERIAL

A. Materials

The dried leaves, fallen from the deciduous trees, mainly jackfruit trees, were collected from the Institute's garden, based in Mumbai, India. Navdeep Chemicals Pvt. Ltd, Mumbai, India, provided Sodium xylene sulfonate (Na-XS) and sodium cumenesulfonate (NaCuS).

B. Experimental procedure

The dried leaves were cleaned using a slightly wet cloth and were subjected to particle size reduction in a mixer and sieved to obtain the particle in the size range of 50-160 µm. The study involved using the hydrotrope solutions (10 -40 % w/w) of suitable concentrations to suspend a specified amount of powdered leaves (2.5 - 12.5 % w/w) in a fully baffled cylindrical glass reactor (0.25 kg capacity).Then the suspension was stirred using a turbine impeller of 0.025 m diameter, at a selected temperature (333- 388 K) at an agitation speed (600-1000 rpm) to ensure complete suspension of solid particles and their vigorous mixing.

After a stipulated extraction time, the mixture was filtered to separate the solid residue and the hydrotrope solution containing the lignin extract. The solid residue was washed with distilled water at temperature 353 K to isolate the traces of hydrotrope and the lignin extract that adhered to the solid leaf residue. The solids were then dried and weighed to verify the extent of extraction. The lignin, dissolved in a hydrotropic solution, was recovered by precipitation from the hydrotropic solution by diluting the extract with hot distilled water. Then the suspension was filtered under vacuum at -325 mm of Hg. The solid residue was washed with hot distilled water and dried in the oven at 378 K for 5 h. The diluted filtrate was evaporated to recover the concentrated solution of the hydrotrope.

The percentage of delignification of the dried leaves was calculated based on their original lignin content, determined by the method described in the literature [16]. The weight of dried leaves extracted in hydrotropic solution during the operation was noted as the percentage delignification.

$$\%\ Delignificatio = \frac{weight\ of\ lignin\ extracted}{amount\ of\ the\ dried\ leaves\ taken} \times 100$$

C. Analytical methods

The moisture content of the dried jackfruit tree leaves was determined by the NREL procedure, wherein the leaves were kept in the oven for drying at 60°C for 24 h [16].

The Ash content of dried leaves was determined using the standard method of AOAC[17].

The Cellulose content of the dried leaves was determined by following the procedure as described in the literature [18].

The Hemicellulose content of the dried leaves was determined by following the procedure as described in the literature [18].

The Lignin content was determined by 72 % sulphuric acid treatment as per the process described in the literature[16].

The UV spectra of lignin dissolved in hydrotrope solutions (working sample) and only in the hydrotrope solution (reference cell) were recorded on a Chemito 2700 Double Beam UV–vis spectrophotometer (Chemito Instruments Pvt. Ltd., India).

The IR spectra of the solid residue obtained after the extraction were recorded at 298 K in the region 4000–400 cm^{-1} using a KBr pellet on a Bruker/Vertex 80V Fourier Transform Infrared spectrophotometer (FTIR) (Bruker Corporation, Germany).

The recovered lignin was suspended in 30 % v/v ethanol and was sonicated in a bath sonicator. The supernatant was subjected to Gas chromatography and mass spectroscopy using a Finnigan LCD Advantage Max mass spectrometer (LCQAD 30000, Thermo Electron Corporation, USA). The instrument was equipped with a capillary column and a Quadrupole detector. Nitrogen was used as a sheath gas with a flow rate of 40 x 10^{-6} $m^3.min^{-1}$, and auxiliary N_2 flow rate was maintained at 18 x 10^{-6} $m^3.min^{-1}$. The capillary temperature was maintained at 548 K with a voltage of 420 V and ion spray voltage at 5 kV.

The isolated lignin was analyzed by Differential Scanning Calorimetry (DSC) of Shimadzu DSC-60 (Japan) make to study the degradation rate of the extracted lignin and to confirm that the extract is lignin. The analysis was performed at a heating rate of 283 K min^{-1}.Nitrogen was used as the purge gas during the DSC analysis.

The X-ray diffraction (XRD) and spectra of isolated lignin were recorded on D8 Advance Bruker X-ray diffractor (Bruker Corporation, Germany) at the wavelength 1.5406 Å.

The surface morphological structure and the average size of the extracted lignin were determined by Scanning Electron Microscopy (SEM-JEOL-JSM). The extracted lignin was coated with silver at 15 mA and the accelerating voltage of 20–30 Kv.

The average molecular weight of the extracted lignin was determined using GEL permeation chromatography (GPC) (Waters India Pvt. Ltd., India) equipped with HPLC-515 pump, Styragel HT column (7.8 x 300 mm, molecular weight range of 500–30000), equipped with

refractive index (RI) detector. For, this the extracted lignin was solubilized in dimethyl sulfoxide (DMSO). The polystyrene (molecular weight range of 3000–800000) was used as a standard and THF at 0.8 cm^3. min^{-1} was used as the mobile phase.

D. Mass transfer model for dried leaves delignification

A mass transfer model for the extraction of active materials from a solid matrix was used to mathematically describe the delignification process of the dried leaves. Since the particle is assumed of a flat shape; thus, Fick's second law of diffusion was applied to model the mass transfer. The general equation (1) for the solid-liquid mass transfer model reduces to equation (2) for flat plate geometry:

$$\frac{dC(t,x)}{dt} De \frac{1}{x^{(\Phi-1)}} \frac{d}{dx} (x^{(\Phi-1)} \frac{dC(t,x)}{dx}) \quad (1)$$

$$\frac{dC}{dt} = De(\frac{d^2C(t,x)}{dx^2}) \quad (2)$$

where C, t, x, ϕ, and D*e* are solute concentration, reaction time, distance, geometric shape factor, and effective diffusivity coefficient, respectively. The finite difference method was used to discretize the differential equation and the set of equations along with the solution mass balance equation for solute by the Crank-Nicolson method to match the experimental concentration profile of extracted lignin for estimating the *De*. The theoretical lines obtained were plotted in the studies to indicate the diffusion coefficient of the process [4].

E. Activation Energy

The amount of energy required for the extraction of lignin was calculated by plotting Ln (Rate of extraction of lignin) versus1/Temperature. The slope of the line gives the activation energy of the process.

III. RESULTS AND DISCUSSION

Initially the properties of the dried leaves were determined to set suitable hydrotropic extraction process. Table 1 gives the composition of the leaves of a jackfruit tree

Table 1: Composition of jackfruit tree dried leaves.

Parameter	Values
Moisture content	5.6-6.4 % w/w
Oven dry weight	1.2 ± 0.2% w/w
AIR (acid insoluble residue)	42.65 ± 0.03 % w/w
AIL (Acid insoluble Lignin)	20.71 ± 0.2 % w/w
ASL (Acid soluble lignin)	0.3 ± 0.01% w/w
Total lignin content	20.96 % w/w
Ash content	1.228 ± 0.003 % w/w
Cellulose content	49.12 ± 0.01 % w/w
Hemi- cellulose content	18.23 ± 0.02 % w/w
Organic composition of lignin (Elemental analysis- Dumas method)	C: 42.10 %, H: 5.22 %, N: 0.64 %, S: non-detectable

The hydrotropic de-lignification of the dried leaves at determined temperatures as a function of time enabled a maximum of 81 % w/w de-lignification with 30 % w/w of Na-XS. Thesolubilization of lignin was noted as the darkening of the hydrotropic solution. The separation of the hydrotropic solution was easy by filtration without any significant pressure drop across the filter. The solid residue was washed with water 1:50 to remove the traces of hydrotrope in the interstitial space between solid particles. The extracted lignin was further washed before drying to remove the traces of hydrotrope from the lignin.

The physical characteristic of the lignin product was comparable with the reported literature [19–28]. The delignification of dried leaves by hydrotrope (81 wt%) was more than that reported in the literature for lignin extraction by 80% v/v solution of 1, 4-butanediol [21]. Further, it was also more than the delignification of woody materials with aqueous sodium xylene sulfonate solution (30%, w/w)[30]. The extraction of lignin (97%) from bagasse by using ionic liquid (IL), i.e. 1-ethyl-3-methylimidazolium as cation and a mixture of alkyl benzene sulfonates as anions, was, however, higher than the present investigation but the process required much higher temperatures (463 K) and isolation of ionic liquid and lignin was a real hurdle in IL based approaches [31].

