

RECOVERY OF SODIUM HYDROXIDE FROM EMBILIPITIYA BLACK LIQUOR BY ELECTRODIALYSIS

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ABSTRACT

A new type of electrolysers unit to fractionate the Embilipitiya black liquor into sodium hydroxide, lignin and organic acids has been proposed and experimented in this work. Lignin deposition on and the consequent damage to the anode-side cellophane membrane that are generally associated with electrodialysis have been eliminated in the proposed unit. Also, bubbling of liquor in the anode compartment has been eliminated and erosion of anode electrode has been minimized. Even with the use of an ordinary membrane, such as cellophane, the cathode compartments of the proposed unit yield sodium hydroxide solutions of strength 0.1M or more which has a good market value. Lignin which has a very high fuel value can easily be isolated from the end products of electrodialysis. Most importantly the polluting black liquor, upon electrodialysis followed by filtration, yields an almost colourless liquor with a pH of 6.1 and a TDS of 0.23 g/l which could be discharged on land for irrigation purposes as per the environmental standards of Sri Lanka. Thus an environmentally hazardous black liquor has been changed to an environmentally friendly liquor with valuable byproducts.

Introduction

Black liquor, a liquid effluent produced by the Embilipitiya pulp mill, is rich in valuable chemicals such as sodium hydroxide, lignin as sodium lignate and low molecular weight polysaccharides (Ray et al. 1992). Black colour of the waste liquor is owing to the presence of lignin which is isolated from straw during the pulping process in which straw is cooked with sodium hydroxide at specified pressure and temperature. In this soda-pulping process, lignin in straw is converted into sodium lignate which exists in black liquor as sodium ions and lignate ions.

The concentration of the ions in black liquor can be quantified by measuring the total dissolved solids (TDS) content of black liquor which is about 9.74 g/l in the case of the Embilipitiya black liquor. The allowable TDS value for industrial effluent to be discharged on land for irrigation is 2.1 g/l (National Environmental Act 1990). Also, the biochemical oxygen demand (BOD) and the chemical oxygen demand (COD) of the black liquor are about a 100 times higher than the allowable limits for discharge of industrial effluents and the pH of black liquor is above the allowable range of pH which is 5.5 - 9.0 (National Environmental Act 1990).

An almost continuous release of black liquor of the above mentioned characteristics into a water body, as it is in the case of the Sri Lankan black liquor, has the potential to kill all life-forms in the water body and eventually turn it into a dead one (Shanthini and Arulanantham 1995). Thus, black liquor is too hazardous an effluent to be let into the environment without treatment. This paper discusses briefly the treatment methods available and proposes a new type of an electrolysers unit in order to treat the Embilipitiya black liquor before it is discharged into the environment.

Available Treatment Methods

Black liquor from soda-pulp mills, where wood is the raw-material for paper, is successfully treated to recover energy and sodium hydroxide in a process known as the conventional chemical recovery process (Basu 1968, Panda 1991, Sinha 1970). Non-wood based black liquor, as in the Sri Lankan case where straw is used in place of wood, has a relatively high content of silica (Tandon et al. 1989) that causes problems such as formation of hard silica scales on the walls of the chemical recovery units (Misra 1967/68). Frequent shutdowns of the recovery unit and an increase in the maintenance and replacement costs are the consequences (El Ebiary 1983, Panda 1989, Veeramani 1977). Nevertheless, a conventional chemical recovery plant has been available at the Embilipitiya paper factory for more than a decade which has of course never been of any use (Wanigasundera 1995). Neither the straw-based black liquor nor the wood-based black liquor can be treated in the recovery plant of the Embilipitiya mill.

