Treatment of black liquor derived from non-woody feedstocks

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Abstract

Black liquor disposed from paper mills using rice straw as a feed stock was treated via sequenced chemical-aerobic biological process. Lignin separation was achieved by chemical coagulation using anionic polymer and at a low pH-value. The lignin removal efficiency reached 80% at 1.5% lignin concentration; whereas the removal of the COD reached 53%. The delignified effluent was subjected to biological oxidation using activated sludge process. The effects of three different concentrations of the delignified black liquor were studied using activated sludge as a post treatment. The post treatment of the delignified effluent removed up to 75% and 72% of the chemical and biological oxygen demands, respectively. These values decreased as the concentration of the spent liquor increased. The treated wastewater was amenable for wastewater discharge into the sewerage network according to the Egyptian standards.

1 Introduction

Black liquors are highly concentrated wastewater discharged during the production of chemical pulps in paper industries that don't employ technologies for the recovery of pulping chemical. However, conventional recovery processes are not economically viable for small paper mills and in those using non-woody materials with a high silica content [1]. Consequently, soda-pulping liquors are classified as hazardous wastes. Black liquors derived from non-woody feedstock are poorly biodegradable, highly toxic and contain high color level. Rice straw is a non- woody ligno-cellulosic feedstock. To show that the black liquors from non-woody feedstock are equally problematic as those from woody feedstock,

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the composition of rice straw and two commonly used woody feedstock is given in Table 1.

Table 1: Chemical composition and characteristics of some wood and rice straw fibrous raw materials.

Type		Non-wood	Softwood	Hardwood
Constituents		Rice straw[1]	Pine[2]	Birch[2]
Cellulose	(%)	40	41	38
Hemicellulose	(%)	28	24	37
Lignin	(%)	17	28	20
1% NaOH solubility	(%)	NA	10-15	14-20
Fiber length	(mm)	1.0-1.4	3.0	1.1
Fiber width[3]	(μm)	10-20	38	20

[1]Misra[15]; Bolton, [4].
[2]Biermann, [3]; Rydholm, [19].
[3]Mc.Dougall et al., [14]; Calting & Grayson, [5].

During the soda pulping, primarily the lignin and hemicellulosic components of the lignocellulosic feedstock are dissolved. Consequently, the resulting liquors are composed for the most part of lignin and products of hemicellulose degradation such as sugars and organic acids. The fatty fraction of lignocellulosic feedstock, known as "resin", is also dissolved during the soda pulping and thus the resinous compound are present in the black liquor as minor components.

Untreated pulp and paper mill effluents display acute lethal and chronic inhibitory effects to fish and aquatic organisms in the ecosystms. The organic matter concentration of black liquor is high, values ranging from 25 up to 120 g COD/l are reported [21]; [1]; [22]; [23]. Since the soda pulping process itself involves the addition of alkali, the resulting black liquors characteristically have very high pH values ranging from 9 to 14.

By far, no economically feasible process was developed yet to alleviate the detritus environmental impact of the black liquor, so that some of the plants were closed. A novel process was patented by El-Shall, [7]; to easily separate the lignin, but the liquor after lignin separation still contain high concentration of organic matter; and should be subjected to a proper treatment process to decrease its organic matter concentration to the required limits for wastewater discharge into surface water or sewage net works.

Therefore, the aim of the present study is to evaluate the treatment of the black liquor derived from the rice-straw feed stock, chemically as a pretreatment step for separating the lignin then followed by activated sludge process as a post treatment.

2 Materials and methods

The black liquor used in this study originates from the soda pulping of rice straw and it is disposed at a concentration of about 1.5% (as total solids, TS). The liquor contains mainly lignin in addition to minor amounts of carbohydrate and hemicellulose and has a pH >8. The liquor directly produced from the pulp separation has a concentration in the range of 9 to 7% total solids (TS) but in the production cycle, 3-steps washing were applied and the washing waster were added to the original liquor decreasing its concentration to 1.5% TS.

Chemical treatment: The black liquor was mixed with the optimum amount of a anionic poly-electrolyte polymer ("Magna floc 3236" Siba Specialty Chemicals Water Treatment Limited) and at a pH 2.5. The lignin was instantaneously separated and filtered using filter cloth of 24 mesh Tyler (0.85 mm) under atmospheric pressure. The process was performed batch wise.

