

Treatment of Black Liquor and Utilisation of Waste Materials Generated in Small Paper Plants

Swamy Y.V., Mohanty J.N., Murthy B.V.R., Tripathy H.K. and Tripathy A.K.

ABSTRACT

Black Liquor generated from straw based paper plant was treated to bring down BOD and total solids to environmentally acceptable limits. The BOD and total solids could be brought down effectively by conditioning the liquor with acid followed by clariflocculation. A cationic polyacrylamide (flocculant) was found to be effective in lowering BOD and total solids. It was possible to reduce BOD to 400-600 mg/l from the initial value of 2400-3200 mg/l as well as to remove all most all the suspended solids and more than 50% of the dissolved solids by clariflocculation followed by lime/sludge treatment. BOD could be further reduced to less than 100 mg/l by advanced oxidative process. The sludge obtained from the clarifier was blended with various solid waste materials generated from the paper plants and coal fines to make briquettes which can be used as domestic as well as industrial fuel.

INTRODUCTION

Paper industry is one of the highly polluting industries generating significant quantities of solid and liquid wastes. Pollutants from the plant discharge include suspended solids like fibres, sodium salts, chlorinated lignin compounds, resin acids, clays etc.. The discharge of untreated waste, therefore, create serious water polluting problem resulting toxicity to aquatic life, deterioration in water quality and increase in the cost of water treatment. The colour due to lignin, dioxins formed by the action of chlorine during the bleaching on lignin causes aesthetic pollution and persists in the water streams for long distances.

There are about 380 small paper mills in India(1). Large number of paper mills in India are based on agricultural residues like bagasse, straw, etc. Medium and large mills are generally based upon bamboos and hardwoods. Due to shortage of forest based raw materials and with an objective to conserve the forest cover, the raw materials for the future mills will be mainly agro wastes, out of which bagasse will have

a 60% share and rest will be straw, grasses and other fast growing plants. Out of the total paper plant installed capacity of 4.55 millions tonnes per year (1), about 50% of the total production is from small units. Size of these mills does not allow to install a full-fledged effluent treatment and recovering system. As a result, substantial quantity of organic mass dissolved during pulping is discharged as waste into open stream. A 30 tonnes per day paper mill discharges organic residues (2) equivalent to 30 tonnes of coal. Lignin based wastes constitute nearly 60-70% of the total organic residues and is a major source of pollution. Lignin is having high energy potential due to its high carbon content (60%) with heating value of 4,500 kCal/kg. In an integrated paper mill, lignin is used as a source of fuel in boilers to recover caustic and energy. The paper mills in developed countries co-generate energy to the tune of 70-80% of their requirement, whereas integrated paper mills in India

**Regional Research Laboratory (CSIR)
Bhubaneswar-751 013 (ORISSA)**

co-generate only 30-40% of the energy requirement of the paper mill. The small paper mills, because of high capital investment, do not install the recovery system and effluent is discharged to the environment.

Waste waters are generated from operations which include chipper house, digested house, pulp washing, bleaching and paper machine. The pollution load of the waste waters from each of the above section vary from each other as well as the same section from different mills. In recently established mills, different combinations are used to segregate the waste water (3). The purpose of segregation is to facilitate devising treatment methods at source, treatment for colour removal from a small volume concentrated waste water.

LITERATURE REVIEW

The quality of effluent desired and mode of its final disposal determines the type of treatment to be adopted. However, no single process will reduce all major pollutants and hence a combination of methods need to be used which include, (i) physical, (ii) physico-chemical, (iii) biological, (iv) solar detoxification, etc.

In physical methods, mechanically cleaned grit chambers are used to remove grit, debris and floating materials. Sediments of individual and combined waste water to remove the suspended solids in classifiers appears to be the only treatment process. Sedimentation could reduce 70% of the suspended solids and 25-30% BOD. Chemical coagulants have also been used primarily for removal of suspended solids and partly colour but the high chemical requirement and sludge disposal problems make the process uneconomical.

Physico-Chemical treatment methods have been tried to remove colour due to lignin. Chemical coagulants with CaO, Fe₂SO₄, FeCl₃, AlCl₃, Al₂SO₄ has varied colour removal efficiency of 25-95%. The resulting sludge did not settle rapidly and created problems for dewatering and disposal (4). Chinese alkaline straw pulp liquor (5) has been treated with 5.5% aluminium sulphate to coagulate the fibre particles and reduce COD. The resultant sulphate ion in the filtrate is being precipitated as calcium sulphate by addition of calcium oxide. The CaSO₄ is reacted with ammonium carbonate to form a liquid fertiliser. The COD of the remaining filtrate is reduced using 10% carbon residue of coal cinder. Application of activated carbon for colour removal from pulp wastes has been tried (6) and this process is found to be

economical if reuse of treated effluent is considered for massive lime treatment (7) for colour removal. This method achieved 90% colour removal besides 20-40% reduction in BOD.