Removal of silica from black liquor prior to treating it in the conventional chemical recovery unit was seen as a way to treat non-wood based black liquor (Govindan and Radhakrishnan 1989, Tandon et al. 1989). Excess silica can in theory be removed by lime treatment but was found unsuccessful owing to many operational problems and economical concern (Bleier 1989). Desilication by pH reduction through controlled carbonation is another possibility and pilot plant units were installed in Egypt, Indonesia and China (El Ebiary 1983, Leguen 1987, Marcks and Schildhauer 1986). Most of these units were later shut down mainly due to excessive foaming during desilication (Panda 1991, Yong 1993). Central pulp and paper research institute of India has developed another type of reactor for desilication by controlled carbonation (Kulkarni et al. 1989) and a pilot plant unit has been installed in India (Govindan and Radhakrishnan 1989) where again foaming is reported to be causing problems (Francis et al. 1989).

Recovery of chemicals from black liquor by fractionating electrolytes from non electrolytes of the black liquor by the process of electrodialysis has been reported to have tremendous industrial potential almost three decades ago (Basu 1968). Electrodialysis, in contrast to desilication followed by an extensive chemical recovery process, appears to be a suitable one step method to recover chemicals from black liquor. Spent sulfite liquor, for instance, has been successfully separated into pulping chemicals and lignosulphonic acids in pilot plant electrodialyser units (Basu 1968, Mishra and Bhattacharya 1984). Investigations on the influence of operating parameters on the performance of a three-compartment electrodialyser unit have been carried out with soda-pulped straw-based black liquor by Joshi and Basu (1973) and Mishra and Bhattacharya (1984). Both these works used cellophane membrane as well as cation-exchange membrane in order to recover sodium hydroxide from black liquor. No further work on electrodialysis has been found in the literature to the best of our knowledge and therefore we experimented into electrodialysis of the Embilipitiya black liquor in this research work and the results obtained are reported in this paper.

Experimental Setup

A three compartment electrodialyser unit similar to the one described by Mishra and Bhattacharya (1984) was constructed with perspex and is shown in Fig. 1. The unit has a rectangular cross-section of dimension 38.9 cm by 7.2 cm and a height of 9.0 cm. The compartments were separated from each other by cellophane sheets since cellophane is the only membrane that is available in the Sri Lankan market. The black liquor used in the experiments was obtained from the Embilipitiya pulp mill and 900 ml of it was filled in the middle compartment. The outer compartments were each filled with 450 ml of distilled water. Stainless steel electrodes of 6.85 cm height were used. Two electrodes, one per compartment, were placed in the two

outer compartments. The electrodes were connected to a d.c. power supply unit such that one electrode acted as anode and the other as cathode. During the experiment, the current was maintained constant by varying the voltage.

During electro dialysis cations, that are mainly sodium ions, in black liquor moved through the membrane to the cathode compartment and sodium hydroxide was formed there. Concentration of the sodium hydroxide in the cathode compartment was measured using the conductivity meter Hach 44600. Anions in black liquor moved towards the anode of which the lignate ions were held by the membrane because of the molecular size of lignin which was larger than the pore size of the membrane. Consequently, a lignin layer formed on the anode-side membrane. Anions of organic acids passed through the membrane to the anode compartment where organic acids were formed and retained.

The lignin layer formed on the anode-side cellophane membrane increased the cell resistance which in turn resulted in considerable increase in voltage required to maintain the current constant. In addition, damage of anode-side membrane due to lignin deposition and bubbling of the liquor in the anode compartment due to rise in temperature were observed. Pitting of anode electrode was also observed. These were problems that were encountered also by Mishra and Bhattacharya (1984). They reported that when the cellophane membranes were replaced by ion-exchange membranes there was an increase in the sodium hydroxide recovery. We nevertheless decided to retain the inexpensive and locally available cellophane as the membrane in our experiments but to modify the electro dialyser unit as follows to increase the recovery rate of sodium hydroxide.

The stainless steel electrodes placed in the two outer compartments containing 450 ml of distilled water each were turned into cathodes and a third stainless electrode was placed in the middle compartment in which there was 900 ml of black liquor. This third electrode was the anode. During electro dialysis, the cellophane membranes were intact as expected but the lignin molecules reaching the anode electrode deposited on the surface of the electrode itself. The lignin covered anode drastically reduced the rate of fractionation and eventually inhibited the process of electro dialysis itself.

