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RESEARCH ARTICLE

Selective separation of biomass from black liquor waste by inorganic and organic acids

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Abstract

Lignin biomass has been investigated over the last few decades as a promising resource of many green chemicals and materials. It forms basis of sustainable development but needs scientific support and exploration. In the present work lignin biomass was precipitated from the Kraft black liquor of hardwood and bamboo by using inorganic and organic acids at pH 2, 4, 7,9,10 respectively in order to estimate optimum isolation conditions. A comparative study was performed among the lignin biomass so obtained, based on yield and chemical structure and thermal stability. The results showed that the best conditions occurred with lignin precipitation, at 9 pH temperature 50 ^{o}C, using H_3PO_4 and acetic acids for maximum yield. The residual lignin biomass was subjected to physico - chemical characterization by TGA and DTG to evaluate the lignin for various possible value added applications. The investigations showed that biomass from different acids differ significantly in Td (Thermal decomposition value in ^{O}C) values as follows $Td_{H3PO4}=304<Td_{H2SO4}=342<Td_{HCl}=352.63<Td_{AA}=384.52$.

INTRODUCTION

Globally changing climatic conditions, deteriorating environmental health and energy crises have drown much attention to the development of cleaner and greener technology based on renewable resources, necessary for ensuring sustainable development(1). One of such non-exhaustible material is lignin biomass, available abundantly from black liquor (BL) waste of pulp and paper industry (2, 3). Removal of biomass containing lignin and lignin related compounds (L & LRC) from BL would offer several advantages like, recovery of valuable chemicals, increasing the pulp capacity, and decreasing the load on environment, since COD and BOD of resistant BL waste is reduced (4,5).

Identifying the role of biobased economy in present scenario, for its promotion and implementation the governments of many countries, and several industrial-academic-associations, at international level have set goals for replacing fossil derived chemical commodities by lignin biomass such as lignoBoost, LigniMatch, and Cascading of Biomass13 Solutions for a Sustainable Biobased Economy, so as to evaluate possible upgrading of lignin into value-added products that can substitute fossil-based alternatives in sustainable manner (6-8).

Kraft lignin constitutes of various functional groups, main groups in unmodified lignins are hydroxyl (aromatic and aliphatic), methoxyl, carbonyl, and carboxyl, because of the reactions involved in the pulping processes modify the properties of the native lignin, and the separation method adopted for its recovery which determine its potential applications. The solubility of the lignin is affected by the proportion of these functional groups; most lignins are quite soluble in alkaline solution due to the ionization of hydroxyl and carboxyl functional groups (9,10).

Out of the two available techniques of separation biomass from of black liquor, ultrafiltration and precipitation, the later provides superior separation with less ash content at a lower cost owing to possible gravimetric separation, as compared with ultrafiltration, as reported by Uloth and Wearhg (11). Precipitation can be done by using CO_2, SO_2 gases and acids including waste generator acids from chlorine plant. A comparative study showed that later option, gives higher yield, as exhibits in the same phase, facilitate enhanced mass transfer to occur, and work in wider pH range, with much simpler operational designing (12-15). Therefore this option was found realistic for the small as well as large scale industries.

In this paper, separation of lignin biomass by precipitation from Kraft black liquor, obtained from mixed raw material of hardwood and bamboo was investigated. The precipitation was carried out using different inorganic and organic acids at pH 2, 4, 7,9,10 with the focus being on quantifying separation properties of the lignin material to determine the optimal conditions. The reason for selecting various acidifying agents was that the different acids supposed to introduce different ions in the extracted biomass and that may affects its properties and application (16). The study also aims at investigating complete utilization of the isolated lignin biomass material in both, residual and filtrate form and its possible application as value added products. The residue available in the form of higher molecular weight fraction, and a comparative study was performed among the different lignin biomass samples so obtained, based on yield; chemical structure and thermal stability. For low molecular weight lignin in filtrate biodegradability was investigated by comparative study of %COD reduction.