A. Effect of type of hydrotrope on delignification

The maximum delignification of the dried leaf using 30 % w/w Na-XS (81%) was higher compared to de-lignification obtained using Na-CS (42%), at 115℃ temperature in 4 h. Thus, Na-XS was a more effective hydrotrope for de-lignification compared to Na-CS (Fig. 1). Ansari and Gaikar [4] work on the de-lignification of bagasse with 30% (w/w) aqueous solutions of Na-XS and Na-CS also showed similar results. Depending on the hydrocarbon chain length, the efficiency of hydrotropes to extractactive materials from plant matrices varies [15, 32–34]. Hence, the NaCS, involving the propane chain (long-chain), has to be more efficient compared to NaXS, which involves two methyl groups (short-chain) [15, 32, 35-36].

However, in the current study and as reported by Ansari and Gaikar, the extraction of lignin using NaCS was less than NaXS[4]. So, the current study did not explainthe reason for NaXS to be a more effective hydrotrope for the de-lignification of dried leaves. Nevertheless, it could be because of the much larger molecular weight of Lignin [28, 37]. Thus, in further experiments and analysis, NaXS was used.

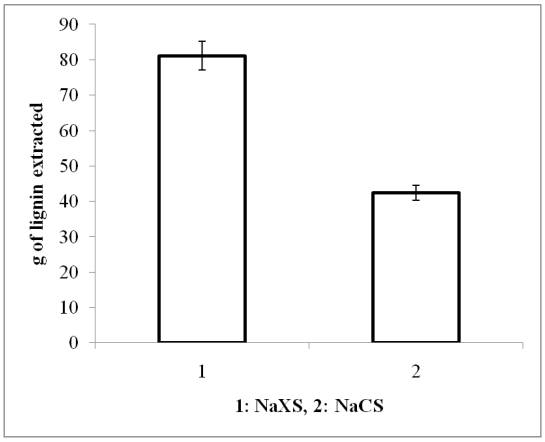

Fig. 1. Effect of type of hydrotrope on de-lignification of dried foliage at 900 rpm, 100℃, 5 % w/w leaf loading concentration, 300 min extraction time.

B. Effect of hydrotrope concentration

The percentage extraction of lignin from dried leaves increased significantly with hydrotrope concentration starting from 10 % w/w up to 30 % w/w NaXS. However, the incremental change in the delignification percentage beyond 30 % (w/w) of hydrotrope was insignificant. The model curves obtained using the finite difference method to generate the concentration versus time data in the solution agree with the experimental data of lignin extraction (Fig 2). The standard deviation of repeated runs was in the range of 0.01-0.025 %, with the statistical p-value of 0.38 > 0.05.

The hydrotropes have the minimum hydrotropic concentration (MHC) at which they form self aggregates. The MHCs are similar to the critical micellar concentration (CMC) of the surface-active compound. The increase in hydrotrope concentration improves the permeabilization of active material from the plant matrix. The formation of MHCs and co-clusters with the active compounds improves the permeabilization of active material [33]. The scanning electron microscopy (SEM) reports of various plant matrices treated with hydrotrope reveal the cell wall distortion and permeabilization [4, 14-15, 32, 34].

The viscosity of 30 % hydrotropic solutions containing the leaves was 2 $\times 10^{-3}$ kg.m^{-1}.s^{-1},and the density of the solution was 1164 kg. m^{-3}. The viscosity of the 40 % w/w hydrotropic solution containing the powdered leaves was 3 x 10^{-2} kg.m^{-1}.s^{-1} almost 1.5 times more than that attained with 30% w/w NaXS concentration. The high viscosity of the solution beyond 30 % w/w NaXS can be another reason for the no improvement in yields with 40 % w/w NaXS solutions.

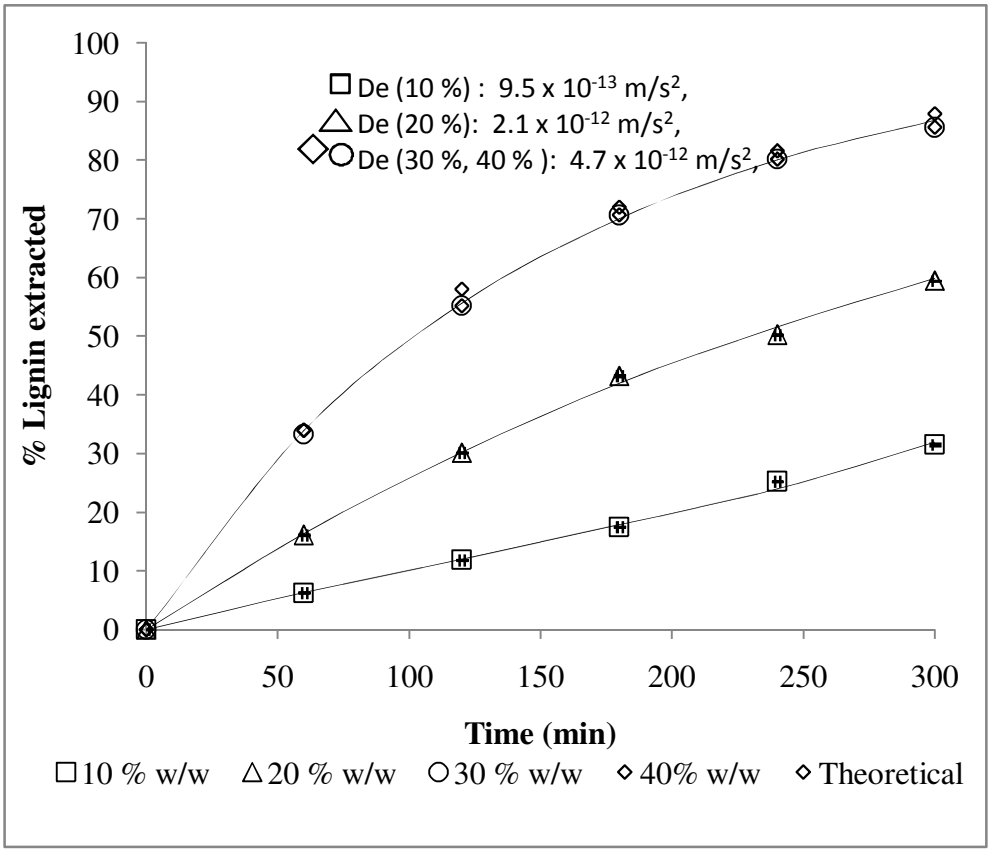

Fig. 2. Effect of Concentration of NaXS on de-lignification of dried foliage at 900 rpm, 100℃, 5 % w/w leaf loading concentration, 300 min extraction time.

C. Effect of temperature on delignification

With the incremental change in the temperature from 333 K to 373 K, the lignin extraction improved from 31.5 % w/w to 81.1 % w/w, while above 373 K, the de-lignification was insignificant (Fig. 3). The repeated runs showed variation in the yields of 0.01 to 0.08 % with a statistical p-value of 7.05 x 10^{-5}< 0.05, indicating data to be statistically significant. Thermal energy applied during the process disturbs the bonds within the lingo-cellulosic structures and increases the movement of the molecules and subsequently increases the mass transfer, and assists in the solubilization of the plant material [32]. The time-based analysis of lignin extraction was significant upto 240 min. Beyond that, the results were not effective (Fig. 3).

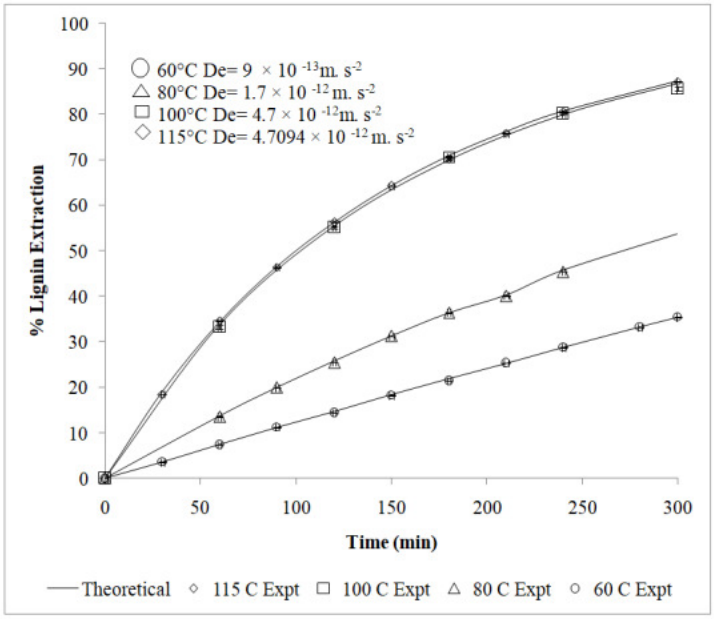

Fig. 3. Effect of temperature on hydrotropic extraction of lignin at 5 % w/w leaf loading concentration, 900 rpm, 300 min extraction time, 30 % hydrotropeNaXS.