Biological treatment: Batch laboratory experiments were carried out using activated sludge process. Two liters plexiglas laboratory columns were used. The black liquor was inoculated with activated sludge from a plant treating domestic sewage. On daily basis, the aeration was stopped to let the sludge to settle then the supernatant was drained and the column was refilled again with the spent solution (delignified black liquor) till a considerable amount of adapted sludge was produced. To study the effect of aeration period and the waste concentration on the activated sludge, several experiments were conducted. A fixed amount of sludge (3-4g/l) was transferred to different columns to which variable concentrations of the delgnified black liquor was added. To compensate the deficiency of nutrients, ammonium sulfate and potassium phosphate salts has been added prior to the bilogical process. Detention periods ranging from one hour to twenty-four hours were examined. Characterization of the treated wastewater was carried out after 60 minutes settlement.

Analysis: Raw black liquor and the treated effluents were analyzed for chemical oxygen demand (COD), biological oxygen demand (BOD_5) and total suspended solids (TSS) according to the standard methods for water and wastewater analysis [2].

3 Results and discussion

3.1 Characteristics of black liquor

Analysis of the black liquor and the spent solution after lignin separations at the concentration of 9, 7 and 1.5% (based on TS) are recorded in Table 2. These data indicated that the pH-value of the spent solution was acidic, whereas that of the original black liquor was alkaline. This was due to the acidification process at the optimum pH value of 2.5 at which maximum lignin separation (about 80%) was achieved. It is also observed that both the COD and BOD values of the liquor were enormously decreased after lignin separation but the residual values in the spent solution did not comply with the National Regularity Standards for wastewater disposal into sewerage network.

From these results, it may be seen that wide variations in the characters of the wastewater were exhibited in COD, BOD, and suspended solids. The results showed that the percent of the BOD to the COD reached only 30%. This indicated that the rice straw black liquor was only partially biodegradable. This may be due to the presence of recalcitrant organic matter. Also, it was obvious that there was a deficiency in the nitrogen and phosphorous for the biological treatment; thus it must be compensated prior to the aerobic biological treatment.

3.2 Lignin separation

The main objective of the separation process was to achieve instantaneous separation of lignin once the black liquor and the acid come into contact. This means that the retention time was extremely short which has a great impact on the economy of the process, as no voluminous reactors will be required. The main factors affecting the separation process were the polymer concentration and the pH value of the medium. Both factors were thoroughly studied and the effect of these two variables on the filtration rate of lignin was also investigated.

The effect of the polymer dose on the extent of lignin recovery and the filtration rate was illustrated in Tables 2 & 3 and Figure 1. These tests were carried out at an optimum pH value of 2.5.

The results showed that by increasing the black liquor concentration the dose of the polymer was increased whereas the filtration rate decreased.
This was related to the increase of viscosity of black liquor by increasing its concentration. It is worth to mention that at black liquor concentration of 1.5%, lignin was separated and floated on the surface of the solution, which allows its easy removal from a stirred tank by a simple skimming process.

The moisture content of the separated lignin was very high (80-90%) and it was fluffy in nature, which may introduce a problem in its subsequent handling. On the other hand, application of vacuum filtration causes destruction of the flocks and its flow through the filter cloth. Therefore, the lignin was separated using filter cloth of 24 mesh Tyler (0.85 mm) under atmospheric pressure.

3.3 Biological treatment

Biological treatment commonly helps in the elimination of the soluble organic matter, which is difficult to remove by chemical means. The role of the aerobic post treatment was to reduce the recalcitrant compounds in the black liquor wastewater. For example, resin acids are aerobically degradable [13]; [9]. Aerobic treatment of the pulp and paper industrial wastewater as a post treatment has been found capable of eliminating the acute toxicity in the pre-treatment [20].

Table 2: Average characteristics of the black liquor at different concentrations and the efficiency of lignin separation Process at the predetermined optimum pH and polymer dose.