Material and Methods

The black liquor was procured from nearby pulp and paper industry using Kraft pulping process and hardwood and bamboo as raw material, it was collected at 3 different locations in a multiple effect evaporators. The following Tables 1 and 2 summarizes the properties and elemental analysis of BL, as determined in the laboratory. The precipitation was carried out in on laboratory scale using inorganic acids such as concentrated HCl, HNO_3, H_2SO_4, ortho-H_3PO_4 and organic acetic acid. The BL obtained was used within 15 days of storage time, and was stored in opaque plastic containers at cool place.

Preparation of biomass

In present study a glass beaker with mechanical stirrer arrangement was taken and to this 100 ml of black liquor was added. Then the beaker was placed in the water bath for 1 hour in order to reach the target temperature and stirred (10rpm /min.) well for every 10 min. The temperature was varied between 30^oC and 60^oC. After obtaining the target temperature, acid was added slowly, and the pH of the solution was monitored continuously with an electronic pH meter. When the desired pH was reached, addition of acid was stopped and the solution was stirred for another 10 minutes. Again the pH of the solution was checked, if necessary it was adjusted by adding few drops of acid. Foam formation was observed during addition of acid. The precipitate so formed was allowed to settle for overnight for a period of 15-18 hrs (17), and then filtered through a Bücher funnel using a Whatman filter paper No 41, by applying vacuum slowly (18). The residue started collecting on the filter paper, and the filtrate in the filtering flask. The residue so obtained was washed and dispersed in distilled water having the same pH as that of the precipitate and filtration was carried out as mentioned in earlier step. The residue (solid biomass) so obtained was air dried for 48 hrs, and then oven dried for 6 hrs at $100 \pm 1\ ^0C$ (17, 19). After drying its weight and ash content was determined and then stored in air tight plastic bags. Fig. 1 gives schematic representation of steps involved in precipitation of BL and preparation of solid biomass. The detailed process parameters are given in Table 3.

Table 1 Properties of Black Liquor

S.No	Location	Designation	pH	% Solids
1	Entering the Ist evaporator	BL/18	12.45	18
2	Leaving the Ist evaporator	BL/22	12.75	22
3	Leaving the 2nd evaporator	BL/33	13.17	33

Table 2 Composition of Black Liquor

Element	C	H	N	S	P	K	Ash	O
%	31.63	2.78	0.25	2.01	0.09	0.04	48.0	15.00

Table 3 The parameters in the precipitation process

BL	Temperature ^{0}C	Acid	pH
BL/18,BL/22, L/33	40	H_2SO_4	~9
BL/33	30,40,50,60	H_2SO_4	~9
BL/33	50	HCl, HNO_3, H_2SO_4, H_3PO_4, Acetic acid	~9
BL/33	50	HCl, H_2SO_4, H_3PO_4, Acetic acid	~10,~9,~7,~4,~2