In biological treatment methods (8), ponds (9,10), aerated lagoons (11), activated sludge process (12) and trickling filters (13) are adopted depending on local conditions. Several studies on land application of pulp and paper mill waste waters revealed that productive crop irrigation programme yield revenue thereby reducing treatment cost.

The total decolorisation of the effluent can be attributed to the difficulty in identifying and isolation of colour bearing compounds. The industries concern is about the colour of the organic origin "chromophores", the groups which generally absorb ultraviolet (UV) light through their functional groups having excess electrons such as C=C, -C=C-, six carbon aromatic rings, nitro, sulphur and oxygen containing groups and heterocyclic compounds containing oxygen, nitrogen or sulphur and oxygen containing groups and heterocyclic compounds containing oxygen, nitrogen or sulphur as a member of the cyclic ring. The colour not only deteriorate the aesthetic appearances of the stream, but also inhibit the natural process of photosynthesis due to absorbance of sun light resulting in oxygen deficiency, affecting aquatic growth. Some of the treatments like alums co-precipitation, massive lime treatment, ozonolysis and biogenetics have been tried and the ozonolysing seems more promising.

The massive lime treatment has effectiveness (14) in removing colour but due to high lime requirement, a high volume sludge is generated which can not be disposed directly for the landfill. KMnO₄ is an active decolorisation agent and it primarily attacks the C=C. The ultimate product MnO₂ brown in colour is eliminated from the effluent by filtration. Similarly hydrogen peroxide (H₂O₂) is useful in removing colour of those materials which are easily oxidisable (15). The ozone (O₃) being the highest oxidation potential, Nobel et al. (16) reported that under large excess of O₃ phenol will be completely oxidised to carbon dioxide and water. Extensive work has been carried out (17,18) using ozone and observed that it helps in reduction of BOD and COD. Colour removal is carried out effectively using granular activated carbon (19). Low molecular weight dyes are absorbed in the micropores of the activated carbon. Methods have been developed for processing paper mill sludge to prepare granular active carbon known

as pyrochar. Phrochars produced by these processes have been successfully used for removal of colour and organic matter along with heavy metals from various waste waters (20,22).

Advanced oxidation processes (AOP) of UV/H₂O₂, UV/O₃ and UV/H₂O₂/O₃ are effective for on-site destruction of organic pollutants in industrial water. Intermediate (23) addition of H₂O₂ and catalyst, Fe²⁺, reduce COD of waste water within a reasonably short time span than one time addition of reagents. AOP based upon hydrogen peroxide, ozone and ultraviolet radiation have been among the most commonly investigated (24,25). There is a growing number of commercial application of these AOP and their combination (26,27).

Solar de-toxification technology (28) use UV light from the Sun or electric lamp to drive photocatalytic redox reaction used in the destruction of toxic chemicals. Natural process is slow, but this can be augmented by light-activated catalyst. The process of water purification is further hastened by the addition of oxidants like oxygen (O₂), ozone (O₃) and hydrogen peroxide (H₂O₂) as well as lamps that produce mostly ultraviolet rays. The photocatalytic (TiO₂) is very well suited for applications to treat waste water.

During black liquor treatment, huge quantity of black sludge is generated. Besides a substantial quantities of solid combustible wastes are generated at different stages of the paper plant. The economy of the plant depends heavily on the extent of energy recovery through waste utilisation. The solid wastes can be utilised either to generate energy for the plant for the use as domestic fuel.

In this paper, an attempt has been made to characterize and treat the paper mill effluent to bring down the total solid and BOD to a desired level by clariflocculation and, also, to utilise the sludge and other paper mill wastes in the form of briquettes to recover energy.

EXPERIMENTAL

Raw materials

Black liquor generated from straw based paper plants, straw dust from straw handling plant, screen rejects, sludge (black), sludge (white) from pulp washing and other fibre materials are used in the present study. The study has been carried out using two black liquor samples (Sample A and B) and the

Table-1
Characterisation of black liquor.

Parameters	Sample A	Sample B
pH	8.70	8.10
Total solids g/l	18.50	26.50
Suspended solids g/l	5.20	4.00
Dissolved solids g/l	13.50	22.50
Silica g/l	1.28	1.40
BOD mg/l	2340	2600
COD mg/l	9500	10250
Specific gravity g/cc	1.015	1.017

analysis of the BOD and total solids including suspended and dissolved solids are shown in Table-1.