Concentration / Characters	9%			7%			1.5%		
	Black liquor	Spent solution	% Removal	Black liquor	Spent solution	% Removal	Black liquor	Spent solution	% Removal
pH	10.3	2.5	-	9.3	2.5		8	2.5	-
COD mgO_2/l	69210	21345	69	36500	8150	78	5775	2728	53
BOD mgO_2/l	15000	6300	58	9150	2500	73	1237	805	35
Total Organic Nitrogen mg/l	145	75	48	95	36	62	50	14	72
Total phosphate mgP/l	40	16	60	28	10	64	19	6	68
Total suspended solids mg /l	21120	5920	72	6450	360	94	277.5	166	40
Total solids, %	9	-	-	7	-	-	1.5	-	-
Lignin g/l	41.0	7.7	81	27	5.7	79	8.0	1.5	81
NaOH,%	1.67	-	-	1.5	-	-	0.3	-	-

Table 3: Effect of polymer concentration on lignin recovery and filtration rate at various black liquor concentration.

Black liquor concentration* %	Polymer concentration ppm	Lignin recovery %	Filteration rate Kg lignin/m^2/day
1.5	20	79.3	75.8
3.0	40	75.8	52.4
5.7	50	79.2	16.6
7.0	60	79.5	18.5
9.0	80	81.2	11.9

* Based on Total Solids

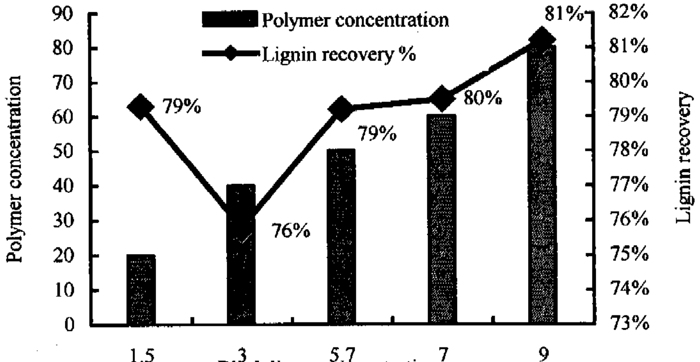

Figure 1: Effect of polymer concentration on lignin recovery at various black liquor concentration.

To study the feasibility of improving the quality of the chemically treated effluent via post treatment, the chemical treatment was complemented with a batch operated activated sludge process. The mixed liquor suspended solids was adjusted at 3g/l and it was fed with the diluted spent liquor (1.5%). The detention time was maintained at 24hrs for almost one month.

During the acclimatization period, average COD and BOD removal values were 63% and 82%, respectively. After reaching the steady state; mixed liquor suspended solids was kept around 3-4g/l. To study the effect of different concentrations of the black liquor, three concentrations were investigated; the first was the 1.5% TS; the second was the black liquor (7%) diluted with 50% sewage and the third was the concentration 7% spent liquor which its COD reaches 7300 mgO_2/l. The aeration periods ranging from one to twenty four hours were investigated.

The results obtained are given in Table 4a,b,c and illustrated graphically in Figure (2). From these results, it can be seen that at low concentration of spent liquor namely; 2260 mg COD/l, the treatment efficiency was high. The BOD, COD and suspended solids removal values reached 72%, 74% and 58% respectively after four hours aeration. By increasing the detention period to 24 hours, the COD and BOD_5 removal values increased by only 3% and 10%, respectively. Based on these data, it can be concluded that four hours aeration was suitable for post treatment of the delignified effluent of rice straw black liquor.

At higher concentrations of the spent liquor namely; 4068 and 7300 mg COD/l, the removal efficiencies of the COD and BOD_5 were decreased by 6% and 12% and by 15 % and 11%, respectively. These results indicated that upon increasing the lignin content in black liquor, the efficiency of biological treatment was decreased. This may be attributed to the fact that lignin was recalcitrant in aerobic treatment. This result is in agreement with Kern andKirk [11] which indicating a poor biodegradability of high molecular weight lignin by aerobic treatment. The occurrence of lignin biodegradation is only restricted to low molecular weight derivatives [6]; [16]. Since most of the lignin present in chemical pulping wastewater belonged to the high molecular weight [17], very little removal of lignin may be expected by biological treatment. No color reduction was observed. On the contrary, the aerobic effluent intensified in color levels. This observation has been previously mentioned by Rintala & Vuoriranta [18] and Kortekass et al.[12]. This may be due to biological removal of methoxy groups from aromatic ring [10]. The resulting phenolic compounds bearing neighboring hydroxyl groups were susceptible to auto-oxidative modifications, which led to the formation of the colored compounds [8].