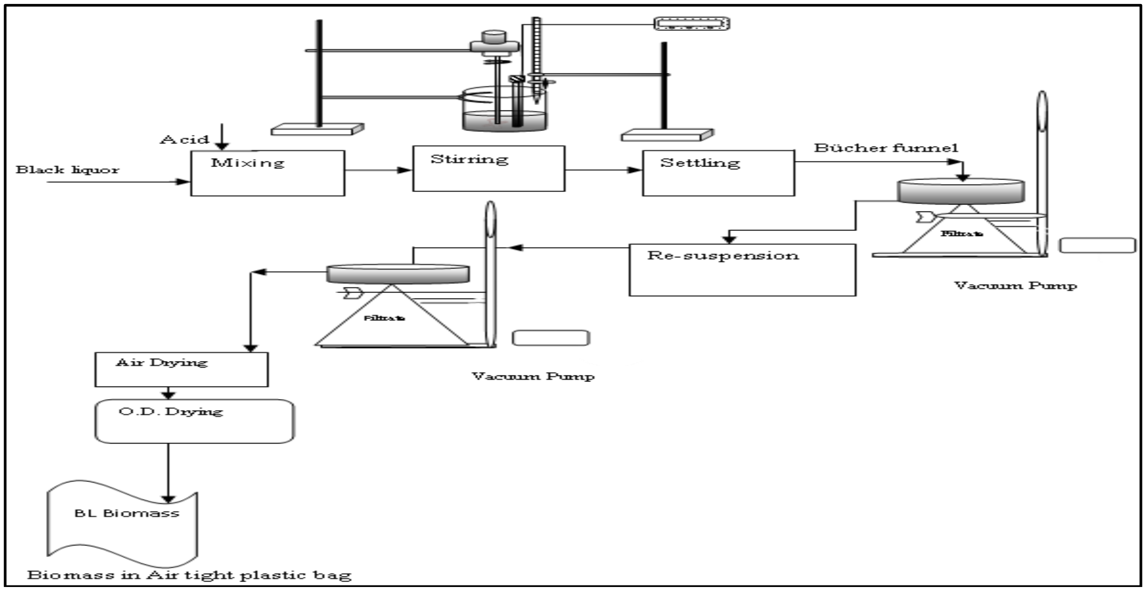


Fig. 1 Schematic representation of precipitation of black liquor and preparation of solid biomass

Results and Discussion

The results of the experiments have been compared and elucidated in the graphs and in tabular format. Acidification decreases pH of black liquor, and precipitated biomass separated out as higher molar mass fraction in the residue. BL was with solids content 18%, 22%, and 33%, it was found that as the solid content increases, % yield of lignin biomass also increases in the order BL/18< BL/22< BL/33 also reported in the literature (20), the corresponding values of ash content were 26.7%,31.7%, and 34.1%. Thus ionic strength was increased with increased solid content, caused significant differences in the yield values, as shown in Fig.2. Therefore black liquor BL/33 was found more relevant for present studies.

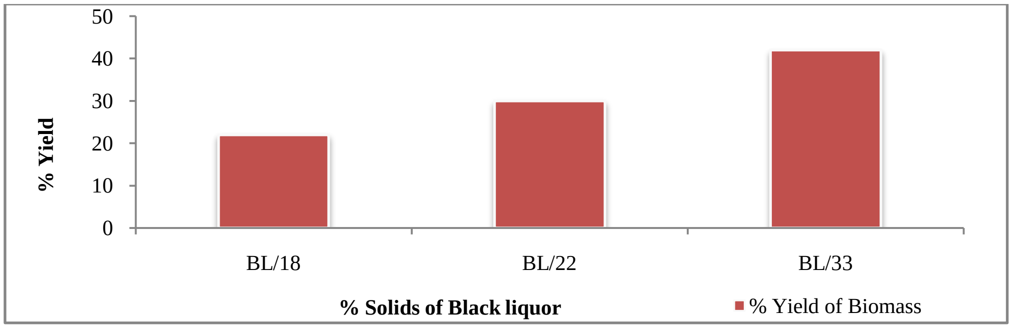


Fig. 2 Variation in yield with % solid content (source point of black liquor)

The influence of temperature on yield value is depicted in Fig.3. As temperature increases from 30 to 50 ^{o}C, yield of biomass also increases till temperature 50 ^{o}C and removes maximum biomass, but thereafter it seems to remain constant at 60 ^{o}C. Hence precipitation was carried out at 50 ^{o}C.

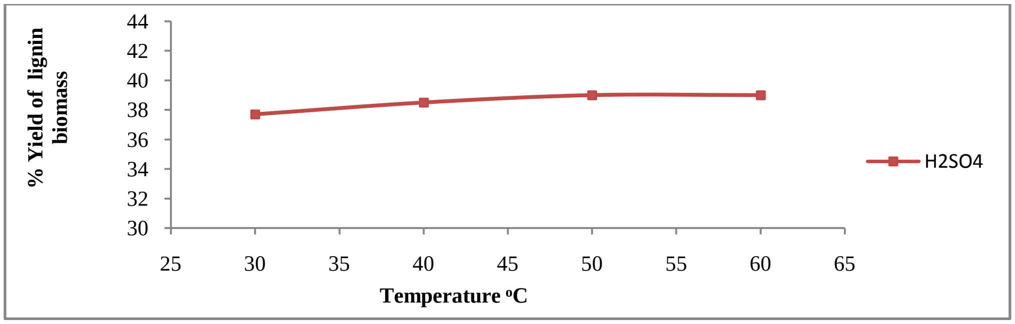
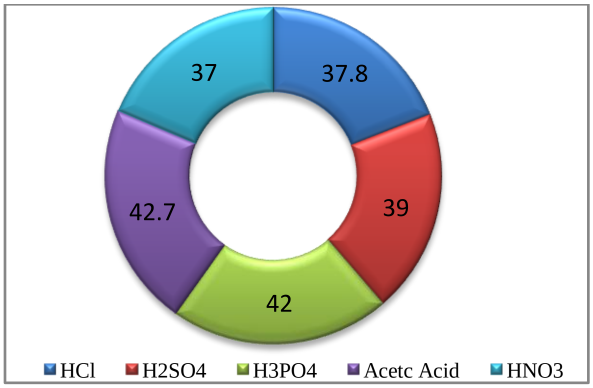


