

Synthesis, characterization and metal adsorption capacity of *Acacia* lignin based resin

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Abstract

The present study is focused on the synthesis of ecofriendly adhesives based on *Acacia* lignin. Alkali lignin extracted from *Acacia* wood was used for preparation of bio-based resin. Resin was synthesized using lignin as the replacement of petroleum-based phenol through condensation polymerization reaction catalyzed by sodium hydroxide. Structural characterization was performed using Fourier transform infrared spectroscopy (FTIR), Differential scanning calorimetry (DSC), Thermo-gravimetric analysis (TGA) to measure the glass transition temperature and thermal degradation, respectively. FTIR, revealed *Acacia* lignin resin resemblance in structure with control resin along with higher reactivity. DSC study suggested that the *Acacia* lignin based resin exhibited higher glass transition (T_g) temperature ($T_g = 475.19^\circ\text{C}$) as compared to commercial lignosulphonate based resin ($T_g = 263.05^\circ\text{C}$). The weight loss rate of the synthesized lignin based resin presented slightly different weight loss curves, wherein the main pyrolysis stage was observed at 200-515 $^\circ\text{C}$. The formulated *Acacia* lignin based resin exhibited uniform morphology and enhanced temperature stability compared with commercial lignosulphonate based resin. Further, the highest metal adsorption capacity was presented by alkali lignin (86%), followed by lignosulphonate based resin (79%). The improved properties of the product were attributed to the increased covalent interaction among phenol-formaldehyde and lignin. Thus, lignin based resin can be utilized as adhesive as well as for the formation of composite materials.

Key words : *Acacia* lignin, Bio-based resin, FTIR, DSC, Metal adsorption capacity.

INTRODUCTION

The recent development in global manufacturing industries led to increase utilization of petroleum and petrochemicals. The excessive use of petroleum and petro products has enhanced environmental pollutions. Thus the search for novel and ecofriendly alternative of petrochemicals, is crucial for investigators. Phenol-formaldehyde (PF) resins are mostly synthesized using petrochemicals like phenol and formaldehyde under alkaline catalyst^[1]. PF resins are used in the wood industry for their excellent performance, including high bonding strength, excellent water resistance, heat resistance and chemical stability, but its toxicity and high cost production limit its uses^[2,3]. Hence the reduction of cost and substitution of petrochemical based raw materials is important for synthesis of resins.

Nowadays, the progress of polymers from renewable resources is a field that is gaining increased attention due to features like sustainability, environmental control and low production cost^[4,5]. Lignocellulosic biomass, such as agricultural and forestry residues, contains a significant amount of lignin, a polyphenolic aromatic molecule, at up to 30-40 % of its dry weight^[2]. Lignin and its derivatives are one of the most extensively employed biomaterials, hence lignins, such as kraft lignin and lignosulfonates, have been studied as a raw material for partial substitution or replacement of phenols^[6,7]. Lignin and phenol are structurally similar for possessing more phenolic hydroxyl groups which make it possible for lignin to be used as a substitute for the phenol in the synthesis of PF resin. It is an amorphous three-dimensional phenyl-propanoid structures synthesized by enzymatic polymerization of three monomer i.e. *p*-coumaryl alcohol, coniferyl-alcohol and sinapyl-alcohol^[8]. The resulting structure is a complex macromolecule with a great

variety of functional groups. Conventionally, lignosulphonate (lignin resulting from the sulfite or kraft pulping process) has been the only type of lignin widely used in the production of lignin based product such as dispersants, emulsifier, resins etc.^[3].

