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Electrochemical Treatment of Bleach Effluent of Pulp and Paper Mill Waste

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ABSTRACT : Treatment of paper effluent by electrochemical method of waste water of pulp and paper was studied. The objective of this study is to bring the chemistry and physical processes involved into perspective and to focus attention on those areas critically needing research. Electrochemical Treatment is a method of treating polluted water whereby sacrificial anodes corrode to release active coagulant precursors (usually aluminum or stainless steel cations) into solution. Accompanying electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode. Electrochemical Treatment has a long history as a water treatment technology having been employed to remove a wide range of pollutants. Batch and continuous modes of treatment were studied. The batch mode aims to optimize coagulant concentration, pH and current density at fixed treatment duration. The current density is the most significant factor in the suspended solids elimination followed in decreasing order of importance by coagulant concentration and pH. Physicochemical characterization of the effluent was done before and after the treatment in batch and continuous mode to improve the efficiency of this process. This characterization included pH, Turbidity, conductivity, COD, suspended solids.

Keywords : Electrochemical treatment, COD, Pulp, Suspended solids.

INTRODUCTION

The production of paper started two thousand years ago in China and was considered as a secret activity until XII century when it was developed.

Nowadays, paper is produced from wood and the variation of the proportion of its components makes possible the obtaining of a large variety of paper quality. The production of paper gets through several stages like slashing, boiling in a solution of sodium hydroxide, dilution and washing. Such stages operate with a large quantity of water and hence quantities of wastewater are generally important.

This waste water generally large quantities of suspended solids; it also contains considerable amount of COD and BOD. Conventional physicochemical treatment of paper effluent consists of classic pretreatment such as coagulation /flocculation, sedimentation and sludge handling etc. and they have noted that for wastewaters which contain colloidal particles, fine bubbles produced by electrochemical Treatment can very effectively float them. Janssen and Koene have shown that electrochemical techniques are one of the competitive and interesting technologies in this field. Electrochemical techniques are highly versatile. Quantity of water due to a passage of electric current between an anode and a cathode is a process which produces fine oxygen and hydrogen bubbles as shown in the following reactions:

Anodic oxidation:

$$2\ H_2O \leftrightarrow O_2 + 4\ H^+ + 4e \qquad \ldots (1)$$

Cathodic reduction:

$$4H_2O + 4e! \leftrightarrow 2H_2 + 4OH \qquad \ldots (2)$$

His process is complex because of its dependence on several factors. Indeed, the current density influences directly the number and size of bubbles. The pH is a parameter which influences the mechanism of electrochemical owing to the fact that the hydrogen bubbles are the smallest with neutral pH and

For the oxygen bubbles their sizes increase with pH. Other than pH and current density there are several other parameters which affect this process such as the state, the arrangement of the electrodes, the nature of water to be treated and processing duration.

MATERIALS AND METHODS

First the bleach effluent of an integrated pulp and paper mill was studied. Characteristics of these effluents are shown in table. A laboratory scale electro-chemical treatment unit with flexibility to use either stainless steel or aluminum electrodes was used in the study. Spacing between the electrodes was 12 mm and effective surface area of the electrodes was 300 cm^2. Electrochemical treatment of the wastewater was carried at different pH values for different durations of electrolysis.

For the pH adjustment of the wastewater sulfuric acid was used. All the experiments were conducted on 700 ml of wastewater at 5 volts voltage using both the electrodes (stainless steel and aluminum). During the treatment, current measurements were made. Wastewater after the electro-

chemical treatment was allowed to settle for 2 hours and in the supernatant COD and turbidity was measured for assessing the treatment efficiency.

A. Material

(*i*) *Effluent characteristics*

These effluents are taken in a way to respect the standards of sampling and are stored in the cold storage during experiment days. A physicochemical characterization of the effluents is carried out before the treatment.

Table 1: Characteristics of Bleach effluent.

S. No.	*Parameter*	*Untreated*
1	pH	8.1
2	Turbidity (JTU)	137
3	Total Solids (mg/l)	5200
4	Total Suspended Solids (mg/l)	300
5	Total Dissolved Solids (mg/l)	4900
6	COD (mg/l)	2400

We note that these effluents present a high rate of COD and a considerable rate of suspended Solids which makes effective an eventual treatment by electrochemical.

(*ii*) *Experimental Setup*

A laboratory scale unit was used to conduct the experiments in the present study. The unit includes two components: The Reactor and the Power system. The reactor is made up of acrylic material and its capacity is of 700 ml. it includes two electrodes (a cathodes and an anode). Two types of electrodes Aluminum and Stainless Steel, each of 50mm width, 200 mm length and 2 mm thickness were used in the present study. In any single experiment, both the electrodes used were of same metal. A schematic diagram of the experimental set-up is shown in Fig. 1. Spacing between the two electrodes was 12 mm. The power system was used to supply Direct Current (DC) at desired voltage to the electrodes.

