

Chemically Activated Carbon from Lignin

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Chemically activated carbons were prepared from the lignin by pyrolysing with chemical reagents. The spent liquor obtained from Kraft pulping process produced at MPM pulp manufacturing unit was used as the source of lignin. The lignin was precipitated from the liquors by adjusting the pH to 2 to 3 by the addition of 2N H_2SO_4 . In the Mysore paper mills the pulp and paper manufacturing units and sugar production units are integrated. They have their own Chemical recovery, heat recovery, and industrial waste utilization units. In CSRMP (Cold soda Refined Mechanical pulp) BSW Filtrate causes water pollution due to colour, BOD and COD. By Isolation of lignin from BSW filtrate there is a reduction to a level of 80 to 90% in colour, BOD and COD. The recovered lignin subjected to pyrolysis at 500°C in presence of Nitrogen atmosphere with suitable chemical reagents like H_3PO_4 , H_2SO_4 , $ZnCl_2$ and $CaCl_2$ activated carbon is obtained. The activated carbon is used as decolourising and de-odourising agent. Decolourisation tests were performed on a 50 Brix sugar syrup.

The aim of this project is to utilize the polluting waste from pulp mill in prevention of environmental pollution. Replacing Sulphitation process in sugar industry for decolourisation by using activated carbon. Economical development of a process for industrial production of activated carbon from lignin and its application in sugar process will help in protecting the environment from pollutants.

INTRODUCTION

The yearly growth of the world forests is about 8-10 billion M^3 of bio-mass. During the production of 150 million tons of cellulose and pulp from a part of this Bio-mass, about 50 million tons of lignins are formed, over 95% of the lignin residue is used as an energy source for the recovery of inorganic pulping chemicals or disposed as a waste.

The most important non cellulosic portion of wood is known as lignin. It can be defined as a non fibrous, non cellulosic material having the skeleton structure of Phenyl-propane monomers. It is resinous binding material between the cellulosic fibres which gives strength, rigidity and densities to the plant. Lignin is hydrophobic, mainly contains

methoxy- OCH_3 and hydroxyl-OH groups. The Lignin is an important source material for the preparation of variety of chemicals. In our present work we have used the lignin is isolated from black liquor by acid precipitation for the preparation of chemically activated carbon. The pyrolysis of the lignin in the technique used in the process.

The Mysore paper mills is of a 300 TPD capacity and have chemical and heat recovery units to prevent the pollution. In mechanical pulp mill e.g. CSRMP (Cold Soda Refined Mechanical Pulp) Chemi-mechanical pulping process, the Brown Stock Washer (BSW) filtrate contains 4000-4100 ppm of COD around 2000 ppm of BOD, 700-1100 ppm of

lignin in dissolved form Newsprint mills use mechanical pulps which forms a major constituent of the newsprint furnish. The use of mechanical pulp makes the newsprint production economically viable apart from imparting necessary properties like opacity to the newsprint, because of its higher yield and lower brightness. Mechanical pulps produced from short fibre and hardwoods have lower strength properties and there is always a necessity of the use of reinforcing pulp which is normally a chemical pulp.

In order to have high yield of mechanical pulp, pulping is carried out with minimum chemical dosages. As a result a very small portion of lignin, hemicellulose and resinous material gets solubilized in the pulping process. The low chemical dosage does not make it economically viable to operate a chemical recovery unit. Hence the effluents of mechanical pulp mills will be problematic environmentally due to its high colour and high pollution load.

EXPERIMENTAL

The Brown Stock Washer filtrate was subjected to acidification with dilute H_2SO_4 in small quantities. Lignin gets precipitated out. This is colloidal and hydrophobic in

nature. The precipitated lignin is filtered, washed and dried.

PYROLYSIS OF LIGNIN

The dried lignin is mixed with chemical reagents like H_3PO_4 , H_2SO_4 , $ZnCl_2$, and $CaCl_2$ followed by different tests. The samples are dried in an oven overnight and pyrolysed in a furnace. The furnace consisted of a silica tube and a silica boat. A thermo couple measured the temperature precisely in the centre of the tube and regulated furnace heating. Nitrogen gas was used to blanket the boat in the reaction tube. A mass of 5.0 g. pure reagent was diluted in 100 cm^3 water and added to 10 g. of dried lignin cake in a 400 cm^3 beaker. The contents were dried overnight in an oven at $105\text{ }^\circ\text{C}$, transferred to silica boat and placed in the furnace. The mass was heated to 500°C over 30 minutes and maintained at this temperature for at least 3 hours. The resulting carbon was well washed with distilled water on a filter. The running were collected and evaporated to dryness and recovered chemicals mass determined. (Details in the table no. 1.) The activated carbon was dried at 105°C and weighed.