EXPERIMENTAL PROCEDURE

The effluents, black liquor, collected from paper plants were monitored continuously. The liquor was conditioned to a required pH before loading with coagulant. The coagulated liquor was flocculated using suitable flocculating agents (cationic and anionic polyacrylamide). The flocks were allowed to settle in a settling tank and the clarified liquid was separated. The pH of the clear liquor obtained after clarification was adjusted to a neutral solution using lime/sludge treatment. The BOD and various forms of solids and silica were analysed at different stages of the treatment. The BOD was estimate (29) using revised winklers iodometric method IS 3025 (Part 44): 1993,296.

The liquor samples collected from poacher at different washing stages were characterized and tested with different dosages of coagulants and flocculants. The change in pH and BOD was monitored continuously for a period of time to estimate the requirement of various reagents.

Clariflocculation experiments were carried out in 60 litre batch capacity. A 60 litre translucent PVC tank, with conical bottom, was used for the purpose. The settling of the sludge was observed visually. The clarified liquor was collected from three outlets attached at various depths in the reactor. The sludge was discharged from the discharge port attached at the botom of the conical potion.

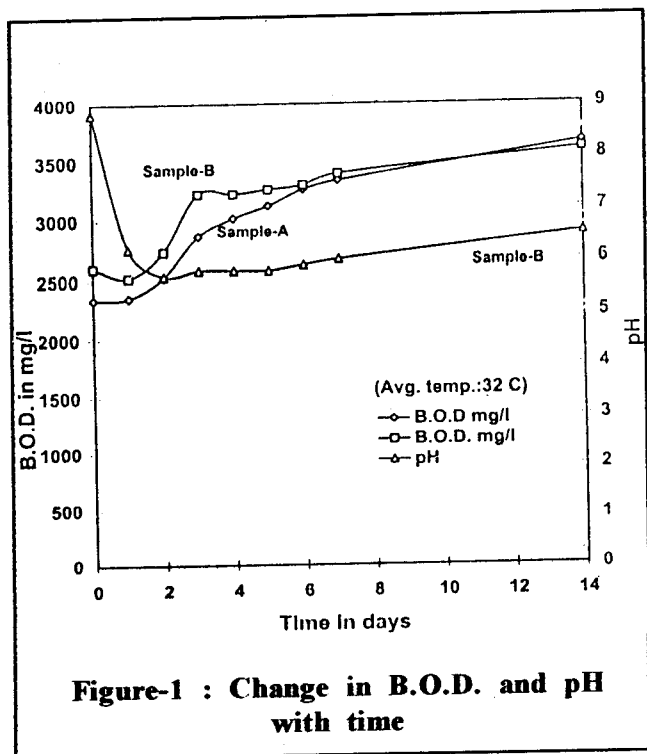
Briquettes were made using straw dust, screen

Table-2
Composition of waste materials from paper plants.

Solid waste	% Moisture	% On Dry Basis						
		Organics	SiO ₂	Free alkali	Na	Ca	Mg	Cl
Screen dust	38.50	75	15.8	0.95	0.45	0.23	0.09	1.26
Sludge (black)	35.00	40.5	41.0	9.74	2.2	0.90	0.21	3.47
Sludge (white)	38.20	54.3	46.0	0.46	0.11	0.72	0.20	1.50

rejects, black and white sludge in a laboratory briquetting press. The composition of solid waste materials is shown in Table-2. Other additives were tried keeping in view of the end use of the briquettes. The green strength of the briquettes were tested before and after drying. Study was made by supplementing coal fines to increase the calorific value of the briquette.

characterised (Table.1). The black liquor is also collected from poacher at different washing stages. The change in pH and BOD is monitored continuously by storing the liquor in an open tank. The liquor analysed from poacher at different washing stages indicates an average composition and characteristics similar to the sump sample. Hence, the study has been carried out using sump samples only. The change in pH of the liquor with time is shown in Fig.1. It is observed that the initial pH (8.9) of the liquor has come down to a pH of 5.7 within 2 days and decreases gradually to the pH value of 5.8 in 4 days. It is reported (30) that the decrease in pH may be due to the degradable organic material which makes the digestion very active causing rapid development of acetone and formic acid. The change in BOD of the liquors (Sample A and B) is shown in Fig.1. It is observed that the BOD increases rapidly in both the samples up to 4 days and reaches a maximum of around 3600 mg/l in 14 days. It is also observed that the rate of increase in BOD is uniform in both the samples. It can be seen from the Fig.1, that with time there is decrease in pH up to 4 days after which there is an increase in pH. It is also observed that there is an increase in BOD with time up to 8 days beyond which there is no significant change.



