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Lignin Separation From Black Liquor of Agro based Medium and Small Scale Paper Industry for Sustainable Development

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ABSTRACT

The pulp and paper industry is one of the most important segments of chemical industry and having more than 400 units in India. About 80% of them are based upon the agriculture residue raw materials. Now the problem is that black liquor has very high range of COD (1,25,000-1,50,000ppm) , high range of pH (12.5-14) and very dark blackish brown color which is posing a serious threat to the water bodies like rivers, lakes, ponds and even ground water. In paper mills, boilers and recovery furnaces are used for the separation of organic and inorganic chemicals. Most of the organic chemicals are burnt in the recovery furnace to generate the heat energy which is further utilized for steam generation. It is having a lot of financial burden on new paper mill installation due to costly equipment, and about 40% cost of the paper industry is mainly for installation and running this unit. So we need simpler process which requires less labor intensive, less capital cost and lower the pollution load for handling the black liquor. In this direction, present research work has been done to find an innovative process based on treatment of black liquor with hydrochloric acid. The recovered lignin can be used in number of new upcoming products like biocomposites and new bio based materials for 3D printing manufacturing.

KeyWords: Agro based Paper Industry, Hydrochloric Acid, COD, pH

Introduction

Agricultural Biomass such as wood, bagasse, wheat straw, rice straw, bamboo and reeds are used for paper making and are mainly composed of cellulose 50%, hemicelluloses 25%, and Lignin 25%. The use of rice straw and wheat straw has been studied in earlier reported research works. (Sinha, 2011; Sinha et al., 2011; Sinha, 2012). The main constituent of the Black Liquor is Lignin. Which is again second most abundant renewable raw material present on Earth it has unique characteristics as a natural biopolymer which can be used for many industrial applications? But 98% of Lignin obtained by pulping process is burnt for its fuel value in chemical recovery furnace and only 2% separated beginning from Biomass is used for other purposes. Lignin can be recovered and used for high value industrial applications resulting in better process economy. (Kumar, et al., 2016). Lignin recovery Bio-char production and decolourization of coir pith back liquor has been studied. Coir Pith Black Liquor obtained by delignification process has been decolorized using H2S O4 in different concentration and pH of solution before and after lignin recovery where found in the range of 1.65 to 3.21 and 1.70 to 3.05 respectively. The study has shown significant lignin recovery and decolourization of Black Liquor after treatment with sulphuric acid. (Rojith, et al., 2012). A research work has been done on selective separation of biomass from Black Liquor and it was found that Lignin precipitated from craft Black Liquor of hardwood and bamboo using organic and inorganic acids. The separation study has been done at pH 2,4,7,9, 10 respectively in order to estimate optimum isolation conditions. The optimum condition of Lignin precipitation was found at 9 p h, 50 degree centigrade temperature using phosphoric Acid H3PO4 and acetic acid. (Kamble, et al., 2015). The Pulp and Paper Industry generates large volume of water effluent which has dark colour and colour removal is difficult due to presence of Lignin and other Non Biodegradable organic compounds. This also reduces the possibility of reuse of water and causes synthetic problems in receiving water bodies. A study of decolourisation of Pulp and Paper Mill waste water has been done using Ozone as the reactant for colour removal dose of 10 gram Ozone per meter cube of effluent lowered the colour significantly. (Madhavan, et al 2016). Water resources are limited and India is facing lot of problems due to increase of water consumption in domestic and industrial uses. Moving bed bio-film reactors (MBBR) is found as a suitable upcoming Technology for wastewater treatment which can handle the paper industry effluent. (Pinto, 2016). A study has been done to development efficient method for recovery of Lignin and silica from Black Liquor of rice straw rice straw was pre-treated with dilute acid resulting in hydrolysis places and followed by alkaline peroxide treatment for delignification. Lignin was precipitated from black liquor using dilute sulphuric acid by reducing the pH of Black Liquor the addition of H2So4 in Black Liquor precipitated about 70% of Lignin present in Black Liquor. (Menu et al., 2012). The Lignin separated from Black Liquor obtained from Pulp and Paper Industry has been study for utilization as the precursors for preparing activated carbon by physical activation with steam results of the study demonstrated that low cost activated carbon can be prepared from Black Liquor lignin (Fu et al., 2013). Lignocelluloses plant biomass is a renewable and