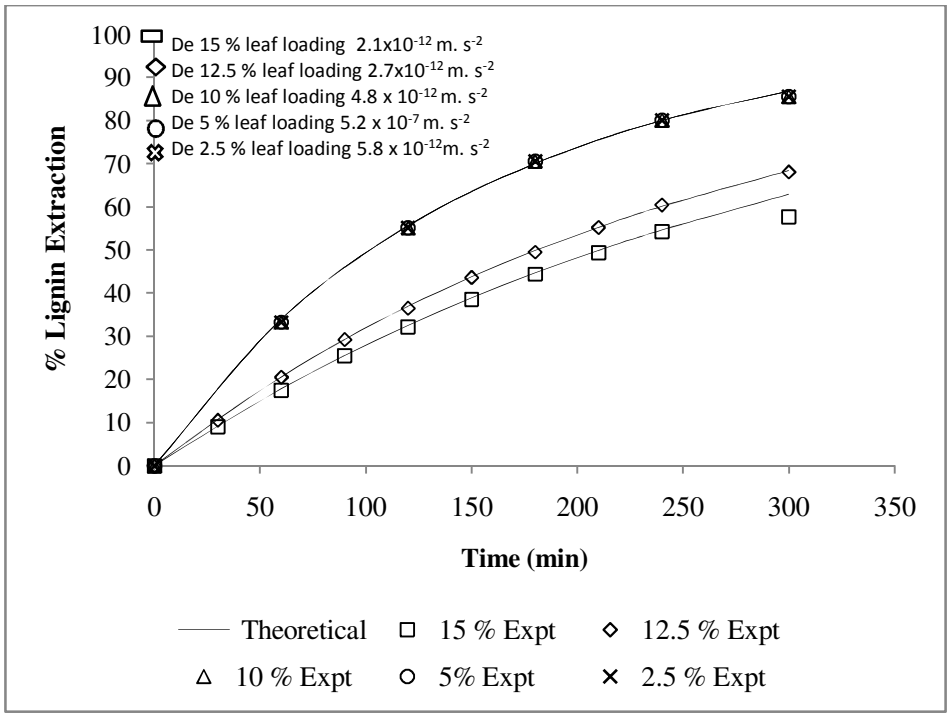

Fig. 4 a: Effect of dried leaf loading concentration on the percentage of Lignin extraction at 80℃, 30 % w/w hydrotrope NaXS, 900 rpm, 400 min extraction time

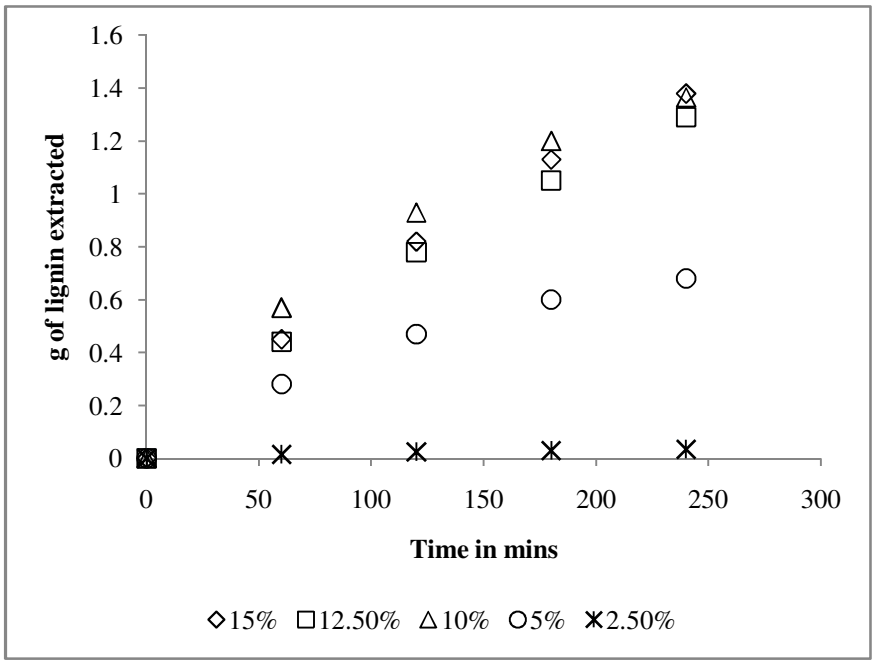

Fig. 4b. Effect of the percentage of dried leaf loading concentration on Lignin extraction in gram unit.

D. Effect of foliage loading concentration

The lignin extraction increased with an increase in leaf loading from 5 % w/w to 10 % w/w. The percentage of lignin extracted was 80 to 81 % w/w at 10 % dry leaf loading concentration, but at and above 12.5 % w/w of leaf loading concentration, the percentage of lignin extraction decreased (Fig. 4 (a), (b). The variation in the repeated runs was 0.1 -0.5 % with the statistical p-value of 0.000481 < 0.05.

Hence, the solid loading concentration was limited to 10 % w/v to allow the proper mass transfer and to improve contact of lignin with extracting hydrotrope. In literature reports, such limitations for the solid loading concentration are observed [38].

E. Activation Energy

The activation energy estimated for extraction temperatures from 343 K to 373 K was 52.9 KJ.mol^{-1} (Fig. 4.c). Indicating the process is diffusion controlled. In literature, Yanbo and Zhou *et al.*, [39] stated that activation energy is less than 20 KJ. mol^{-1}, the process is diffusion-controlled.

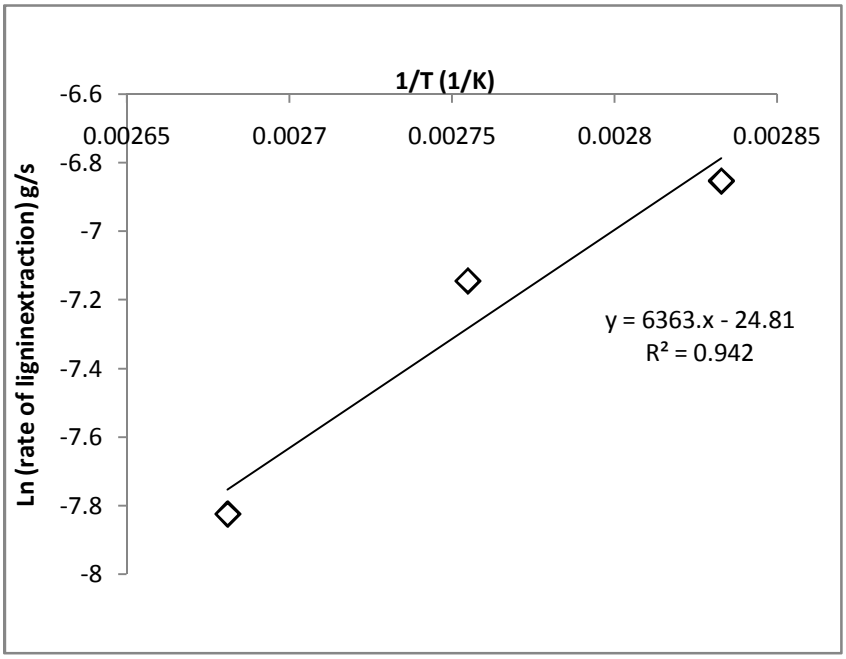

Fig. 5. The rate of oil extraction v/s temperature, activation energy plot (at hydrotropic delignification temperature 60-115℃, 900 rpm agitation speed, 10 % Leaf loading concentration, 30 % NaXS)

F. Recovery of Lignin and hydrotrope

Three parts of water enabled the precipitation of lignin from the hydrotropic solution. Further, the solid hydrotrope was recovered from the diluted hydrotrope solution by evaporating water. The total recovery of hydrotrope after the first delignification step was approximately 98.3 % w/w. The loss of 1.7 % w/w hydrotrope during the processing steps was due to the handling. The recovered hydrotrope enabled the extraction of lignin from fresh leaves and hence was re-usable.