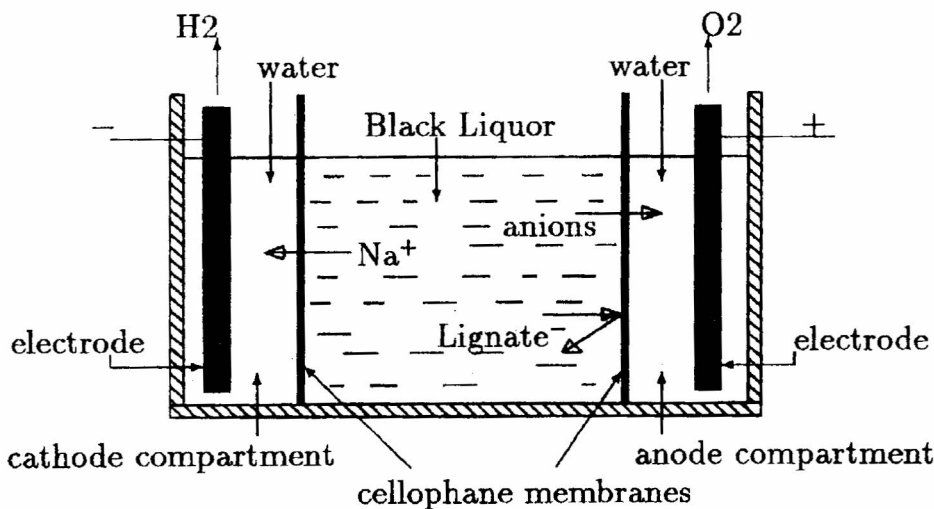


Fig. 1. A three compartment electro dialyser unit as described by Mishra and Bhattacharya (1984).

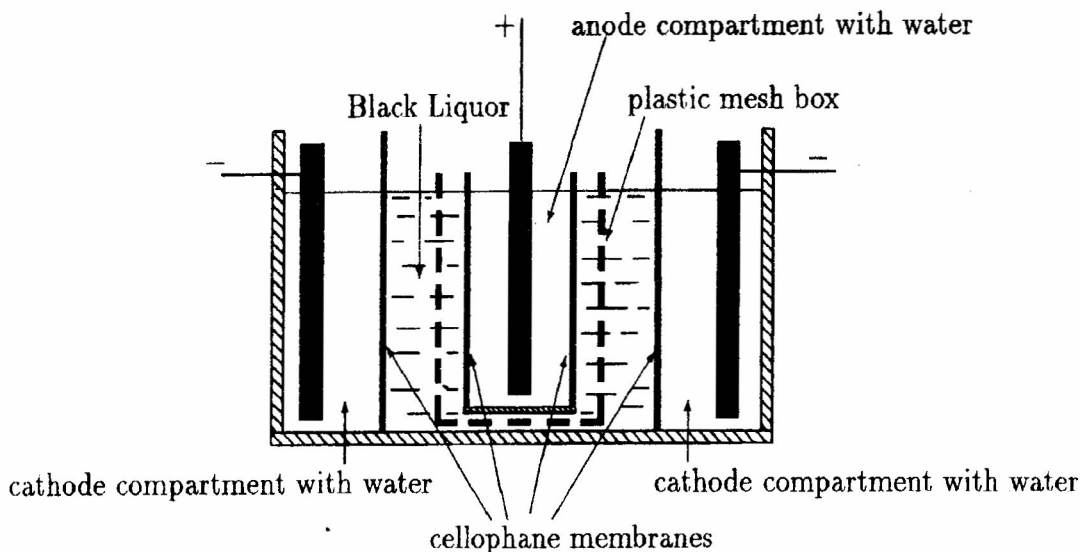


Fig. 2. Modified electrolysers unit which is proposed and experimented in this study.