abundant source for the production of bio-based fuels, chemicals and chemical building blocks. Efficient fractionation and conversion of these feed-stocks are an essential step in the valorization of the cellulose, hemicelluloses and lignin fractions. The use of a new two-stage alkaline oxidation (AlkOx) process has been investigated for the pretreatment of softwood in presence of sodium carbonate. (Servaes K. et al 2016). Lignocellulosic feedstock bio-refineries may play a major role for sustainable production in the future. In the presented work, findings of four separate studies were combined. These experimental and process simulation works included one study regarding the production of organosolv liquors to investigate lignin and carbohydrate solubilization and the precipitation of lignin's, The focus lies on the possibilities of concentrating the organosolv liquor by nano-filtration for lignin separation and production.(Weinwurm et al ,2016). The aim of this study was to study the conversion of black liquor under hydrothermal conditions and its integration in a pulp mill. Three sulfur-free black liquors produced from caustic soda cooking of pre-hydrolyzed softwood, pre-hydrolyzed hardwood and non pre-hydrolyzed hardwood chips were converted. Finally, results obtained with a Kraft softwood lignin were compared to those obtained with softwood black liquor. (Huet M. et al 2016). The conversion, in a sustainable way, of paper industry wastes such as black liquor into value-added molecules is still challenging. For these reasons, the use of hydrophobic ionic liquids for the liquid–liquid extraction of these phenols has been investigated. The influences of the side chains of symmetric and asymmetric imidazolium-NTf2 as well as operational conditions (stirring rate and temperature) have been studied. As a result, [C1C6Im][NTf2] has been found to be efficient in one-step total extraction phenol components contained in the solution issued from the catalytic conversion of black liquor. This study showed that the catalytic hydro-pyrolysis of black liquor could be considered as an alternative source of phenol compounds to conventional fossil resources. (Garron A. et al., 2015). The aim of this study was to study the conversion of black liquor under hydrothermal conditions and its integration in a pulp mill. Three sulfur-free black liquors produced from caustic soda cooking of pre-hydrolyzed softwood, pre-hydrolyzed hardwood and non pre-hydrolyzed hardwood chips were converted. Finally, results obtained with a Kraft softwood lignin were compared to those obtained with softwood black liquor. Results show that bio-crude yields were greater with black liquor, whereas platform molecules production was higher with lignin. Presence of carbohydrates derivatives in black liquor is identified as a major parameter for bio-crude production as it would favor bonding between phenol species. (Huet M. et al., 2016). The implementation of wood extraction prior to pulping (pre-hydrolysis), with subsequent recovery of hemicelluloses, is expected to affect the operation of a conventional kraft pulp mill. The magnitude of impacts will depend especially on the extraction conditions. In this specific work, the consequences of integrating the auto-hydrolysis process are studied using a detailed mill balance. In turn, this would enable the simultaneous recovery of lignin and hemicelluloses. To make this process economically feasible, the extra revenue from the sales of lignin and hemicelluloses products would need to compensate for the additional operating costs in the pulp mill. (Hamaguchi M. et al., 2015). Extractions of hard- and softwood chips were carried out using green liquor with varying alkali charges (1%, 3%, and 5% on dry wood weight). The pulp yield of a mill was sustained while producing a by-product stream of extracted hemicelluloses. The liquid–liquid extractions were performed at different temperatures (25–65 °C) and pH values (0.5–3.5) for 36 min. The extraction potentials of trioctylphosphine oxide (TOPO) and trialkylphosphine oxide (TAPO) were compared to determine their application in industrial-scale extraction. It was determined that the acetic acid extraction efficiency of TAPO was higher than that of TOPO. The maximum acetic acid extraction yields for the extracts derived from hard- and softwood were 83.1% and 82.1%, respectively, using TAPO as an extractant at 25 °C and pH 0.5.(Hamaguchi M. et al 2013). Five lignin fractions were obtained by precipitation at pH 4.8, 4.0, 3.0, 2.0, and 1.5, respectively, from the black liquor of oil palm empty fruit bunch (EFB) fibre pulping after isolation of the polysaccharide degradation products, and one lignin fraction was obtained by direct precipitation at pH 2.0 from the black liquor prior to isolation of the polysaccharide degradation products. The results showed that the predominant component in the alkaline nitrobenzene oxidation mixtures was syringaldehyde, together with vanillin as the second major phenolics monomer and less p-hydroxybenzaldehyde, which corresponds to the results obtained by the non-destructive techniques such as 13C