Several reports have been published on the synthesis of lignin based phenolic resin from the forestry and agricultural residues lignin^[2,3,9], and the chemical or structural modification of lignin to increase the reactivity of lignin for the synthesis of ecofriendly resins^[9,10]. Recently, lignin efficacy as a binder or resin or adhesives by biochemical modification and novel extraction process like acid hydrolysis and organosolv process have been reported^[10,11,12,13]. *Acacia* species are one of the most dominant tree found in tropical region of India including Chhattisgarh. They are basically used in a timber mill for making furniture's and a large amount of *Acacia* wood powder is thrown as waste. It can be easily available with low nominal cost and also a good source of lignin^[14]. In addition, *Acacia* lignin can also be used as reducing and stabilizing agent for the synthesis of metal nanoparticles^[15]. Hence, the use of *Acacia* wood powder as a raw material for lignin extraction could be better for economic and environmental concern point of view.

In the present work, *Acacia* wood dust was used as a raw material for lignin extraction. Lignin extracted using alkali extraction method have been applied for the preparing of lignin-PF resin. The synthesized lignin based resin was chemically and thermally characterized. Further, metal adsorption capacity of lignin based resin was also investigated.

MATERIALS AND METHODS

Acacia wood powder was collected from a local timber mill of Bilaspur, Chhattisgarh, India. Phenol, formaldehyde, sodium

hydroxide, liginosulphonic acid and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Hi-media laboratory Pvt. Ltd, Mumbai, India. All others chemical reagents used in these experiments were analytical grade. Ultrapure water was used throughout the experiments.

Extraction of lignin from Acacia wood powder

The *Acacia* wood powder was obtained from the local timber mill of Bilaspur, Chhattisgarh, India. The dried wood powder of *Acacia* was first dewaxed using toluene-ethanol (2:1, v/v) in a soxhlet extractor and dried in an oven at 60 °C before lignin extraction. Lignin was extracted from dewaxed *Acacia* wood by alkali extraction method as described by Aadil et al. (2014)^[14]. In brief, alkali extraction dried wood was treated with 0.2 N NaOH solution (solid/liquid ratio 1:15 (w/v)) at 120 °C for 45 min. The dark brown liquor was separated by filtration and concentrated in oven at 60 °C to decrease the volume. Dissolved hemicellulose fraction was removed through precipitation by reducing the pH of filtrate up to 5.5 with 5 N HCl followed by adding three volumes of 95 % ethanol. After removing hemicellulose fraction by filtration, soluble lignin fractions were obtained by re-precipitation of lignin at pH 1.5-2.0.

Synthesis of phenol-formaldehyde (PF) and lignin based resin

In order to synthesize lignin/PF resin, 6.4 g of phenol, 15 ml formaldehyde, 0.5 g alkali lignin pre extracted from *Acacia* wood dust and 0.5 g of sodium hydroxide was mixed in a beaker equipped with a stirrer and thermometer. The mixture was heated for 45 min at 80 °C. In order to stop the reaction, the mixture was

quickly cooled to 40 °C. Finally, the obtained resin was cured at 110 °C for 3 h in an oven. Similar concentration and conditions were used for preparation of control resin i.e. pure phenol and commercial liginosulphonic acid. The photograph and possible reaction mechanism for the synthesis of lignin based resin is presented in Fig.1.

Characterization of resin

Fourier transform infrared spectroscopy (FTIR) analysis

The chemical structure of lignin/PF resin was analyzed by Fourier transform infrared spectrophotometer (FTIR) (Affinity 1, Shimadzu, Japan) at the resolution of 4 cm^{-1} in the wave number region 400-4000 cm^{-1} . Spectra of samples were obtained from discs containing about 1.0 mg sample in approximately 100 mg potassium bromide (KBr).

Differential scanning calorimetry (DSC) analysis

Glass transition (T_g) and melting temperatures were determined by using Differential scanning calorimetry (DSC 60, Shimadzu, Japan), scanned between 25 to 600 °C, under a nitrogen atmosphere (35 ml/min) with a constant heating rate of 50 °C/min. α -Alumina (α - Al_2O_3) powder provided by the Shimadzu Corporation, Japan was used as standard. Data were analyzed by the Thermal Analyzer (TA-60 WS Acquisition status) software.