To keep the surface of anode electrode free of lignin deposit, the electrolysers unit was modified as shown in Fig. 2. An open box of 11.6 cm by 5.5 cm rectangular cross-section was constructed with a perspex bottom and four cellophane side walls of 5.0 cm height reinforced by a perspex grid. This box was filled with 400 ml of distilled water and the anode electrode was placed inside it. The whole set up was placed in the middle of the compartment holding 600 ml of black liquor. Placed in the black liquor was another open box of 17.3 cm by 5.9 cm rectangular cross-section and 9.0 cm height made entirely of plastic mesh which surrounded the small anode compartment on all four sides and at the bottom. The two outer compartments were each filled with 450 ml of distilled water and cathode electrodes were placed in them.

Experimental results and discussion

Fig. 3 shows the experimental results obtained up to 3 hours of electrolysers in the units shown in Fig. 1 and Fig. 2. Circles (o) represent the results obtained with the unit of the type of Mishra & Bhattacharya (1984) and pluses (+) represent the results obtained with the modified unit. Both results were obtained maintaining 500 mA current throughout the electrolysers. It can be seen in Fig. 3 that the sodium hydroxide recovery, which was quantified as concentration of NaOH in gram per litre (g/l) in the cathode compartment, is much higher in the modified unit than in the unit duplicating the one used by Mishra & Bhattacharya. It can also be seen in Fig. 3 that the duration of electrolysers in the old type unit was only 2 hours and it was because of the increased cell resistance owing to the lignate layer formed on the anode-side membrane. Whilst, the electrolysers in the modified unit was carried out for three hours and could have been carried out for more than three hours, if needed. Lignate ions moving towards the anode electrode of the modified unit did not form a lignin layer on the cellophane walls of the anode compartment. Lignin instead accumulated on the plastic mesh bottom of the space between the plastic mesh walls and the cellophane walls. Cellophane membrane of the anode walls being lignin free was in fact the

cause for the performance of the modified unit being better than that of the Mishra and Bhattacharya type unit.

Asterisks (*) of Fig. 3 represent the results obtained with the modified unit at 1000 mA current which show that the NaOH recovery in the modified unit increases when the current is increased. It is of considerable importance to note that the modified unit allowed currents as high as one ampere owing to lignin-free cellophane as anode walls whereas such high current was not possible in the old setup. Presence of plastic mesh walls near the anode compartment walls seemed to contribute towards the advantageous phenomenon of lignin-free cellophane as anode walls. When the plastic mesh was replaced by a wire mesh the results showed very little difference as can be seen from Fig. 4. This observation perhaps implies that the mesh contributes by offering only physical resistance to the flow of the lignate ions moving towards the cellophane membranes of the anode walls. This resistance to the flow resulting in reduction of the velocity of the ions perhaps causes the lignin particles to settle down before they reach the anode walls. The results of Fig. 4 completely rule out the possibility of the mesh acting as a secondary anode in interrupting the lignate ions. Further investigations are nevertheless being carried out at present to thoroughly investigate the contribution of the mesh box close to the anode wall surrounding it towards the maintenance of the anode-side cellophane free of lignin deposit. Though the environmentally friendly wire mesh was preferred to plastic mesh, corrosion limited the life span of the wire mesh to about 17 hours of electro dialysis only. The plastic mesh on the other hand could be used as many hours as it was required. Fig. 4 also shows that after about 17 hours of electro dialysis with 1000 mA current, the average concentration of the NaOH solution in the cathode compartments of the modified unit went up to 8 g/l, that was about 0.2M strength. Such a strength of NaOH solution has indeed an admirable market value. Purity of the cathode solutions has, however, not yet been fully analyzed owing to lack of sensitive analytical equipment in the department and should somehow be carried out in the future for the completion of this research work. The black liquor in the middle compartment, after about 17 hours of electro dialysis, was observed to turn into a light brown liquor with suspended and settled solids. When these solids were removed by filtration, an almost colourless liquor was obtained as the filtrate. The pH of the filtrate, when measured with the pH meter TOA HM-5ES, was 6.1. This pH value falls within the range of 5.5 - 9.0 which is the acceptable pH-range for a liquid effluent to be discharged onto the environment as per the environmental standards of Sri Lanka (National Environmental Act 1990). The TDS value was 0.23 g/l, when measured with the conductivity/TDS meter Hach 44600, which is acceptable if the filtered liquor is to be released onto the land for irrigation purposes. To release the filtered liquor to an inland surface water body, the TDS has to be reduced as low as 0.05 g/l. This low value for TDS may be achieved by subjecting the filtrate to conventional biological waste treatment processes since the filtrate is free of lignin which in fact resists biodegradation.