G. Characterisation of extracted Lignin

a. UV-absorbance

The UV absorption spectra of the lignin in the hydrotrope solution are shown in Table 2, where the UV-spectra of the hydrotrope solution was considered a blank. The UV absorbance of lignin showed two maxima, one at 240 and 290 nm wavelengths (Fig 6). The earlier literature reported 241 nm and 292 nm wavelengths for lignin extracted from baggase [4]. The absorbance in the spectral region of 240 nm indicated the presence of unconjugated phenolic compounds rather than conjugated phenol structures of Lignin [25] and at 290 nm showed the presence of phenolic hydroxyl groups of Lignin [19, 27]. Balasubramanium and Burghard [40] have confirmed that the unconjugated phenols exhibit peaks between 250 and 300 nm while conjugated phenols showed the maximum close to 370 nm, which is close to the obtained UV peaks.

Table 2: UV absorption spectra of hydrotrope solution with lignin.

S.No.	Reference	Peak (nm)	Group
1.	Current Work	240 and 290	Unconjugated Phenolics and Phenolic hydroxyl groups
2.	(K. B. Ansari & Gaikar) [4]	241 nm and 292	Unconjugated Phenolics and Phenolic hydroxyl groups
3.	(Vallejos *et al.*,) [25]	240	Unconjugated phenolic
4.	(Saariaho *et al.,)* and (Boeriu *et al.*,) [19, 27]	290	Phenolic hydroxyl groups
5.	(Balasubramanian & Burghard) [40]	250 and 300	unconjugated phenols
6.	(Balasubramanian & Burghard) [40]	370	conjugated phenols

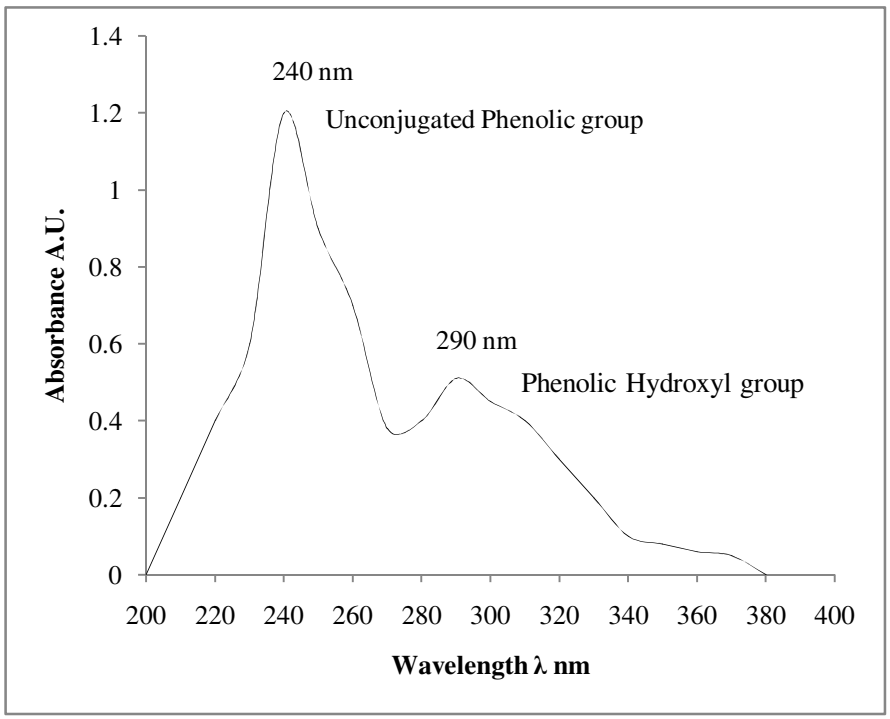

Fig. 6. UV-Vis absorption spectrum of extracted NaXS extracted lignin.

b. IR spectra of the extracted lignin

Fig. 7 shows an IR spectrum of the lignin extracted by Na-XS solutions. The peak at 3427.51 cm^{-1} indicated the stretching of phenolic and hydroxyl units of Lignin [20, 41].Cyclic hydrocarbons and aromatic methoxy groups of the lignin structure were identified by the peaks at 2922–2852 cm^{-1}. The peak at 1639.49 cm^{-1} indicated the carbonyl group stretching for methoxyl group of lignin, aromatic ring stretching, and methyl group (CH_2/ CH_3) stretching, respectively [24]. The absorbance of the guaiacyl structure of the lignin was found at 1375–1347 cm^{-1}. The p- hydroxyl phenyl structures of lignin showed peaks at 1261 cm^{-1} and 1162 cm^{-1} [24]. The ether linkage of the lignin structure was seen at 1043 cm^{-1}. Comparing the identified functional group peaks of the extracted lignin with that mentioned in the literature indicates that the recovered solid is Lignin [31] (Table 3).

Table 3: Comparison of the Infra-red identified functional groups of the extracted lignin with that mentioned in the literature.

S.No.	Reference	Peak (cm^{-1})	Group
1.	(Mai *et al.*, Faix and Böttcher) [20, 41]	3427.51	Functional groups of lignin extracted by Na-XS
2.	(Lisperguer *et al.*,) [24]	2922–2852	Cyclic hydrocarbons and aromatic methoxy group
3.	(Lisperguer *et al.*,) [24]	1375–1347	Guaiacyl structure of the lignin
4.	(Lisperguer *et al.*,) [24]	1261 cm^{-1} and 1162	p- hydroxyphenyl structures of Lignin
5.	(Tan *et al.*,) [31]	1043	Ether linkage of the lignin

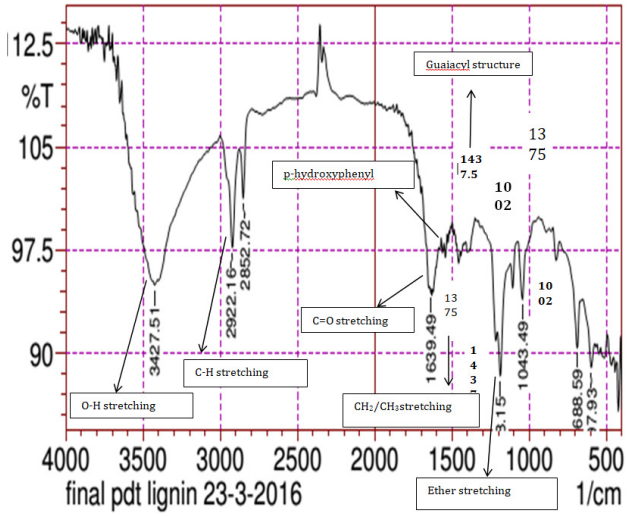

Fig 7. Infrared spectrum of A. NaXS and B. NaCuS assisted extracted lignin

c. Gas chromatography Mass spectroscopy

The lignin recovered using NaXS was sonicated for 180 min with two solvent systems, namely ethanol-water (60:40) and ethanol-water (70:30). The dissolved fractions of lignin in both ethanol-water mixtures were analyzed by Gas chromatography - Mass Spectroscopy. The solvents facilitated degrading and solubilizing the different fractions of lignin, as Ni and Hu [26] stated. The compounds obtained included m/z of 94, indicating p-hydroxyl phenyl, m/z of 122 indicating the guaicyllignin (softwood lignin), m/z of 129.22, indicating the presence of 4-hydroxymethyl-tetrahydro-fura-3-carbaldehyde. Finally, the m/z of 138 peaks was found, indicating no syringyl lignin (hardwood lignin). Thus, the lignin extracted is softwood lignin, as illustrated in the literature for the lignin-derived compounds [4, 22].

d. Differential Scanning Calorimetry analysis

The DSC of the Lignin extracted using NaXS was performed by following a program where a heating rate of 283 K min^{-1} was used under a nitrogen atmosphere. The DSC curve of lignin showed three distinct peaks (Fig. 8). The first peak was observed at 396 K (123°C), and it appeared as exothermic. The second peak and third peak were observed at 485 K (212°C) and 345°C (618 K), and these peaks were endothermic. The DSC result was comparable with the literature, endothermic peaks of lignin at 100 ^{0}C (373 K) to 180°C (453 K) corresponding to loss of water and exothermic at 280 ^{0}C (553 K) to 390°C (663 K) corresponds to the melting point peak, and the peak at 420°C (693 K) and beyond 500°C (773 K) correspond to degradation peak of Lignin [42].