Also, the results obtained indicated that the sludge settling characteristics were generally satisfactory in terms of sludge volume index, which ranged from 42 to 63 with an average value of 45 at the low concentration of the spent liquor. As the concentration of the wastewater increased the sludge settling decreased. Average value of sludge volume index was 37 at the higher concentration of the spent liquor (7%).

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Table 4a: Biological treatment of spent liquor (1.5% TS).

Time/hours Characters	Raw	1	2	3	4	5	6	24
pH	7.6	8.3	8.6	8.6	8.5	8.4	8.4	8.2
Chemical Oxygen demand mgO_2/l	2260	124 3	954	633	598	607	554	529
% Removal		45	58	72	74	73	76	77
Biological Oxygen demand mgO_2/l	510	350	224	163	145	134	117	90
% Removal		31	56	68	72	74	77	82
Total suspended solids mg/l	220	160	124	110	92	98	87	86
% Removal		27	44	50	58	56	60	60
Sludge Analysis Volume ml/l		220	205	210	190	230	230	210
Total sludge weight g/l		3.5	3.7	4.1	4.5	4.7	3.9	3.7
Sludge Volume Index		63	55	51	42	49	60	57

Table 4b: Biological treatment of spent liquor (7%) diluted with 50% sewage.

Time/hours Characters	Raw	0	1	2	3	4	5	6	24
pH	7.2	7.6	8.3	8.6	8.6	8.5	8.4	8.4	7.5
Chemical oxygen demand mgO_2/l	4068	334 2	274 8	150 0	142 8	128 4	127 2	129 6	110 4
% Removal		17	32	63	65	68	69	68	73
Biological oxygen demand mgO_2/l	1058	905	805	443	421	365	250	210	185
% Removal		15	24	58	60	66	76	80	83
Total suspended solids mg/l	262	260	220	214	202	170	132	156	148
% Removal		-	19	21	26	38	51	43	46
Sludge Analysis Volume ml/l		140	120	110	140	130	140	140	120
Total sludge weight g/l		2.6	3.9	4.3	5.1	3.3	5.7	4.3	3.7
Sludge Volume Index		53. 8	30. 7	25. 6	27. 5	39. 4	24. 6	32. 6	32. 4

Table 4c: Biological treatment of concentrated spent liquor at (7% TS).

Time/hours Characters	Raw	0	1	2	3	4	5	6	24
pH	7.1	7.3	8.8	9.0	8.9	9.01	9	9.24	8.9
Chemical oxygen demand mgO_2/l	7300	7230	6825	3360	3580	3020	2920	2720	3100
% Removal		-	6	54	51	59	60	63	58
Biological oxygen demand mgO_2/l	2336	2254	1911	1198	1074	1022	934	895	905
% Removal		4	18	49	54	56	60	62	61
Total suspended solids mg/l	360	360	355	270	285	300	298	287	300
% Removal			1	25	21	17	17	20	17
Sludge Analysis Volume ml/l			170	140	120	90	90	95	90
Total sludge weight g/l			2.6	2.6	2.6	3.2	3.6	4.0	4.5
Sludge Volume Index			65	53	46	28	25	24	20

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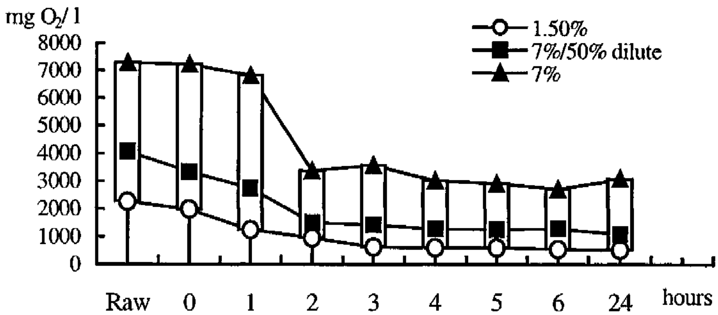

Figure 2: Effect of aeration period on the COD concentration at different spent liquor concentration.