The main drawback of the modified unit was that the liquor in the anode compartment, which was mainly organic acids, got heated up during electro dialysis. The temperature at times went up to 70 °C in the anode compartment which caused leaks at the joints of the perspex unit. In order to maintain the temperature of the anode liquor at 40 °C, the anode liquor was circulated through a water-cooler by use of a pump. The results obtained from the modified unit with and without cooling at 1000 mA current are shown in Fig. 5. It can be observed that the recovery of sodium hydroxide with cooling is higher than the results obtained without cooling. In addition, maintaining the temperature at 40 °C saved the unit from developing leaks. Also, evaporation losses of the anode liquor at high temperatures were avoided. Investigations are carried out at present about the influence of the temperature of the anode liquor on the recovery of NaOH.

As the modified unit was found suitable for electro dialysis of the Embilipitiya fresh black liquor, which was partly straw-based and partly wood-based, we decided to test the performance

of the modified unit with the accumulated black liquor of Embilipitiya. The accumulated black liquor is stored in large stabilization ponds covering a land area of about 35 acres in the vicinity of the pulp mill before being discharged into the Walawe river. This land space for storing black liquor does of course increase as and when the pulp mill produces black liquor provided there is no continuous release of black liquor into the Walawe river. Evaporation of black liquor indeed accounts for some losses in its volume.

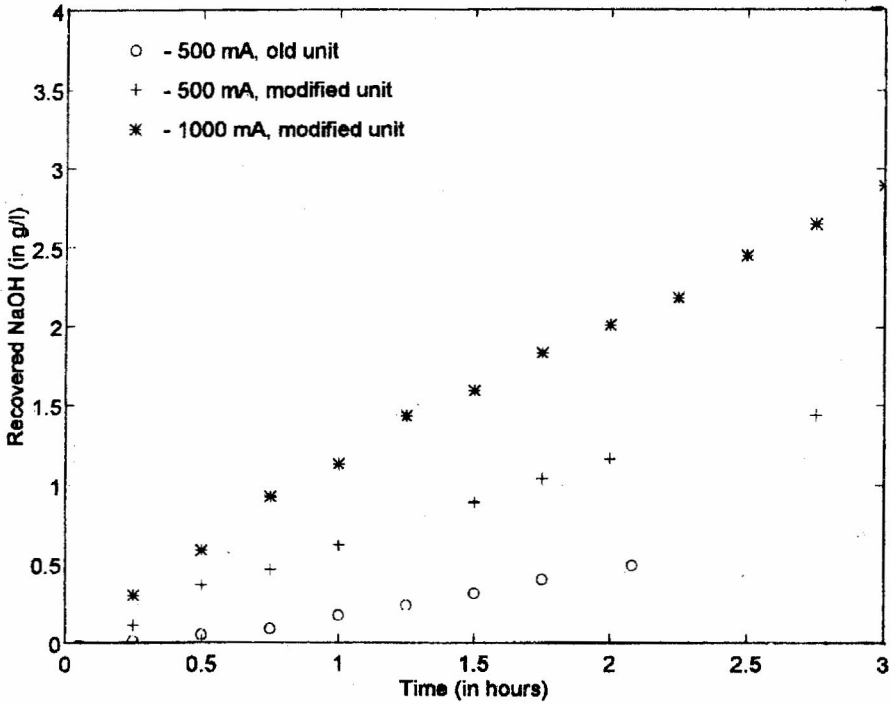


Fig. 3. Concentration of NaOH recovered during electro dialysis of Embilipitiya fresh black liquor as a function of processing time in two different type of units.