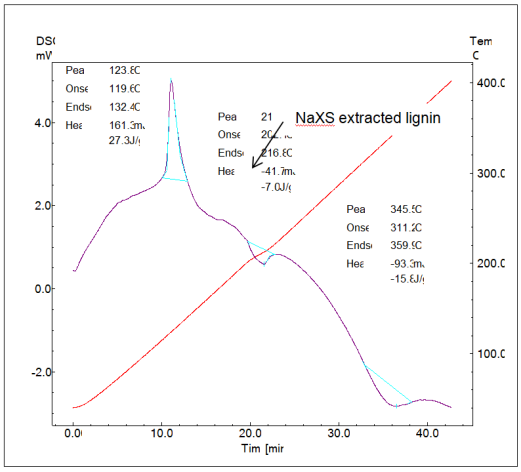

Fig. 8. Differential scanning calorimeter graph of NaXS extracted lignin.

e. X-Ray Diffraction

The X-ray diffraction measurement of the free-flowing lignins powder extracted using NaXS and NaCuS showed a weak peak at 22.37 (**1**) (2 θ value) (Fig. 9 a, b), indicating that the extracted lignin was amorphous. The amorphous nature of the extracted lignin obtained by the XRD pattern was comparable with the results studied by Luo *et al.,* [23], Ansari and Gaikar [4]. They also reported the recovered dried lignin to be a free-flowing brown-colored powder, thereby presenting physical characteristics of amorphous nature.

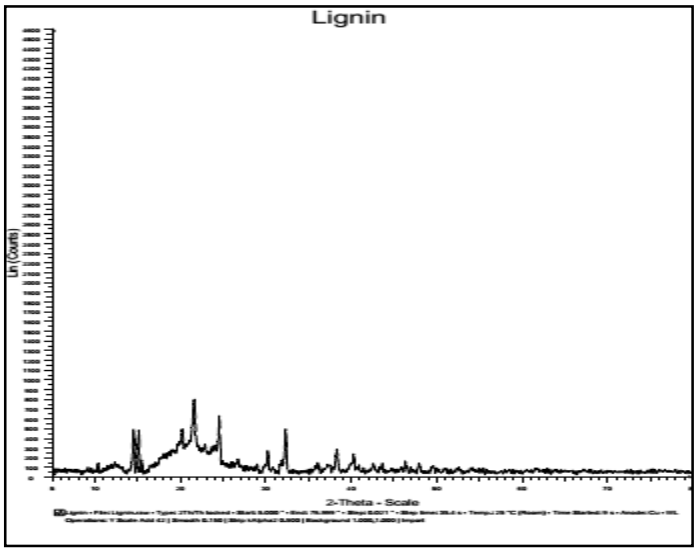

Fig. 9.a: X-ray diffraction spectrum of extracted Lignin from NaXS.

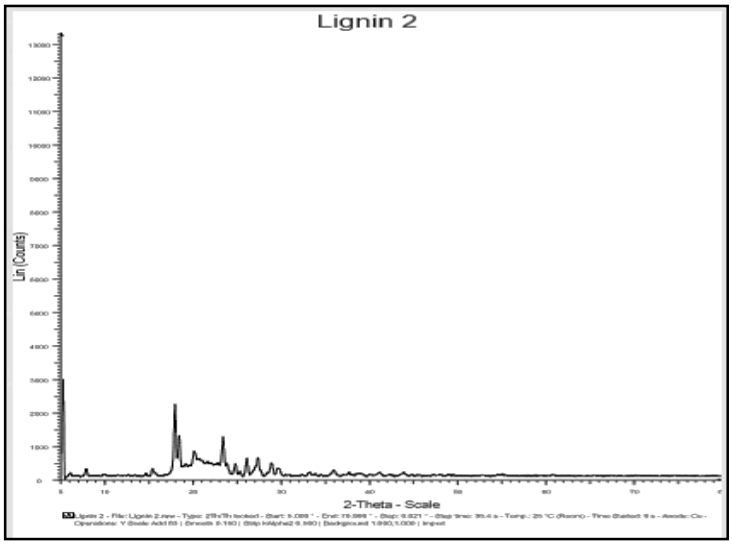

Fig. 9b: XRD of Lignin extracted using NaCuS.

f. Scanning Electron Microscopy (SEM) of extracted Lignin

The SEM images of lignin isolated using Na-XS and NaCuS showed irregular geometries, which are not surprising considering the amorphous nature of the material [4]. Further, the surface of lignin particles was flaky and smooth (Fig.10). Ansari and Gaikar also reported similar irregularities in SEM images of lignin isolated from Na-CS, Na-NBBS, and Na-XS [4].

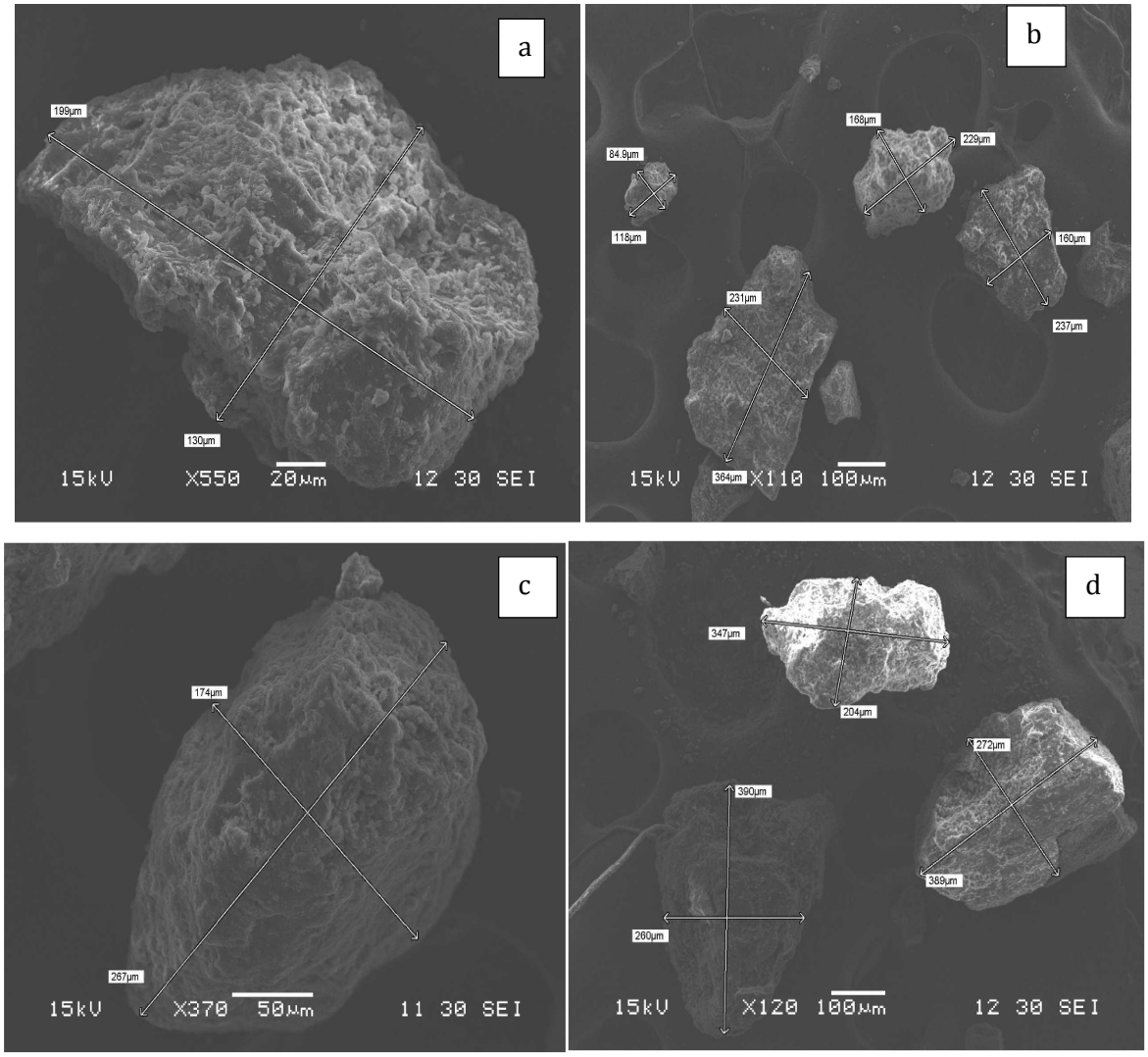

Fig. 10. Scanning electron microscopic images of a, b NaXS extracted lignin, c, d NaCuS extracted lignin.

g. Gel permeation chromatography

The GPC analysis of lignin extracted using NaXS show that the weight-average (MW) and number-average (Mn) molecular weights of lignin are 4509 g.mole^{-1} and 3962 g.mole^{-1}, respectively (Table 4). The molecular weight of the extracted lignin was comparable with the literature reports on the molecular weight of softwood lignin extracted from bagasse using dioxane, hydrotrope, toluene (3405–3868 g.mole^{-1}) (Ansari and Gaikar, 2014), lignin isolated from bagasse by alkali treatment (1680–3020 g.mole^{-1}), and lignin obtained from bagasse using soda process (2160 g mole^{-1}) [43].