RESULTS AND DISCUSSION

BLACK LIQUOR TREATMENT

Black liquor generated from the digestion of various combinations of raw materials is collected and

Experiments are carried out in two different seasons to establish the process parameters in changed climatic conditions; Season I: Temperature varies from 23°C to 41°C (average temperature of 32°C). Season II: Temperature varies from 13°C to 29°C (average temperature of 21°C). The change in pH with climatic conditions, for sample B, is represented in Fig.-2. It is observed that the pH has come down to a value of 5.9 after 2 days from the initial value of 8.9 at an average temperature of 32°C, whereas at an average temperature of 21°C the time taken to reach the pH to about 5.8 is 5 days.

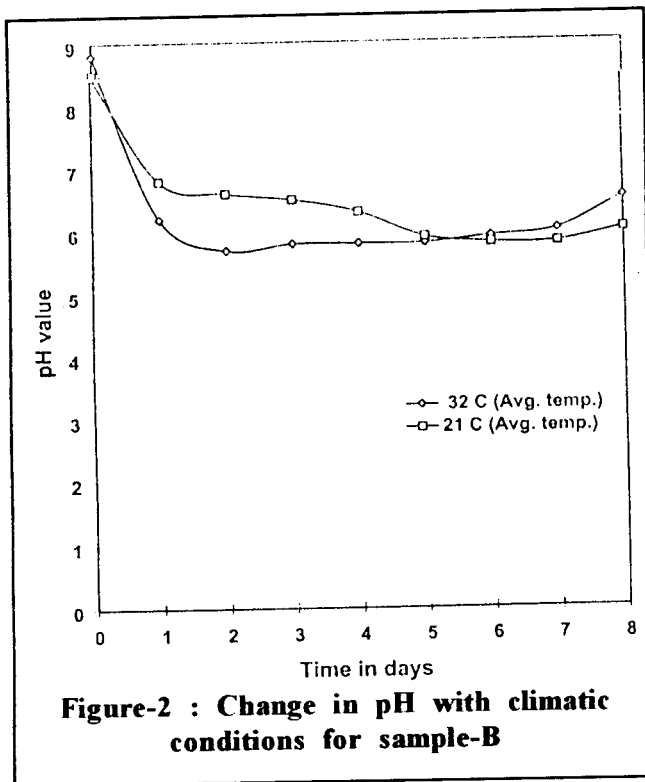


Figure-2 : Change in pH with climatic conditions for sample-B

The response of the liquor to the primary coagulant indicate that the sample has to be conditioned before being subjected to primary treatment. The liquor is allowed naturally to attain a pH of 5.8 to 6.0 followed by conditioning the liquor with acid to further bring down the pH for effective primary coagulation.

After primary coagulation, the liquor is tested with various cationic and anionic flocculants. A synthetic cationic polyacrylamide is found to be very effective in the separation of almost all the suspended solids and partly dissolved solids in the form of flocks.

More than 60-70% of the colour of the liquor is removed at this stage. The absorbance is measured at 420 nm with the help of UV Visible Spectrophotometer. The percentage decolorisation is determined using the formula:

$$D = [(A_i - A_f) \times 100] / A_i$$

Where,

D = % decolorisation,

A_i = Initial absorbance and

A_f = Final absorbance

The sludge obtained after primary clarification, contains higher residual moisture content. The moisture content in the sludge varies depending on molecular weight and dose of the flocculant. Therefore, it is believed that intra-floccular water locked within the floc structure produces a higher residual moisture content than those of the tightly packed unflocculated cakes. The flocculants, both ionic and non-ionic, are water soluble polymers and are strongly hydrophilic. The higher the molecular weight and dose level, the greater the flocculant adsorption on the surface. The hydrophilicity of anionic flocculants is the strongest, followed by cationic and non-ionic. This is one of the major reasons why flocculant cakes usually contain a higher residual moisture content than unflocculated cakes. The water molecules in a hydrated layer are gathered on the particle surface in an orderly or a saturated manner and are difficult to be removed by mechanical means. The thickness of a hydrated layer varies from 10 to 10 cm depending on the particle surface hydrophilicity [31]. The residual water content is enhanced by the reduction in particle size and increase in the specific surface area of particles. It will be possible to lower the cake moisture content and reduce the filtration cycle time by adding the selected flocculants.