Thermo-gravimetric analysis (TG/DTA) analysis

Thermogravimetric analysis (TG/DTA) of synthesized films was performed by using a thermo-gravimetric analyzer (Diamond STA-6000, Perkin-Elmer, Shelton, USA) under a nitrogen atmosphere at a flow rate of 200 ml/min. Resin samples (about 5 mg) were heated from 40 to 700 °C at a heating rate of 10 °C/min to obtain individual spectra.

Metal adsorption assay

In order to investigate the metal adsorption capacity of prepared lignin based resin, 0.5 g of resin was mixed into 50 ml solution of nickel chloride (NiCl_2) (10 mM). The reaction mixture was incubated for 24 h at room temperature under constant stirring. After 24 h the reaction mixture was filtered. The amount of metal adsorbed by resin was determined using atomic absorption spectroscopy (Shimadzu AA 7000). The amount of metal ion adsorbed at equilibrium per unit mass of sorbent was evaluated according to:

$$q_e = C_o - C_e / D$$

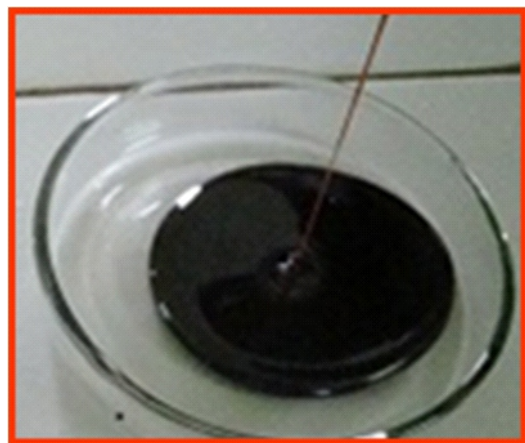


Fig 1a : Photograph of lignin based resin.

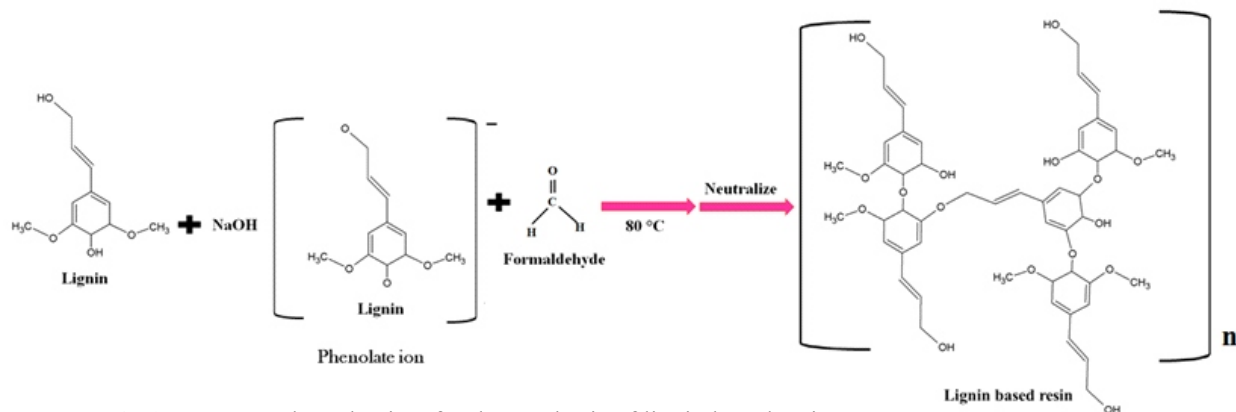


Fig 1b : Proposed mechanism for the synthesis of lignin based resin.

where C_o , C_e denote the initial and equilibrium metal concentration in solution, respectively, and D is sample dose.