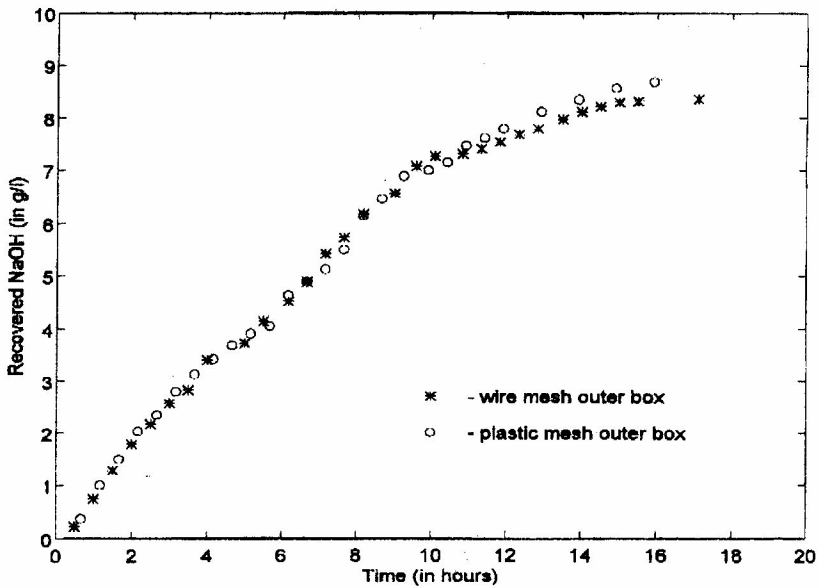


Fig. 4. Concentration of NaOH recovered during electro dialysis of Embilipitiya fresh black liquor as a function of processing time in the modified unit at 1000 mA current with plastic mesh outer box and wire mesh outer box.

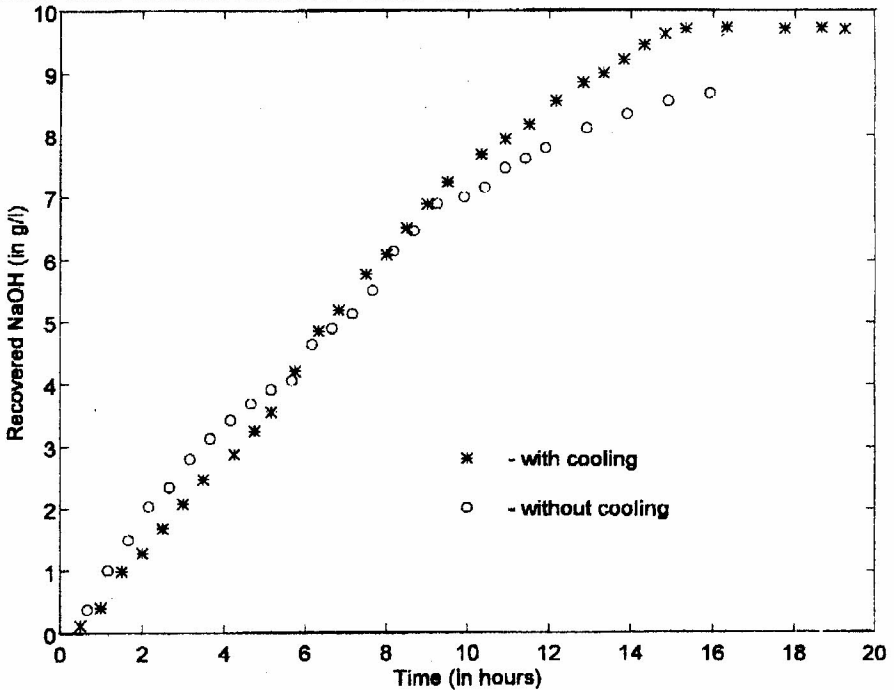


Fig. 5. Concentration of NaOH recovered during electro dialysis of Embilipitiya fresh black liquor as a function of processing time in the modified unit at 1000 mA current with and without cooling of the anode liquor.