Fig. 3 % Yield of lignin biomass at various temperatures

All the selected acids, shows significant variation in % yield (gm.) of biomass as depicted in Fig.4. The observation shows that with increase in number of the hydrogen atoms in the acids, yield value also increases, in the order A.A.>H_3PO_4 > H_2SO_4 > HCl. The influence of pH on yield value is depicted in Fig.5., as pH decreases yield of biomass increases till pH 9, and maximum amount of biomass separated out, further lowering of pH in the neutral range do not significantly increases %yield, whereas in acidic range again %yield increases but to smaller extent, because remaining lignin also gets precipitate. Table 4 gives features of each acid during precipitation of BL, further during the process response of each acid was different, towards filtrate, foam, fumes, smell formation tendencies and physical texture of solid biomass so obtained.



Acid used	HNO_3	HCl	H_2SO_4	H_3PO_4	Acetic Acid
H Ions	1	1	2	3	4

Fig. 4 %Yield of lignin biomass by different acids

Although higher yield was obtained with acetic acid, in comparison with remaining, it proves ineffective in wider pH range. On the other hand nitric acid gives yield less than hydrochloric acid, furthermore, handling of nitric acid during precipitation was quite tedious, due to dense fumes generated, and hence it was discontinued.

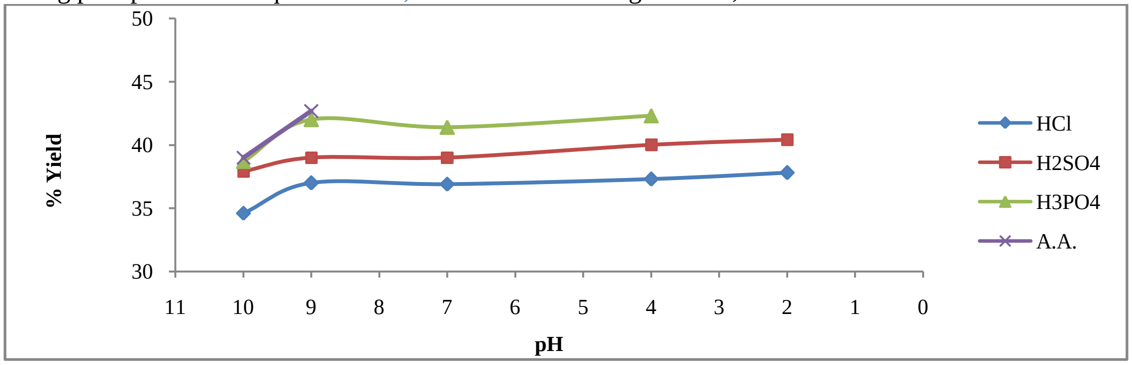
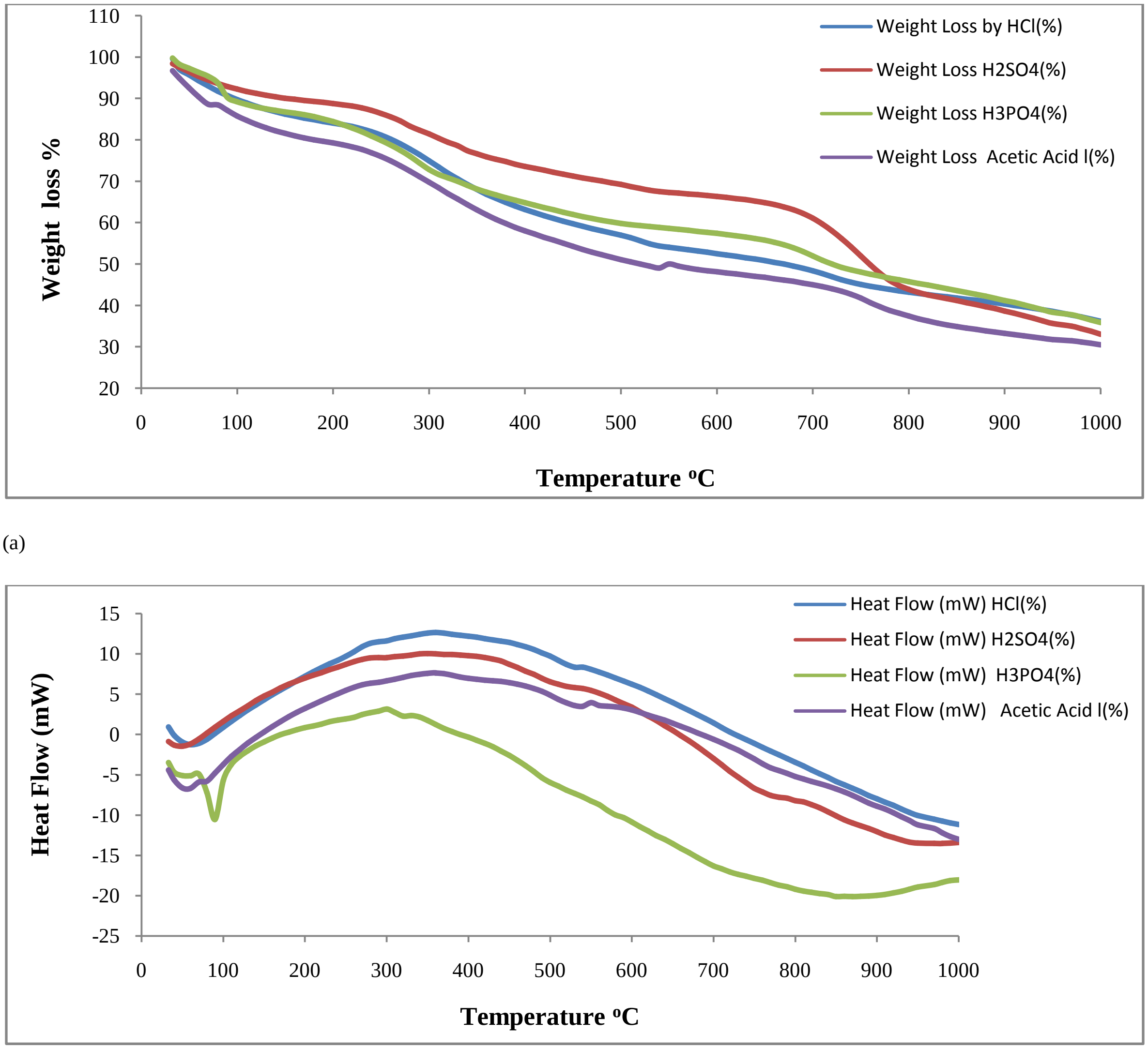


Fig. 5 Yield of lignin biomass at various pH, using different acids

Table 4 Distinguishing features and observations and made during precipitation of BL by different acids

Acid used,	Rise in Temp	Foam formation in ml, settling time (min.) Fume formation, smell tendencies, conveniences of handling	Texture, properties of solid biomass
HCl	3-4 ^{0}C	55ml ,15 min., Moderate, convenient to handle next to A.A.	Brownish chocolate, powder form, few lumps
HNO_3	2-4^{0}C	58ml , 25 min. Dense fume formation of brown color , not convenient to handle	Brownish chocolate, powder form, lump form
H_2SO_4	6-8 ^{0}C	68ml , 30 minutes, moderate,, rotten egg smell (H_2S) , can be handled	Blackish, powder form, lump form
H_3PO_4	5- 8^{0}C	65ml , 35-40 min., moderate ,fume formation ,convenient to handle ,	Dark brownish-black powder ,free flowing, grainy granular
Acetic Acid	3-7 ^{0}C	44ml , 10-20 min., least, most convenient to handle,	Brownish-black powder , free flowing, grainy