RESULTS

FTIR analysis

The FTIR spectra of a representative *Acacia* lignin and lignosulphonate based resin and control phenol-formaldehyde resin is presented in Fig. 2. It was observed that the IR spectra of lignin-PF resin are similar, suggesting the resemblance of the structure of the both resins with reference resin (PF resin). It was further observed that peaks around at 3600 cm^{-1} appeared in both

appeared at $1600\text{--}1500\text{ cm}^{-1}$, which correspond to the aromatic skeleton of lignin. It was also noted that the peak at 1479 cm^{-1} assigned to the methylene groups (CH_2) bridges, appeared at 1479 cm^{-1} in LS resin, whereas these peaks shifted at 1415 cm^{-1} in AL resin and the carbon-oxygen ether band appeared at $1400\text{--}1000\text{ cm}^{-1}$ [16].

Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) and melting temperature (T_m) were determined by DSC analysis. It was observed that the T_g of *Acacia* lignin based resin ($T_g = 475^\circ\text{C}$), was higher than the

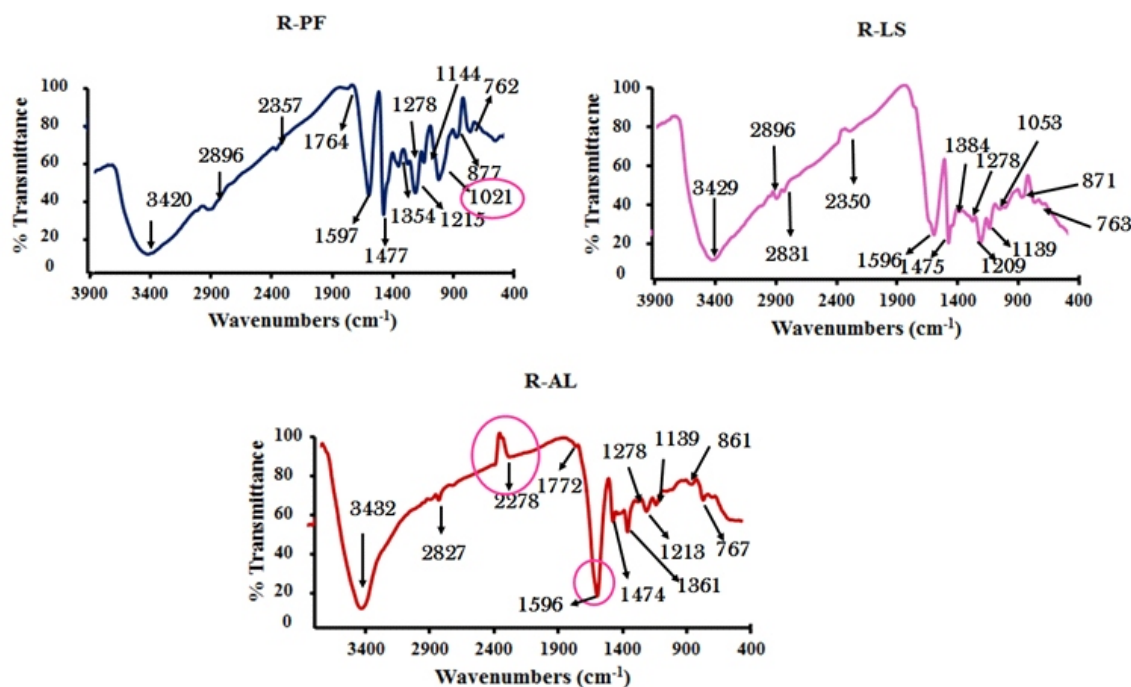


Fig 2 : FTIR spectrum of control, *Acacia* lignin and lignosulphonate based resin.

the resin, which was attributed to hydroxyl groups ($-\text{OH}$) of lignin. The band at 2916 cm^{-1} was attributed to C-H stretch of methylene groups and at 2839 cm^{-1} , typical C-H stretch of methoxy groups (Fig. 2) [6]. The characteristic peaks of lignin

commercial lignosulphonic acid based resin ($T_g = 263^\circ\text{C}$). The DSC study revealed that the lignin-phenol-formaldehyde resin exhibited slightly different curing behavior as compared to commercial lignosulphonic-PF resin (Fig. 3). The DSC profile of