The sludge separated after clariflocculation is dried naturally and is used for making briquettes for energy recovery. The clarified solution is further dosed with lime/lime sludge to bring down BOD and colour of the solution. Around 80% of initial colour of the solution is removed besides bringing down the BOD value of the solution to less than 500 mg/l (Table-3) from an initial BOD or around 3000 mg/l. The solids Removed during the treatment is shown in Table -4. It is observed that almost all the suspended solids and more than 50% of the dissolved solids are removed

Bleaching the above clear liquor could bring down the BOD to less than 100 mg/l. Bleaching with chlorine compounds may produce dioxin which are considered to be toxic. Advanced oxidation processes (AOP) of UV/H₂O₂, UV/O₂ and their combination may be further useful for on-site destruction of organic pollutants in the water [26-27].

BRIQUETTING OF SOLID WASTES

Two types of briquettes have been prepared from the paper mill solid wastes for different end uses. The typical compositions of the briquettes are given in Table-5.

Table-3
BOD of the liquor after clariflocculation.

Sample	BOD original (mg/l)	primary loading agent	Flocculant	BOD overflow (mg/l)	2nd stage treatment	BOD 2nd stage (mg/l)
A	2325	Coagulant	cpa* I	1300	Lime	390
B	2760	Coagulant	cpa II	1380	Sludge	460
A	2325	Coagulant	cpa I	1400	Lime	490
B	2760	Coagulant	cpa II	1475	Sludge	500
B	2760	Coagulant	cpa II	1500	Sludge and AOP**	125

cpa*-cationic polyacrylamide

AOP**-Advanced Oxidative process

Table-4
Percentage solids after clariflocculation.

Sample	Initial solids g/l			Final solids g/l			Dry sludge kl/kl
	Total	Suspended	Dissolved	Total	Suspended	Dissolved	
1.	18.50	5.2	13.3	6.5	0.2	6.3	19.5
2.	18.00	4.8	13.2	7.2	0.4	6.8	18.1
3.	24.00	4.0	20.0	13.4	0.4	13.0	22.4
4.	26.50	5.0	21.5	13.8	0.3	13.5	23.3

The briquettes are prepared in a laboratory briquetting press and the briquettes are cylindrical in shape with 28 mm dia.X 25 mm height. There is no requirement of any binder as the residual liquor in the black sludge has the inherent binding property. Straw dust (generated in raw material section) and screen rejects (undigested material) are fibrous in nature and are ideal for adding strength to the briquettes. The white sludge and black sludge are obtained from clarifiers treating white effluent and black liquor respectively and these sludges are subjected to natural drying before being briquetted.

The green briquettes have strength of 3-4 drops. The green briquettes are subjected to natural drying and the strength increases to more than 10-12 drops after 3-4 days of natural curing.

The briquettes, made of from the plant wastes only are light and are fast combustible. The briquettes to be used for domestic purpose should lignite fast but burn slowly. In order to prepare briquettes for

the purpose of domestic fuel, inert materials like clay is added to control the combustion process without compromising the strength of the briquettes.

In order to prepare the briquettes for use in the energy recovery stream of the plant itself the calorific

Table-5
Composition of briquettes.

Solid waste	Briquettes for Domestic use (%wt/wt)	Briquettes for Plant use (%wt/wt)
White sludge	60	65
Black sludge	7	8
Screen rejects	7	8
Straw dust	7	8
Clay (inert)	19	-
Coal fines	-	11

value should be increased and the residual ash content should be as low as possible. Hence, the briquettes from the solid wastes are prepared with coal fines and without clay. The addition of coal fines enhances the calorific value. Coal fines to the extent of 10-12% could be added without adversely affecting the strength of the briquettes.

CONCLUSIONS

The initial pH of the liquor collected from the sump of the straw based paper plant is the range of 8.5-9.0 and lowers down to a value of 5.7 to 6.0 with time.

The decrease in pH is faster during hot climatic conditions (32°C) and slower during cold climatic conditions (21°C).

The BOD and total solids could be reduced effectively by conditioning the liquor with acid to a required pH followed by coagulation, flocculation and lime/sludge treatment. A cationic polyacrylamide is found to be effective for clariflocculation.

It is possible to bring down the BOD to 400-500 mg/l from an initial value of 2800-3200 mg/l by clariflocculation followed by lime/sludge treatment.

BOD could be further brought down from 400-500 mg/l to less than 100 mg/l by advanced oxidative process.

The sludge obtained in the process could be utilised for making briquettes by blending with straw dust and other paper plant waste materials to recover energy.

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