Table 4: Gel permeation chromatogram of NaXS extracted lignin.

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	4767	3962	4509	5060	5577	4981	1.138
Peak 2	158	291	365	467	576	451	1.254

h. Kappa Number

The Kappa number values determined the oxidant demand, the degree of delignification, relative hardness, and biomass bleachability. The Kappa number of the dry leaves was determined by treating the foliage with potassium permanganate ($KMnO_4$) using TAPPI Classical Method T 236 cm-85 “Kappa Number of Pulp” [44]. The estimated Kappa number of the initial foliage

(before hydrotropic extraction of lignin) was 33.6. The kappa number of foliage after delignification were 18.55 and 28.3 for Na-XS and Na-CuS, respectively. The Kappa numbers in the range of 25- 30 and 17 -20 are considered for good pulp quality, i.e. free of Lignin [45]. Further, in the present research, Kappa numbers presented proper lignin content removal in NaXS, thereby indicating suitable quality biomass. The values of the Kappa number obtained in the present research were also found to agree with kappa numbers given by Birchwood [46] for delignification and bagasse delignification studies done by Ansari and Gaikar [4].

G. Mass transfer model

The diffusion co-efficient obtained for 20 % w/w, 30 % and 40 % w/w NaXS were 2.1 x 10^{-12} $m^2.s^{-1}$, 4.7 x 10^{-12} $m^2.s^{-1}$, 4.7094 x 10^{-12} $m^2.s^{-1}$ respectively. The D*e* value for 333 K, 353 K, 373 K and 388 K were 9 x 10^{-13} $m^2.s^{-1}$, 1.7 x 10^{-12} $m^2.s^{-1}$, D*e*= 4.7 x 10^{-12} $m^2.s^{-1}$, 4.7094 x 10^{-12} $m^2.s^{-1}$. The De value for 15 % w/w leaf loading 7.4x10^{-13} $m^2.s^{-1}$ and that for 12.5 % w/w, 10 % w/w, 5 % w/w and 2.5 % w/w leaf loading concentration were 4.89x10^{-12} $m^2.s^{-1}$, 4.8 x10^{-12} $m^2.s^{-1}$, 5.3 x10^{-12} $m^2.s^{-1}$, 5.8x10^{-12} $m^2.s^{-1}$.

As the hydrotrope travels through the interstitial region of the matrix and assists lignin extraction, the process is diffusion-based. The diffusion process involves

i), the collision of species with matrix fibers (*steric interactions*),

ii), as diffusing species diffuse near fibers, restricted thermal motion of water molecules due to proximity to the fibers slows their diffusion (*hydrodynamic interactions*), and

iii), for charged particles (*electrostatic interactions*), the diffusing species interact with charged components of the extracellular matrix, contribute an additional force. Thus, the size, shape, distinctive structure, and charge of the matrix are essential aspects for the lignin extraction and are responsible for the diffusion of hydrotrope molecules [47].

H. Energy calculations

Table 5 below presents the energy calculations

Table 5: Energy Calculations.

Reference	Parameters	Total Energy (kJoules. g^{-1})	Energy fold compared to the current process
(Ansari and Gaikar) [4]	Extraction at 5 % baggase, 900 rpm 353 K, 378 K for 300 min drying	1.08 x 10^2	1
(Fernandez-Bolanos *et al.*,) [5]	Steam 42 $kg.cm^{-2}$, 1 h, 0.1 % w/w H_2SO_4, 236℃, 2 min, 100 g	4920	4.48 x 10^{-2}
(Subhedar and Gogate) [8]	1$g.L^{-1}$, 200 cm^3 cellulase, 50℃, 17.33 $W.cm^{-3}$ for 30 min	1.95 x 10^2	1.78
(Nagula and Pandit) [7]	5 % Napier Grass, 45℃, 300 rpm, 6 h, 50 % duty cycle	9.5 x 10^5	8.65 x 10^3
(Kalogiannis *et al.*,) [48]	175 ^{0}C, 1 h: Acetone Ethanol treatment, evaporation of solvent in vacuum, separation of extract at 4000 rpm, 4℃ for 15 min	3 x 10^2	2.73
(Vallejos *et al.*,) [25]	Ethanol: water: 50 %, liquor: bagasse: 14:1, 30 min to reach temperature, 175℃ for 240 min	8.64 x 10^2	7.87
(Tan *et al.*,) [25]	Steam, 2 h, 3 g raw material, 70℃ with IL for 2 h, 70℃ for 30 min IL evaporation, drying at 60℃ for 18 h	1.34 x 10^4	1.22 x 10^2
(Devendra and Pandey) [49]	5 % w/w raw material, 100℃, 4 h, 900 rpm 4 h extraction, 8500 rpm 10 min	4.55 x 10^4	4.14 x 10^2
Current Process	Extraction at 5 % dried leaf, 900 rpm 353 K, 378 K for 300 min drying	1.08 x 10^2	1

To extractlignin using IL conducted by Tan *et al.*, [25], the energy consumption of 1.34 x 10^4 $J.g^{-1}$ was observed, which is 1.22 x 10^2 times the energy required for the current process. The energy needed for lignin extraction by Devendra and Pandey [49] was 45.5 $kJ.g^{-1}$ which is 4.14 x 10^2 times the energy required for the current process. Vallejos *et al.*, [25] used 50 % of Ethanol: water, liquor: bagasse in the ratio of 14:1 for 30 min, and then at 175℃ for 240 min. Their energy consumption comes to be 8.64 x 10^2 $kJ.g^{-1}$ which is 7.87 times the energy required for the current process.

Fernandez-Bolanos *et al.*, [5] process for lignin extraction required an energy consumption of 4.92 x $10^3$$kJ.g^{-1}$ which is 4.48 x 10^{-2} times the energy required for the current process. Subhedar and Gogate [8] conducted lignin extraction using 200 cm^3 cellulase, 50℃, 17.33 $W.cm^{-3}$ for 30 min. Their energy consumption comes up to 1.95 x $10^5$$J.g^{-1}$ is 1.78 times the energy required for the current process of hydrotropic lignin extraction. The calculated energy required for the process used by Nagulaand Pandit [8] was 9.5 x 10^5 $kJ.g^{-1}$which is 8.65 x 10^3 times the energy required for the current process of hydrotropic lignin extraction.

Kalogiannis *et al.*, [48] performed lignin extraction at 175 0C for 1 h using acetone ethanol mixture. This was followed by evaporation of the solvent in a vacuum and then separation of extract at 4000 rpm, 4 0C for 15 min. Here, the energy calculation showed a requirement of 13 x 102 KJ.g-1 of energy. This is 2.73 times the energy required for the current process of hydrotropic lignin extraction. The energy required for the lignin extraction process used by Ansari and Gaikar[4] where, lignin extraction parameters were 5 % lignin loading concentration, 900 rpm, 378 K for 300 min, showed energy consumption of 1.08 x 102 KJ.g-1. This is equivalent to the energy required for the current process of hydrotropic lignin extraction

It can be inferred from the discussion above that the energy requirements are similar in order of magnitude or

are less than the energy required for the existing literature using other lignin extraction processes.