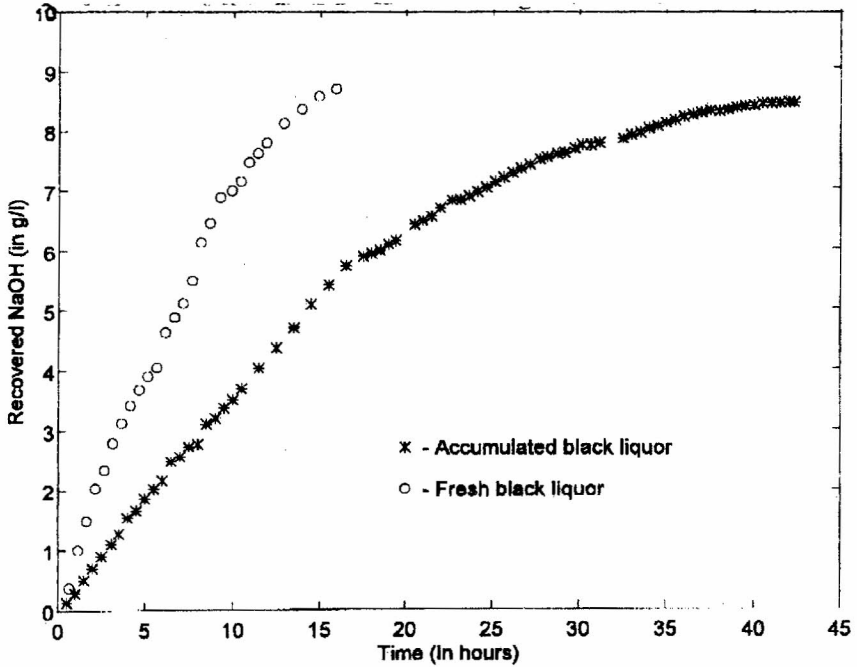


Fig. 6. Concentration of NaOH recovered during electro dialysis of fresh and accumulated black liquors of the Embilipitiya pulp mill as a function of processing time in the modified unit at 1000 mA current.

A single run was carried out at 1000 mA current in the modified electro dialyser with accumulated black liquor. Fig. 6 shows the recovery of sodium hydroxide in cases of both the fresh black liquor and the accumulated black liquor. To obtain the end results similar to that of the fresh black liquor, the accumulated black liquor was fractionated in the electro dialyser unit for 40 hours which was much longer than the time required for fresh black liquor. We at present are trying to investigate into the fine differences between the fresh and accumulated black liquor which once again calls for sophisticated analytical equipment.

Optimization of the influencing parameters and hence possible further modifications to the proposed electro dialyser unit are being investigated at present with the objective of reducing the batch processing time while increasing NaOH recovery. In the cases of both fresh and accumulated black liquor, organic acids were collected in the anode compartment of the modified unit and further research into the anode liquor should be carried out. Also, further experiments will be carried with fresh black liquor that is totally straw-based as soon as it is made available to us by the Embilipitiya pulp mill.

Conclusions

Fresh black liquor of the Embilipitiya pulp mill, which was a mixture of both wood and straw black liquors, is fractionated by the process of electro dialysis in the modified unit into

sodium hydroxide, lignin and organic acids. Also, one of the major environmental problems of Sri Lanka which is the accumulated black liquor stored in large stabilization ponds at the Embilipitiya mills can be fractionated in the modified unit into the chemicals mentioned above. However, our experiments show that the batch processing time required for accumulated black liquor is much longer than the time required for fresh black liquor.

Damage to the anode-side cellophane membrane due to lignin deposition and bubbling of liquor in the anode compartment, both are problems generally associated with electro dialysis of black liquor, have been completely eliminated in the unit proposed by us in this paper. Damage to anode electrode has been minimized. The modified unit even with the cellophane membrane gives valuable caustic soda solutions of about 0.1M strength or more. Black liquor after the process of electro dialysis and filtration is changed into a colourless liquor of 6.1 pH and 0.23 g/l TDS. This liquor is qualified to be discharged on land for irrigation purpose as per the environmental standards for Sri Lanka as far as the pH and TDS are concerned. The environmentally hazardous black liquor can thereby be transformed into an environmentally friendly liquor with valuable byproducts.

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