Figure 1: *Research Lab Digester with in-direct heating used for soda pulping and generation of black liquor*

NMR spectroscopy. The molar ratio of S: V: H in the six lignin fractions was 18–21:10–12:1. (Sun. Run Can et al., 1999). As the attraction of creating biofuels and bio-based chemicals from lignocellulosic biomass has increased, researchers have been challenged with developing a better understanding of lignin structure, quantity and potential uses. Lignin has frequently been considered a waste-product from the deconstruction of plant cell walls, in attempts to isolate polysaccharides that can be hydrolyzed and fermented into fuel or other valuable commodities. During the past decade, various diverse strategies have been employed to elucidate the structure and composition of lignin. This review seeks to provide a comprehensive overview of many of the advancements achieved in evaluating key lignin attributes. Emphasis is placed on research endeavored in the last decade. (S. Jason et al., 2015.)

In this study recovery of lignin's from these processes was conducted, as well as determination of their physicochemical properties amount of Carbohydrates slightly lower hydrogen content but slightly higher oxygen content then soda listening and infrared Spectroscopy result shows that lignin's had lower totally hydroxyl contains then soda Lignin probably indicating that a higher degree of polymerization occur during 10 free treatment despite the use of low temperature and shorter reaction time on the basis of the salient feature of these lignin's potential applications were proposed(Moghaddam L. et al.,2014). The relevant information about the lignin in straw and its applications in the industry is scattered and scarce compared to the wood lignin. This review is focused on the chemical structural and composition of lignin in the straw, and its modification and uses as an adhesive. The review has also shown a great encouragement in studying the lignin within the straw and other herbaceous crops, and the creation of the functionalities of lignin as it does with cellulose and hemicellulose could lead to radical development of lignin as bio-matrix for green composites and biomass as biofuel or other high value added applications. (Hamidreza S. et al., 2013).

Methodology

The black liquor sample was taken from Shriyans paper mills Ltd. which is situated in Ahamedgarh, Punjab .The raw material which is used for the paper making is rice straw. The black liquor sample which comes out from pulp mill contains small amount of hemicelluloses, lignin, caustic and silica which is present in agriculture waste residue. The samples were treated with HCl and effects were studied.

Results and Discussion

By using hydrochloric acid some remarkable results have been revealed which shows that COD, pH and colour reduces significantly. In this direction optimization has been done by taking the different amount of hydrochloric acid, starting from 2% to 14%.

TABLE 1:
Effect of Hydrochloric acid dosing on pH and COD

S. No.	Hydrochloric acid used (%)	Sample used (ml)	pH of each sample	COD of effluent samples.
1	0	100	12.4	146800
2	2	100	10.5	98400
3	4	100	6.6	86400
4	6	100	3.4	44800
5	8	100	2.2	34600
6	10	100	0.7	36000
7	12	100	0.41	38000
8	14	100	0.27	38500