Table 5 and Figures 3 & 4 show the overall removal values as well as the residual concentrations of the treated effluent. The data showed that, at the 7% TS spent liquor concentration, the removal values of the COD and BOD reached 91% and 89%, respectively. At the 1.5% concentration of spent liquor the efficiency was almost the same for both COD and the BOD while the residual values are far less than the 7% concentration.

Accordingly, the quality of the treated black liquor via chemical-biological process was amenable for wastewater discharge into sewerage network. The residual COD and BOD were 598 and 145 mgO_2/l.

Table 5: The Removal efficiency of the overall treatment process at an optimum detention time (4hrs).

Parameters		7%			1.5%		
		Raw	Final Effluent	% Removal	Raw	Final Effluent	% Removal
Chemical oxygen demand	mgO_2/l	3650 0	3020	91	5775	598	90
Biological oxygen demand	mgO_2/l	9150	1022	89	1237	145	88
Total suspended solids	mgSS/l	6450	300	95	277.5	92	67

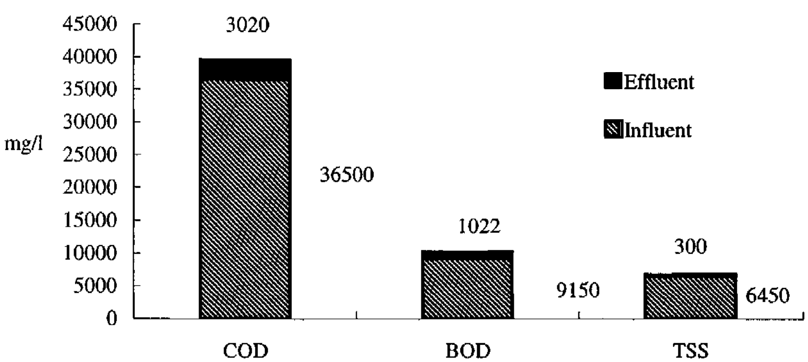

Figure 3: Residual concentration of the final effluent from the 7% black liquor.

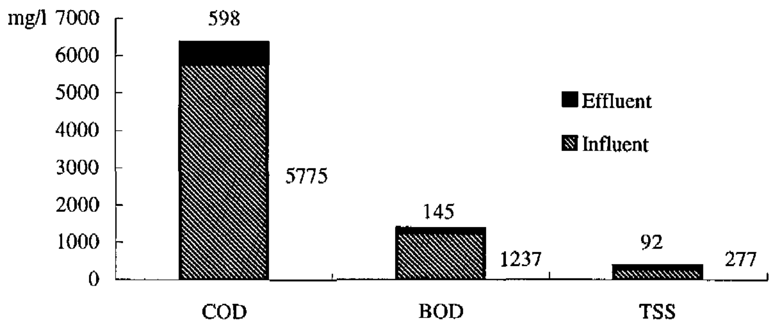

Figure 4: Residual concentration of the final effluent from the 1.5% black liquor.

4 Conclusion

Lignin was successfully separated from the black liquor by using anionic polymer and acidification at pH 2.5. The removal value of lignin reached 80%. Aerobic post-treatment using activated sludge process with aeration time of 4 hrs removed 74% of COD of the 1.5% spent liquor. The residual value of COD was 598 mgO_2/l. The quality of the treated effluent was complying with our National Regularity Standards for wastewater disposal into sewerage network. Increasing the concentration of black liquor from 1.5% to 3.5% and then 7% (based on TS) decreased the efficiency of the sequential treatment.

References

[1] Annonymous, Comprehensive industry document for small pulp and paper (1986) In : Chakrabartii,S.P. & Kumar, A. (ed.)., Comprehensive industry document Series: COINDS/22/1986. Central Board for the Prevention and Control of WaterPollution, New Delhi, India.

[2] APHA (1998). Standard methods for the examination of water and wastewater, 17th ed. American Puplic Health Association Inc., Washington D.C., USA.

[3] Biermann, C.J,(1993). Essentials of pulping and papermaking. Academic Press Inc., London., 42-50.

[4] Bolton, A.J. (1995). The potential of plant fibers as crops for industrial use. Outlook on Agriculture, 24(2), 85-89.