I. Discussion

The current process assists in the selective extraction of lignin, as seen from the characterization studies. With the developed process, the lignin could be recovered simply by dilution with water; thus, the recovery is natural. Unlike several other tedious methods required for recovering as reviewed by Mai *et al.* [41], herein the hydrotrope used is recoverable. The delignification percentage is comparable to that mentioned in the literature, including the extraction obtained by Qiang Wang, Kefu Chen, Jun Li, Guihua Yang, Shanshan Liu [21] using 1, 4 –butanediol. Korpinen & Fardim did the same using sodium xylene sulfonate solution, [30] which is also comparable with that reported for the extraction using ionic liquid (IL) 1-ethyl-3-methylimidazolium as cation and a mixture of alkyl benzene sulfonates as anions [31]. The extraction process using the hydrotrope requires many reduced temperatures than the extraction using ILs [31]. The process helps in the recovery of free-flowing, amorphous, dark brown colored lignin powder. The physical characteristic of the extracted lignin was comparable with those mentioned in the literature [19, 23, 25, 31, 42, 49]. Unlike the reported methods where the lignin is named after the process used for its extraction because the lignin holds properties of the trace materials used in the process taken into consideration [5–10]. The lignin extracted by the current process is free from traces of any solvents and chemicals. Hence, it can be denoted as lignin without giving it any additional suffix or prefixes like kraft lignin or alkali lignin, etc.

IV. CONCLUSION

This study investigates the extraction of lignin from dried leaves successfully using aqueous hydrotropic solutions.. Parameters for delignification such as temperatures, time, hydrotrope concentrations, and suspension loading were optimized. Reusability of hydrotrope was possible for foliage delignification. The current study can solve the issue associated with lignin separation from the lignocellulosic resources usinga solvent and high temperature. Further, it also provides an excellent replacement to the traditional de-lignification processes, where the recovery and generation of an effluent is a significant problem. The entire investigation has focused on developing a green method for delignification, devoid of using any chemicals and solvents. The reported process developed by Ansari and Gaikar for extraction of lignin from baggase is applicable for extraction of lignin from dried leaves as well. Hence gives scope for working in the area of research to extract lignin using hydrotrope.

V. FUTURE SCOPE

The obtained lignin can be subjected to degradation to obtain valuable products which can be used in different applications. Further, the developed process can be an alternate method to the available lignin extraction processes to enable the extraction of lignin from various lignin sources.

Conflict of Interest: Nil.

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REFERENCES

[1]. Kulić, G. J., & Radojičić, V. B. (2011). Analysis of cellulose content in stalks and leaves of large leaf tobacco. *Journal of Agricultural Sciences*, *56*(3), 207–215. https://doi.org/10.2298/JAS1103207K

[2]. Maurya, D. P., Singla, A., & Negi, S. (2015). An overview of key pretreatment processes for biological conversion of lignocellulosic biomass to bioethanol. *3 Biotech*, *5*(5), 597–609. https://doi.org/10.1007/s13205-015-0279-4

[3]. Crestini, C., Crucianelli, M., Orlandi, M., & Saladino, R. (2010). Oxidative strategies in lignin chemistry: A new environmental friendly approach for the functionalisation of lignin and lignocellulosic fibers. *Catalysis Today*, *56*(1), 8–22. https://doi.org/10.1016/j.cattod.2010.03.057

[4]. Ansari, K. B., & Gaikar, V. G. (2014). Green hydrotropic extraction technology for delignification of sugarcane bagasse by using alkybenzene sulfonates as hydrotropes. *Chemical Engineering Science*, *115,* 157–166. http://dx.doi.org/10.1016/j.ces.2013.10.042

[5]. Fernandez-Bolanos, J., Felizon, B., Heredia, A., Guillen, R., & Jimenez, A. (1999). Characterization of the lignin obtained by alkaline delignification and of the cellulose residue from steam –exploded olive stones. *Bioresource Technology*, *68*(2), 121-132. https://doi.org/10.1016/S0960-8524(98)00134-5

[6]. Moniruzzaman, M., Ono, T., Yusup, S., Chowdhury, S., Bustam, M. A., & Uemura, Y. (2013). Improved biological delignification of wood biomass via ionic liquids pretreatment: A one step process. *Journal of Energy Technologies and Policy*, *3*(11), 144–152.ISSN: 2225-0573.

[7]. Nagula, K. N., & Pandit, A. B. (2016). Process intensification of delignification and enzymatic hydrolysis of delignified cellulosic biomass using various process intensification techniques including cavitation. *Bioresource Technology*, *213*, 162–168. https://doi.org/10.1016/j.biortech.2016.03.152

[8]. Subhedar, P. B., & Gogate, P. R. (2014). Alkaline and ultrasound assisted alkaline pre-treatment for intensification of delignification process from sustainable raw- material. *Ultrasonics Sonochemistry*, *21*(1), 216–225. https://doi.org/10.1016/j.ultsonch.2013.08.001

[9]. Triwahyuni, E., Abimayu, H., Cahyono, A., Cahyono, E. T., & Sudiyani, Y. (2015). Alkaline Delignification of oil Palm empty fruit bunch using black liquor from Pretreatment. *Procedia Chemistry*, 1*6,* 99–105. https://doi.org/10.1016/j.proche.2015.12.032