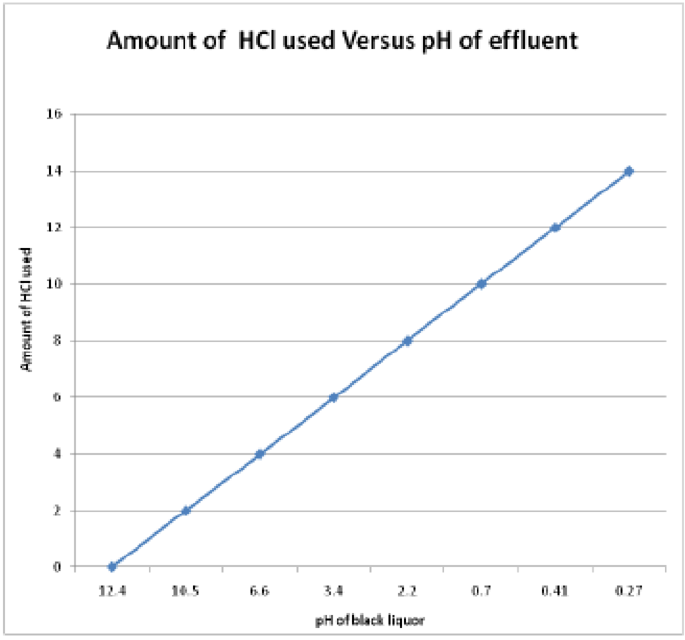

Figure 2: *Trend of decrease of pH after addition of Hydrochloric acid*

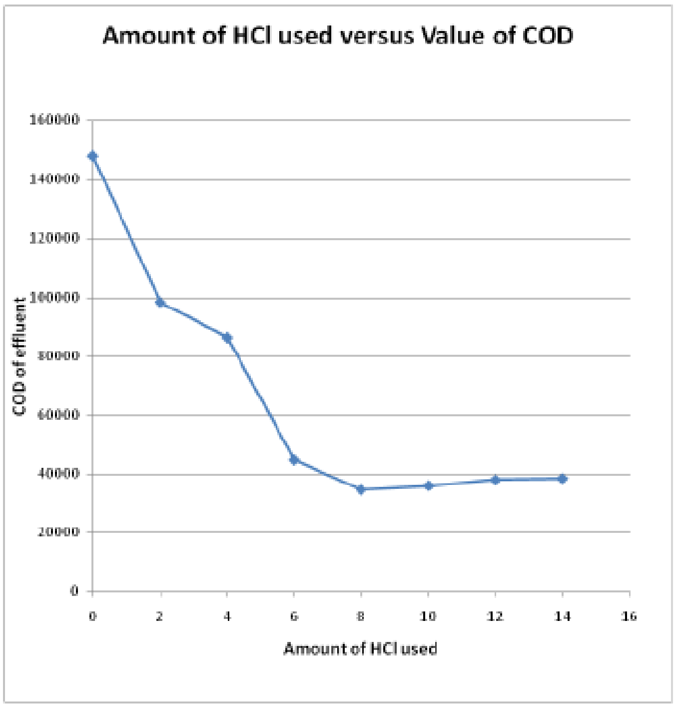

Figure 3: *Trend of decrease of pH after addition of Hydrochloric acid*

The pH was reduced from 12.4 to 2.2 and COD from 1, 46,800 to 34,600 ppm. The visible color was changed from blackish dark brown to light yellowish. Lignin part of Black Liquor precipitated on top of liquor layer and was separated easily by centrifugation methods. Lignin is used as feed in furnace utilized for steam generation, residual caustic can be reused for pulping operations and effluent can be sent to effluent treatment plant for further treatments. If COD and other factors are controlled, the water can be reused for agriculture and industrial purposes also.

As per the recent research work done (Tanase-Opedal, M., et al. 2019), lignin and fiber-based biocomposites are promising renewable materials which can be used as alternatives to petrochemical-based products. The lignin was shown as a very good bio material used for manufacturing biocomposite filaments containing 20%-40% lignin and rest of polylactic acid (PLA) as matrix material. Composites were manufactured by 3D printing by fused deposition modelling. The result showed that biocomposites increased to roughly 50% antioxidant potential/cm^2, for mixture having lignin 40% by wt.

Conclusions

In the present study, results reveal that the optimum use of hydrochloric acid (8%) will give better results as the whole lignin part is precipitated and separated from the effluent. Steam utilization is reduced during multiple effect evaporators which are used in chemical recovery process. This process is environmentally benign as it conserve the environment. This innovative work will generate less pollutants, give economical process for industry and save energy which is used for evaporation of black liquor. The recovered lignin can be used in manufacturing of large number of different types of naturally decaying bio composites and even used as raw material for 3D printing manufacturing process. So this may lead to new integrated paper industry using all the three fractions of lingo-cellulosic raw materials for manufacturing of value added products.

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