[5] Calting, D., and Grayson, J. (1982). Identification of vegetable fibers. Chapman & Hall, London, UK., 71-79.

[6] Colberg, P.J. & Young, L.Y. (1985). Anaerobic degradation of soluble fractions of (^{14}C-lignin) lignocellulose. Appl. Environ. Microbiol. vol.49 (2); pp.345-349.

[7] El-Shall, Hassan U.S. Patent N°. 5,635,024; 3June, 1997.

[8] Field, J.A. and Lettinga G., (1989). " The effect of oxidative coloration on the methanogenic toxicity and anaerobic biodegradability of phenols."

[9] Juna, J. and Rintala, J., (1989).," Evaluation of purification efficiency of activated sludge treatment plants for pulp and paper industry wastewaters in Finland.", International Symposium on waste management problems in agro-industries, Istanbul, Turkey, pp. 253-260.

[10] Kaiser, J.P. and Hanselmann, K.W., (1982). "Anaerobic chemicals through anaerobic microbial conversion of lignin monomers." Exprientia, vol. 38, pp.167-176.

[11] Kern, H.W. and Kirk, T.K. (1987)., " Influence of molecular size and ligninase pretreatment on degradation of lignin by Xanthomonas sp. Strain 99." Appl. Environ. Microbio., vol 53 (9), pp. 2242-2246.

[12] Kortekass, S. Doma, H.S., Potapenko, S., Field, J. and Lettinga, G., (1994) Sequenced anaerobic-aerobic treatment of hemp black liquors. Wat. Sci. Tech., 29(5/6) 409-419.

[13] Leach,J.M., Muller,J.C. and Walden, C.C. (1978)." Biological detoxification of pulp mill effluents". Process Biochemisty, pp. 18-21.

[14] McDougall, G.J., Morrison, I.M., Stewart, D., Weyers, J.D.B.,and Hillman,J.R. (1993). Plants fibers: chemistry and processing for industrial use J.Sci. Food Agric., 62, 1-20.

[15] Misra, D.K. (1987) Ceral straw, In: Hamilton, F. and Leopold, B.(eds.). Pulp and paper manufacture, Vol. 3- Secondary fibers and non-wood pulping. pp. 82-93. Joint Textbook Committee of the paper industry of the United States and Canada. TAPPI-Atlanta, CPPA-Montreal.

[16] Odier, E. & Monties, B. (1983). " Absence of microbial mineralization of lignin anarobic enrichment cultures." Appl. Environ. Mocrobiol., vol. 46, pp.661-665.

[17] Pellinen, J. and Salkinoja-Salnen, M.S. (1985). " Aqueous size exclusion chromatography of industrial lignins." J. Chromatogr., vol. 322, pp.129-138.

[18] Rintala, J.A., and Vuoriranta P. (1988) " Anaerobic-aerobic treatment of thermomechanical pulping effleunts." ;Tappi J. September, pp. 201-207.

[19] Rydholm, S.A. (1965). Pulping processes. Interscience publishers, John Wiley & Sons Inc., New York., 50,96.

[20] Schnell, A., Dorcia, J.H.C., Ashikawa, M., Munnoch, G. and Hall, E.R. (1990).,"Anaerobic and aerobic pilot scale effluent detoxification studies at an integrated new sprint mill." Pulp and Paper, Canada, vol. 91, pp. 75-80.

[21] Sierra- Alvarez, R., Kortekaas, S., Van Eekert, M. and Lettinga , G.(1991) The anaerobic biodegradability and methanogenic toxicity of pulping wastewaters. Wat. Sci. Tech., 24(3/4), 113-125.

[22] Velasco, A. A., Frostell, B., and Greene, M. (1985). Full scale anaerobic-aerobic biological treatment of semichemical pulping wastewater. Proc. 40th Industrial Waste Conf., Purdue University, 297-304.

[23] Zaxuan, W., Lixon, Y. & Nianguo, L. (1983). Disposal of paper black liquid and furfuraldehyde sewage through anaerobic digestion process. Proc. of the Anaerobic Wastewater Treatment Symposium, Noordwijkerhout. TNO Corporate Communication Dept., The Hague, The Netherlands. pp.369-382.