50 g. of 50 Brix Sugar syrup was decolourized

Table 1

Chemically activated lignin	Ash %	% Retention of chemicals	% Removal of Chemicals	% Yield of Activated carbon	% colour removal
$CaCl_2$	30.8	08.6	80.0	52.0	49.0
H_3PO_4	41.1	25.4	46.0	71.2	70.0
H_2SO_4	20.5	00.7	00.2	45.3	19.0
$ZnCl_2$	30.1	15.4	73.5	56.1	53.0
No activation	32.5	—	—	30.2	03.0

Table 2: Analysis of CSRMP BSW filtrate.

SAMPLE	pH	Colour in HU units	BOD in ppm	COD in ppm	T.S in ppm	D.S. in ppm	S.S. in ppm
Before removal of Lignin	10.0	12200	1650	3600	4010	3720	290
After removal of Lignin	6.0	1250	335	850	—	—	—

with 3.0 g. of pulverized activated carbon by stirring at room temperature for 1 hour. The syrup was filtered, corrected to pH 7.0 with 0.1 N NaOH/0.1M HCl, and the absorbance measured at 420 nm in a 10mm cell using the standard ICUMSA colour method or in Hazen colorimeter in terms of HU (Hazen units) details in the table No. 2.

After the removal of lignin from the BSW filtrate there is a reduction of about 80-90% in colour, BOD and COD the values are in the table no. 2.

RESULTS AND DISCUSSION

- Yield of lignin from spent liquor obtained from Kraft pulping process is 110 to 120 gpl (impure) 45 to 48 gpl in pure form of lignin
- Yield of lignin from BSW filtrate is 700 to 1100 ppm
- After the removal of lignin from BSW filtrate there is a reduction of 80-90% in colour BOD and COD
- To control the spent liquor load on evaporator by isolation of lignin
- Elucidate the role of hemi-lignin and glycol-lignin in the formation of colour in pulp. The aim of the present part of the work was to develop a selective method for dissolution of low molar mass lignins without dissolving the glyco-lignin. In mechanical wood pulping the glyco-lignin remain undissolved, where as some of the hemi-lignins are dissolved. The hemi-lignins are responsible for the yellowing of mechanical pulp.
- Activated carbon is used as decolourising agent in sugar mill process. The sugar colour removal tests are arbitrary depending on the colorants in the feed syrup, residence time, dosage of carbon, Brix of syrup and temperature.
- Activated carbon have large surface areas and pore volume that can be adsorb sizeable quantities of impurities and are particularly suitable in environmental protection. Notably in water and effluent treatment. There are many other application range from gold extraction to toxic gas removal. Charcoal filters have been used in sugar decolourisation also.
- Decolourisation of sugar from various chemically activated carbon in the range of 50 to 70%. Replacing the sulphitation process in sugar industry for decolourisation.

- Phosphoric acid activation had the best ICUMSA colour removal for all sugar cane bagasse fractions and the higher yield of activated carbon per unit lignin feed. However the low pH of 1.8 of the decolourising syrup will negative potential use of phosphoric acid . Activated carbon in the sugar industry using the present method. The high colour removal are in a part due to the leaching of the adsorbed acid. The syrup was clarified by a phosphitation process during pH correction to 7.0 as required by the ICUMSA colour method.
- Calorific value of lignin is 6200 cal/g.
- 0.6 g. of Lignin is equivalent to 1.0 g. of coal.
- Lignin is a good adsorbent , Ion exchange and adhesive properties.
- A direct source of various kinds of phenolic and aromatic compounds.
- Good compatibility with several important basic chemicals. High energy content owing to the aromatic nuclei.

CONCLUSIONS

After cellulose and agricultural products , lignin is the largest source of organic matter in the plant kingdom. Utilization of Lignin as activated carbon and other chemicals is concerned. We can proceed along two principal routes either by using the whole unfractionated lignin cellulosic material obtained from the spent liquor, or by extracting certain fractions or high quality chemicals.

Chemically activated carbons were prepared from lignin. Comparison testing showed relatively high retention of the activating chemicals phosphoric acid and carbon gave the best colour removals.

Utilization of industrial waste from pulp mill in prevention of environmental pollution. Economical development of a process for industrial production of activated carbon from lignin and its application in sugar industry will help in protecting the environment from pollutants.

ACKNOWLEDGEMENTS

We express our sincere gratitude to the The Mysore Paper Mills Ltd., management for their co-operation, guidance , providing R & D lab for doing the experiments and also for permitting to publish this paper. And also our sincere gratitude to the dept. of Ind. Chemistry ,Kuvempu University for support and guidance to research work on lignin.

REFERENCES

1. Chemically activated carbons from sugar cane bagasse fractions by--. Bryan peter Lavarack
2. Specialty polymers from Lignin .. J Johan lindberg. University of Helsinki. Finland
3. The chemistry of Lignin...F.E.Brauns
4. Fast pyrolysis of bagasse to produce Bio-oil for power generation K.W. Morris, Int. Sugar Journal 2001. vol. 103
5. Development of Lignin by- products for industrial applications ...Gupta abha. IPPTA Conv. Issue 2001.