The thermal properties of lignin biomass samples were studied by TGA and DTA, under nitrogen atmosphere. TG curves reveal the mass loss of the materials vs. the temperature of thermal degradation, and its first derivative thermogravimetry (DGT) indicates the corresponding rate of mass loss. Fig. 6 (a) and, (b), shows TG and DTG curves of lignin biomass samples by different acids. The peak of this curve expressed as a thermal decomposition temperature can be used to compare thermal stability characteristics of the biomass obtained by various acids. The TGA of these samples are different from the TGA of pure lignin studied by several authors (21). The TGA curve can be distributed into three phase changes; the initial phase corresponds to moisture evaporation, followed by main devolatilization phase, and the last phase by continuous devolatilization (22). The initial moisture loss of the material started at 40 ºC to 50 ºC and reached a maximum at 78ºC to 86ºC, with primarily evolution of H_2O. Lignin is thermally more resistant than carbohydrate wood components, the actual thermal degradation of biomass started in the second phase. The degradation at a temperature range of 200 to 300 C is characteristics of hemicellulosic material (14). Td (decomposition temperature) of lignin biomass has been found to vary as given in Table 5; the events would correspond to the fragmentation of inter-unit linkages between the monomeric units of lignin, generating the release of phenols into a vapor phase. These indicate that thermal degradation of the biomass began above 234ºC (T onset). The onset temperature was 265.99, 323.72, 234.87, and 253.19 for HCl, H_2SO_4, H_3PO_4 and acetic acid respectively and resulted in significant mass losses and breaking of side chains with possible evolution CO, CO_2, and CH_4 and aldehydes (23, 24). Among all samples, Td of lignin biomass obtained from H_3PO_4 was the lowest, indicating the least thermal stability or more reactivity of material. The lignin fractionations made with acetic acid showed higher maximum degradation temperature among all. The cleavage of methyl-aryl ether bonds are identified at below 400 ºC, while above 500ºC some aromatic rings decompose, thus decomposition or condensation of aromatic rings takes place at 400-600 ºC. The next thermal event occurred at temperatures between 550 and 786º C as given in Table 5. All the samples show broad peaks in temperature range, with major degradation in 300 to 450 ºC. The range of DGTmax obtained is in agreement with findings of co-workers (25, 26).



(a)

(b)

Fig 6 (a) TGA, (b) DTG of lignin biomass obtained by different acids

Table 5 Thermal properties of lignin biomass obtained by different acids

Acid	**HCl**	**H_2SO_4**	**H_3PO_4**	**Acetic acid**
Onset (T ºC)	265.99	323.72	234.87	253.19
End (Td)	352.63	342.79	304..40	384.52
Delta	12.97	9.55	9.94	20.184
Onset	500.23	478.24		
End	538.49	549.75		
Delta	2.39	3.157		
Onset	684	699.71		692.30
End	759.34	786		764.86
Delta	4.37	16.455		6.64
Residue at				
600ºC	52.53	66.34	57.50	47.19
800ºC	43.21	43.86	45.77	35.31
1000ºC	36.21	32.52	35.25	28.61

The % residue at 600, 800, 1000 ºC of the lignin biomass are given in Table 5. The high % of residue is due to the presence of inorganic components in lignin. It promoted the demethoxylation, demethylation and dehydration of lignin. After the side-chain functional group were lost, more condensed structure remained (27, 28). Further all TGA graphs shows that the materials were not burning completely even at 1000 ^{0}C, the residue may contained trace amount of $CaCO_3$ and other sodium salt and inorganic material, typical property of Kraft lignin (29).The lignin biomass isolated by H_3PO_4 may find application in preparation of activated carbon and soil conditioner by artificial ammoxidation (30) because of lowest Td value, while acetic acid derived lignin is useful for such applications, which aims higher thermal stability, such as in the preparation of polymer, resin and formaldehyde.