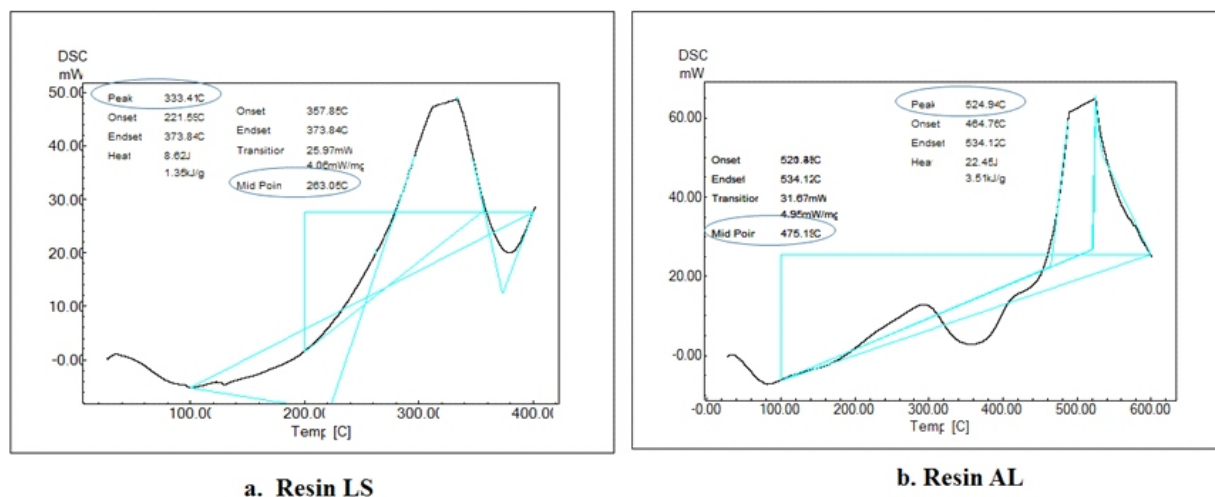


Fig 3 : Differential scanning calorimetry spectra of resins.

LS resin exhibited a main exothermic peak at 333.41 °C whereas in AL resin it was at 524.94 °C, which was higher than LS resin. Main exothermic peaks appeared between 221 to 373 °C in LS resin, while this peak was shifted in AL resin (464-534 °C). The exothermic heat for curing of LS and AL resin was 8.62 J/g and 22.45 J/g, respectively.

Thermo-gravimetric analysis (TGA)

Polymer degradation is most frequently studied under inert atmosphere. Oxidative degradation is equally important because it is closer to the realistic atmospheric condition of degradation^[17]. The thermal degradation of synthesized lignin based resin was determined by thermogravimetric (TG) and differential thermal analysis (DTA) under a nitrogen atmosphere. TG curves (Fig. 4a) relate the weight loss of the materials to the temperature of

500 °C the process is related to the decomposition of some aromatic rings. From Fig. 4a, it was observed that the degradation temperature of AL resin is higher than the LS resin, the 50% weight loss was observed at above 650 °C while in LS resin it was approximately 550 °C. The higher thermal stability of AL resin might be due the strong interaction of AL with phenol-formaldehyde and presence of methylene bridge (CH₂), which provides the thermal stability of resins^[16]. After 700 °C residues were observed, which might be due the inorganic impurities. The results show the similarities with other reports^[2, 16].