[10]. Wang, L., & Weller, C. L. (2006). Recent advances in extraction of nutraceuticals from plants. *Trends in Food Science & Technology*, *17*(6), 300–312. https://doi.org/10.1016/j.tifs.2005.12.004
[11]. Dhapte, V., and Mehta, P. (2015). Advances in hydrotrpic solutions: An update review. St. Petersburg Polytechnical University *Journal: Physics and Mathematic,* *1*(4), 424-435. https://doi.org/10.1016/j.spjpm.2015.12.006
[12]. Dharashive, V., Yelam, K. V., Ajit, G. S. C., & Devne, S. (2016). Effect of Hydrotropes on Solubility of Drugs. I*nternational Journal of Pharmaceutical And Chemical Sciences*, *5*(1), 48–52. http://www.ijpcsonline.com/files/11-01-16/09-1053.pdf
[13]. Saleh, A. M., & El-Khordagui, L. K. (1985). Hydrotropic agents: a new definition. *International Journal of Pharmaceutics*, *24*(2–3), 231-238. https://doi.org/10.1016/0378-5173(85)90023-7
[14]. Sharma, R. A., & Gaikar, V. G. (2012). Hydrotropic Extraction of Reserpine from Rauwolfia vomitoria Roots. *Separation Science and Technology*, *47*(6), 827–833. https://doi.org/10.1080/01496395.2011.635623
[15]. Dandekar, D. V., & Gaikar, V. G. (2003). Microwave assisted extraction of curcuminoids from Curcuma longa. *Separation Science and Technology*, *37*(11), 2669–2690. https://doi.org/10.1081/SS-120004458
[16]. Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., & Crocker, D. (2008). Determination of Structural Carbohydrates and Lignin in Biomass. https://www.nrel.gov/docs/gen/fy13/42618.pdf
[17]. Thiex, N., Novotny, L., & Crawford, A. (2012). Determination of ash in animal feed: AOAC official method 942.05 revisited. *Journal of AOAC International*, *95*(5), 1392–1397. https://doi.org/10.5740/jaoacint.12-129
[18]. Sadasivam S., & Manickam, A. (1992). Biochemical methods for agricultural sciences. Wiley eastern limited.
[19]. Boeriu, C. G., Bravo, D., Gosselink, R. J., &Van Dam, J. E. (2004). Characterisation of structure-dependent functional properties of lignin with infrared spectroscopy. *Industrial Crops Products*, *20*(2), 205–218. https://doi.org/10.1016/j.indcrop.2004.04.022
[20]. Faix, O., & Böttcher, J. H. (1992). The influence of particle size and concentration in transmission and diffuse reflectance spectroscopy of wood. *Holz Als Roh-Und Werkstoff,* *50*(6), 221–226. https://doi.org/10.1007/BF02650312
[21]. Qiang W., Kefu C., Jun L., Guihua Y., Shanshan L., & J. X. (2011). The solubility of lignin from bagasse in a 1,4Butanediol/water system. *Bio Resources*, 6(3), 3034–3043.http://ncsu.edu/bioresources.
[22]. Javor, T., Buchberger, W., & Tanzcos, I. (2000). Determination of Lignin Degradation compounds in different wood digestion solutions by capillary electrophoresis. *Lenzinger Berichte*, *79*, 50–55.https://doi.org/10.1007/s006040070017
[23]. Luo, Q., Peng, H., Zhou, M., Lin, D., Ruan, R., Wan, Y., & Liu, Y. (2012). Alkali Extraction And Physicochemical Characterization of Hemicelluloses From Young Bamboo Phyllostachys Pubescens Mazel. *BioResources*, *7*(4), 5817–5828. http://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/3245
[24]. Lisperguer, J., Perez, P., & Urizar, S. (2009). Structure And Thermal Properties of Lignins: Characterization By Infrared Spectroscopy And Differential Scanning Calorimetry. *Journal of the Chilean Chemical Society*, *54*(4), 460–463. https://doi.org/10.4067/S0717-97072009000400030
[25]. Vallejos, M. E., Felissia, F. E., Curvelo, A. A. D. S., Zambon, M. D., Ramos, L. E., & Area, M. C. (2011). Chemical and physico-chemical characterization of lignins obtained from the ethanol-water fractionation of bagasse. https://ri.conicet.gov.ar/handle/11336/43206
[26]. Ni, Y., & Hu, Q. (1995). All cell lignin solubility in ethanol–water mixtures. *Journal of Applied Polymer Scienc*e, *57*(12), 1441–1446. https://doi.org/10.1002/app.1995.070571203
[27]. Saariaho, A. M., Jääskeläinen, A. S., Nuopponen, M., & Vuorinen, T. (2003). Ultra Violet Resonance Raman Spectroscopy in Lignin Analysis: Determination of Characteristic Vibrations of p-Hydroxyphenyl, Guaiacyl, and Syringyl Lignin Structures. *Applied Spectroscopy*, *57*(1), 58–66. www.osapublishing.org/as/abstract.cfm?uri=as-57-1-58
[28]. Mishra, D., Shukla, A. K., Dixit, A. K., & Singh, K. (2005). Aqueous Enzymatic Extraction of Oil from Mandarin Peels. *Journal of Oleo Science*, *54*(6), 355–359. https://www.jstage.jst.go.jp/article/jos/54/6/54_6_355/_pdf
[29]. Samrot, A. V., Senthilkumar, P., Pavankumar, K., Akilandeswari, G. C., Rajalakshmi, N., & Dhathathreyan, K. S. (2010). RETRACTED: Electricity generation by Enterobacter cloacae SU-1 in mediator less microbial fuel cell. *International Journal of Hydrogen Energy*, *35*(15), 7723–7729. https://doi.org/10.1016/j.ijhydene.2010.05.047
[30]. Korpinen, R. I., & Fardim, P. E. (2009). Reinforcement potential of bleached sawdust Kraft pulp in different mechanical pulp furnishes. *BioResources*, *4*(4), 1572–1585. https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_04_4_1572_Korpinen_F_Reinforcement_Sawdust_KRaft_Pulp
[31]. Tan, S. S., MacFarlane, D. R., Upfal, J., Edye, L. A., Doherty, W. O., Patti, A. F., Pringle, J. M., & Scott., J. L. (2009). Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid. *Green Chemistry*, *11*(3), 339–345. https://doi.org/10.1039/B815310H
[32]. Mishra, S. P., & Gaikar, V. G. (2009). Hydrotropic Extraction Process for Recovery of Forskolin from Coleus Forskohlii Roots. *Industrial & Engineering Chemistry Research*, *48*(17), 8083–8090. https://doi.org/10.1021/ie801728d
[33]. Negi, A. S., & Gaikar, V. G. (2009). Partitioning of o/p Nitro-phenols in the Presence of Hydrotropes in Aqueous Solutions. *Separation Science and*

Technology, *44*(3), 734–752. https://doi.org/10.1080/01496390802625768
[34]. G. Raman & V. G. Gaikar, (2006) Hydrotropic Solubilization of Boswellic Acids from Boswellia serrata Resin, *Langmuir*, *19* (19), 8026–8032, https://doi.org/10.1021/la034611r
[35]. SMishra, S. P., & Gaikar, V. G. (2006). Aqueous Hydrotropic Solution as an Efficient Solubilizing Agent for Andrographolide from Andrographis paniculata Leaves. *Separation Science and Technology*, *41*(6), 1115-1134. https://doi.org/10.1080/01496390600633675
[36]. Mishra, Sanjay P., & Gaikar, V. G. (2004). Recovery of Diosgenin from Dioscorea Rhizomes Using Aqueous Hydrotropic Solutions of Sodium Cumene Sulfonate. *Industrial & Engineering Chemistry Research*, *43*(17), 5339–5346. https://doi.org/10.1021/ie034091v
[37]. Dandekar, D. V., Jayaprakasha, G. K., & Patil, B. S. (2008). Hydrotropic extraction of bioactive limonin from sour orange (Citrus aurantium L.) seeds. *Food Chemistry*, *19*, 515–520. https://doi.org/10.1016/j.foodchem.2007.12.071
[38]. Desai, M. A., & Parikh, J. (2012). Hydrotropic Extraction of Citral from Cymbopogon flexuosus(Steud.) Wats. *Industrial & Engineering Chemistry Research*, *51*(9), 3750–3757. https://doi.org/10.1021/ie202025b
[39]. Zhou, Y., Gao, F., Y., Z., & Lu, J. (2014). Study on the extraction kinetics of phenolic compounds from petroleum refinery waste lye. *Journal of Saudi Chemical Society*, *18*(5), 589–592. https://doi.org/10.1016/j.jscs.2011.11.011
[40]. Balasubramanian, K., & Burghard, M. (2008). Electrochemically functionalized carbon nanotubes for device applications. *Journal of Materials Chemistry*, *18*(26), 3071–3083. https://doi.org/10.1039/B718262G
[41]. Mai, N. L., Ahn, K., & Koo, Y. M. (2014). Methods for recovery of ionic liquids A review. *Process Biochemistry*, *49*(5), 872–881. https://doi.org/10.1016/j.procbio.2014.01.016
[42]. Brebu, M., & Vasile, C. (2010). Thermal Degradation of Lignin A Review. *Cellulose Chemistry & Technology*, *44*(9), 353.
[43]. Mousavioun, P. (2011). Chemical and Thermal Properties of Bagasse Soda lignin. *Properties of Lignin and Poly (Hydroxybutyrate) Blends*, *31*, 44. http://eprints.qut.edu.au/46668/1/Payam_Mousavioun_Thesis.
[44]. Agnihotri, S., Dutt, D., & Tyagi, C. H. (2010). Complete characterization of bagasse of early species of Saccharum officinerum-Co 89003 for pulp and paper making. *BioResources*, *5*(2), 1197-1214. https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_05_2_1197_Agnihotri_DT_Bagasse_Characterization
[45]. Chakar, F. S., & Ragauskas, A. J. (2004). Review of current and future softwood kraft lignin process chemistry. *Industrial Crops and Products*, *20*(2), 131–141. https://doi.org/10.1016/j.indcrop.2004.04.016
[46]. Gabov, K., Fardim, P., &Da Silva Júnior, F. G. (2013). Hydrotropic fractionation of brich wood into cellulose lignin: A new step towards green biorefinery. *Bio Resources*, *8*(3), 3518–3531. https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/3827
[47]. Tylianopoulos, T., Poh, M.Z., Insin, N., Bawendi, M. G., Fukumura, D., Munn, L. L., & Jain, R. K. (2010). Diffusion of Particles in the Extracellular Matrix: The Effect of Repulsive Electrostatic Interactions. *Biophysical Research*, *99*, 1342–1349. http://alumni.media.mit.edu/~zher/papers/Stylianopoulos-etal-BiophysJ.pdf
[48]. Kalogiannis, K. G., Matsakas, L., Aspden, J., Lappas, A. A., Rova, U., & Christakopoulos, P. (2018). Acid assisted organosolv delignification of beechwood and pulp conversion towards high concentrated cellulosic ethanol via high gravity enzymatic hydrolysis and fermentation, molecules. *Molecules*, *23*(7), 1647. https://doi.org/10.3390/molecules23071647
[49]. Devendra, L. P., & Pandey, A. (2016). Hydrotropic pretreatment on rice straw for bioethanol production. *Renewable Energy*, *98*, 2–8. https://doi.org/10.1016/j.renene.2016.02.032

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