It was observed that the COD of BL gets lowed, after removal of biomass. The comparative studies of %COD reduction with respect to the pH of different acids are given in Fig.7, along with corresponding volume of filtrate (ml.) generated. Finally, biodegradability of the filtrate, which is rich in sugar and carbohydrate, a minor fraction of degradation products of cellulose, hemicelluloses and lower molar mass fraction of lignin, was investigated. It was found to be degraded by soil origin fungi such as Aspergillus Niger, Aspergillus Ochraceous, Aspergillus Flavus, Tricoderma, and Penicillin to form humus like material (31). The filtrate may find applications in fermentation process, biogas generation and other green products. The recent research emphasizes that, lignin with high fractions of low molecular weight molecules are rather more reactive than those with high molecular weight molecules, and it is a good raw material for other lignin derivatives such as lignin-based phenol–formaldehyde resins (32, 33).

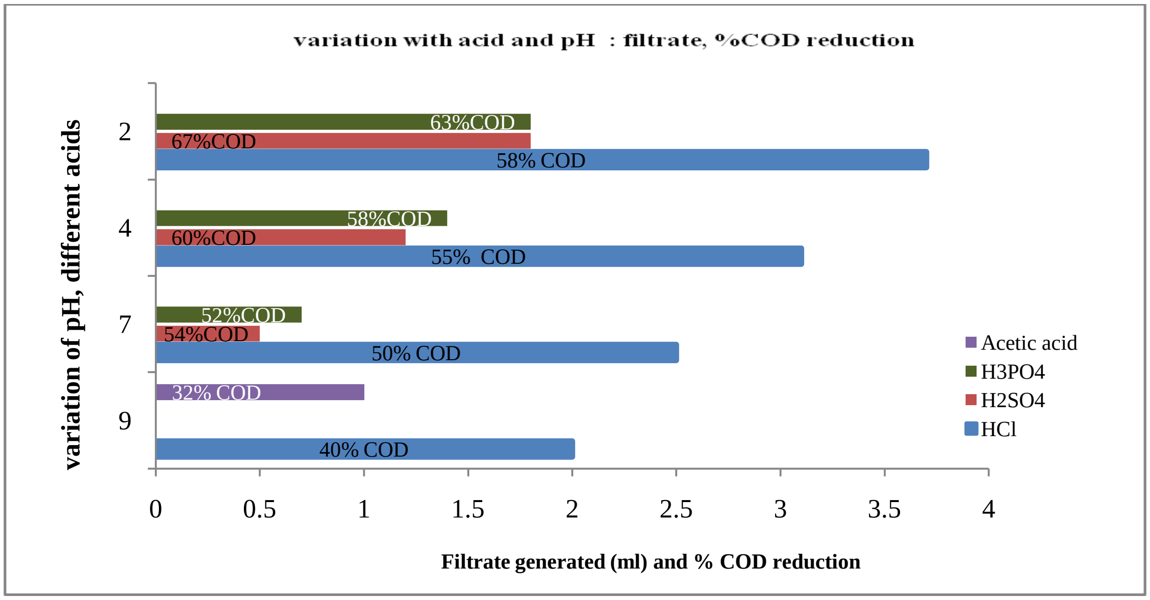


Fig.7 Variation in %COD reduction with pH, of different acids and corresponding filtrate generated (ml.).

Conclusions

A series of lignin biomass samples were obtained from Kraft black liquor of mixed material (hardwood and bamboo) by precipitation with concentrated HCl, HNO_3, H_2SO_4, H_3PO_4 and acetic acids. The conclusion that can be drown from the study are that acidification at higher ionic strength resulted in improvement in the yield of biomass. There are clear differences between the lignin obtained by different acids according to their yields and it resulted in maximum value with H_3PO_4 and acetic acids. Among the various parameters chosen, the best conditions occurred with lignin precipitation was at 9 pH, and temperature 50 ^{o}C with H_3PO_4 and acetic acids. Further, H_3PO_4 removed maximum biomass of 420 gm/l, and reported lowest thermal stability of Td_{H3PO4}=300.4 ^{O}C, may impart added advantage while preparing activated carbon and soil conditioner. Within limited pH range, acetic acid separated highest value of biomass (427 gm/l) and reported highest Td_{AA}=384.52 value, may find applications in preparation of product which requires higher thermal stability, such as preparation of polymer, resin and formaldehyde, and consequently make process more economically efficient.

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