Metal adsorption capacity

Polyphenols have been reported to form complexes with heavy and transition metals. Similarly, different lignins also proved to be good absorbers of heavy metals and consequently, it

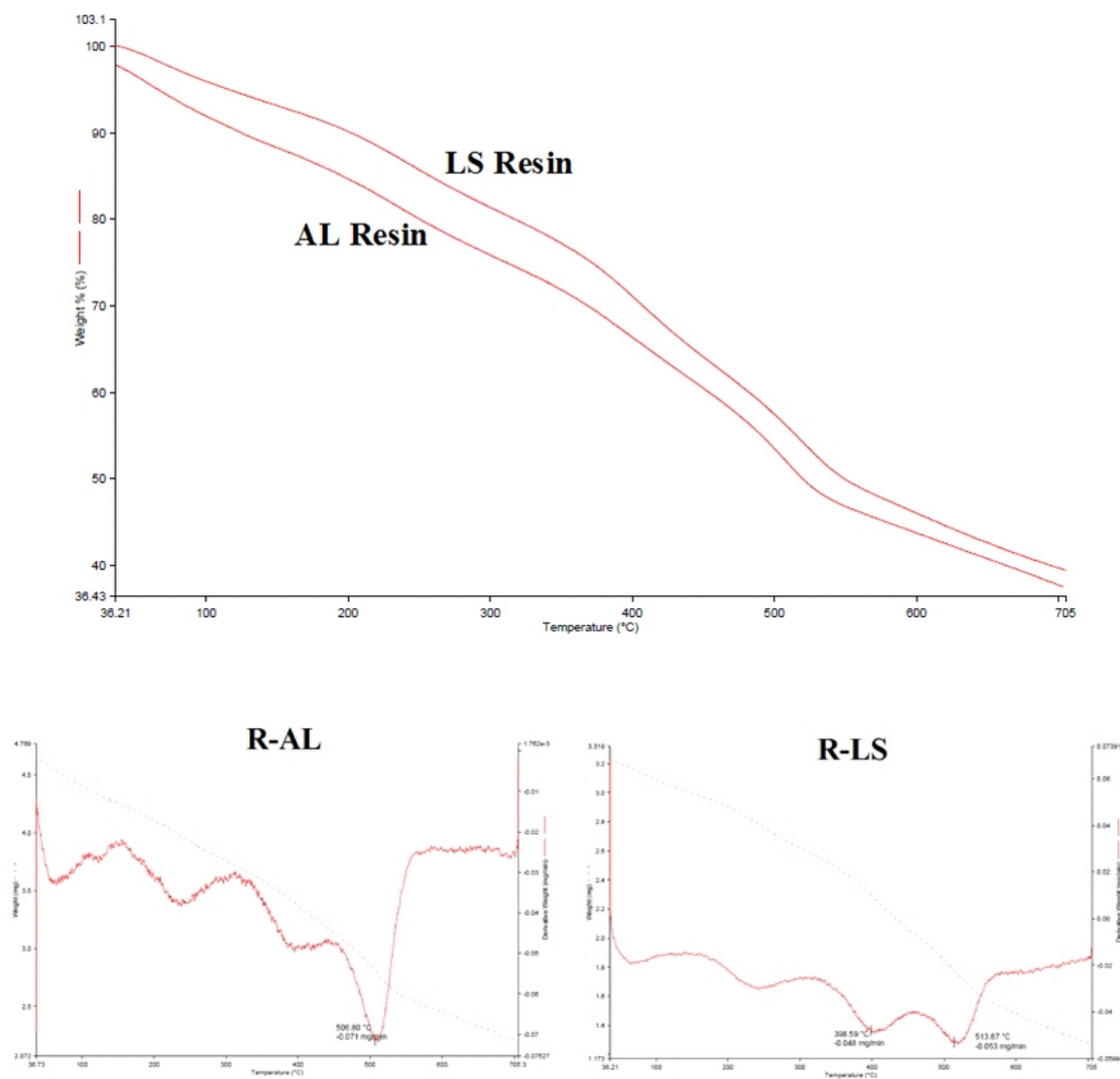


Fig 4 : Thermal degradation profile AL and LS resin
(a) weight loss percentage, (b) Derivative of weight loss

thermal degradation while the first derivative of that curve (DTA) displays the corresponding rate of weight loss^[3]. The DTA appears between 350 and 515 °C in both AL resin and LS resin, as can be seen in Fig. 4b. The pyrolytic degradation in this region mainly involves the fragmentation of inter-unit linkages, releasing monomeric phenol into the vapour phase, while above

might be used for water and other purification systems purification^[18]. The results indicated that the synthesized lignin based resin has the ability to adsorb the Ni²⁺ ion as shown in Table 1. The highest metal adsorption capacity was presented by alkali lignin (86%), followed by lignosulphonate based resin (79%).

Table 1: Metal adsorption by lignin based resin.

Sample	Initial concentration of NiCl ₂ (ppm)	Final concentration of NiCl ₂ (ppm)	Amount of NiCl ₂ adsorbed after test (ppm/g of substrate)	Metal adsorbed (%)
Control PF resin	0.182	0.182	0.182	0.0
Lignosulphonate based resin	0.182	0.036	0.58	79
<i>Acacia</i> alkali lignin based resin	0.182	0.024	0.63	86

DISCUSSION

Acacia lignin has an aromatic and highly cross-linked structure, similar to the network of phenol-formaldehyde (PF) resin. Some of the reports have been published on the synthesis of lignin based phenolic resin from the forestry and agricultural residues lignin^[2, 3, 11, 13]

The synthesis of lignin/PF resin was initiated by the combination of phenolation and polymerization reaction in presence of alkali catalyst (NaOH)^[11]. The results indicated that the *Acacia* lignin based resin has similar reactivity and characteristics as observed for the control phenol-formaldehyde resin which is agreement with the previous reports^[2, 3, 9]. FTIR spectroscopic study of the resin revealed the chemical interaction between lignin and phenol-formaldehyde. IR spectra revealed that the phenolic -OH groups are the most important functional groups in a polymerization reaction during the synthesis of PF resins for activation of the free ring positions to make them react with formaldehyde^[1, 19].

The obtained exothermic peak values for curing of LS and AL resin were found lower than the curing heats for kraft lignin-phenol-formaldehyde resin (81- 100 J/g) reported by Dominguez et al. (2013)^[6]. The difference in melting temperature might be due to the more complex structure of *Acacia* lignin as compared to lignosulphonic acid. The exothermic peaks of lignin based resin mainly appeared due to the exothermic reaction of free formaldehyde with phenol or lignin to form methylphenols^[3, 20]. *Acacia* lignin based resin has higher thermal stability as compared to commercial lignosulphonate based resin. The weight loss rate of the synthesized lignin based resin presented slightly different weight loss curves, wherein the main pyrolysis stage was observed at 200-515 °C as confirmed by thermal analysis. The glass transition values are found higher than the previously reported ammonium lignosulphonate (130 °C) and organosolv lignin (180 °C)^[6, 21]. Further, the highest metal adsorption capacity was presented by alkali lignin as compared to lignin based resin. This could be possibly due to the larger pore size and surface area of alkali lignin as compared to commercial lignin. The adsorption mechanism of Ni²⁺ ion possibly occurred by hydrogen bonding and electrostatic interaction between metal ions and resin^[22].

CONCLUSION

Acacia lignin has been successfully applied for the synthesis of resin. The *Acacia* lignin based resin has similar reactivity and characteristics as observed for the phenol-formaldehyde resin.

FTIR study revealed the chemical interaction between lignin and phenol-formaldehyde. *Acacia* lignin based resin has higher thermal stability as compared to commercial lignosulphonate based resin. Moreover, the *Acacia* lignin based resin displayed higher metal adsorption capacity. Hence, present study suggested that the *Acacia* lignin could be a better alternative of phenol in the synthesis of phenol-formaldehyde resin.

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