The system converted the input Alternating Current (AC) into Direct Current (DC) of desired voltage. Provisions were made in the power system to regulate voltage of the output and to display it on a handy multimeter. An ampere of 0-10A range was fitted in the power system to display the amperage of the power supplied.

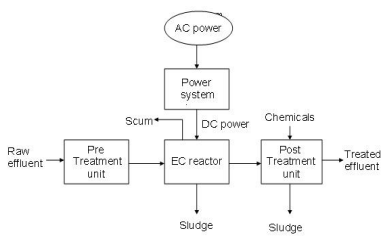
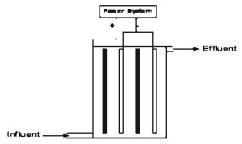


Fig. 1. Schematic diagram of a typical electrochemical treatment.



Fi.g 2. Electro-chemical reactor.

A final experiment was conducted on the wastewater with the superior of the two types of electrodes, and the treated effluent obtained was characterized for different other parameters as well for assessing the treatment efficiency against the untreated waste water.

ANALYSIS AND RESULTS

A. Effect of initial pH

It has been established that the in?uent pH is an important operating factor influencing the performance of electrochemical process. To examine its effect on the treatment of black liquor, the pH was varied in the range 2-8 using low volume of sulphuric acid 0.01N.

Fig. 3 illustrates the removal efficiencies of COD and a change in the pH of the black liquor after electrochemical Treatment, as a function of the influent pH. In addition, it was demonstrated that high pH values will increase Al $(OH)_3$ solubility and lead to the formation of soluble $Al(OH)_4$–, which is useless for water treatment.

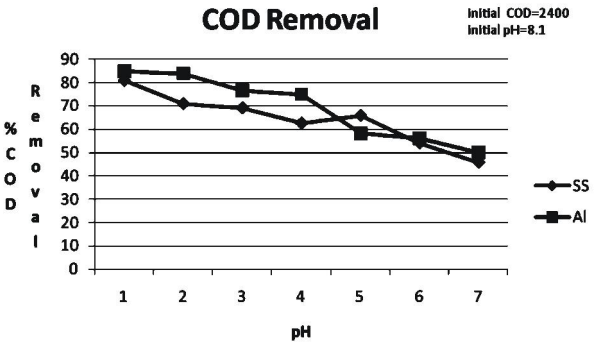


Fig. 3. COD removed as a function of pH.

When initial pH was adjusted in the range 2-7, all aluminum cat ions produced at the anode formed polymeric specie $Al_{13}O_4(OH)_{24}^{7+}$ and precipitated $Al(OH)_3$ leading to a more effective treatment and high removal capacities of COD (85%) and Turbidity (137 JTU). The highest removal efficiencies have been obtained in acidic medium, at pH values in the range 2-7. However, this was contested by Chen et al. [14] who explained this increase by the release of CO_2 from wastewater owing to H_2 bubble disturbance. Indeed, at low pH, CO_2 is over saturated in wastewater and can release during H_2 evolution, causing a pH increase.

B. The effect of Current Density

It is well known that current determines not only the coagulant dosage rate but also the bubble production rate and the size and growth of flocs which can indkuence the

treatment efficiency of the electrochemical. Therefore, the effect of current intensity on the pollutant removal was investigated (Adhoum and Monser, 2004). The Turbidity and COD removals from the paper mill effluent were measured for 15 min at different pH value. The effect of the current intensity on the treatment efficiency of the electrochemical process has been investigated for different wastewaters (Lin and Peng, 1994). During the electrochemical experiments, the small amounts of sludge were scraped off from the top and the bottom of the electrolytic cell, and were evidence of the sedimentation and flotation action.

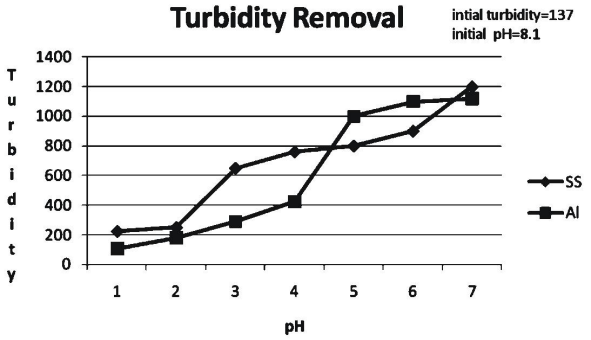


Fig. 4. Turbidity removed as a function of pH.

Since the total surface area of the electrodes was about 300 cm^2, the applied current was readily converted to the current density. Therefore, the removal Turbidity and COD were graphed against current density in Figs. 5-6. Fig. 5 depicts the COD removal efficiency as a function of current density. The percentage of COD removal ups to approximately 374 A/cm^2 was for the Al and 362 A/cm^2 was for SS electrodes. Fig. 6 depicts the Turbidity removal efficiency as a function of current density. The Turbidity removal ups to approximately 108 JTU was for the Al and 224 JTU was for SS electrodes.

However, there was an increase in COD removal by the Al electrode with increasing current density compared with the SS electrode. As expected, it appears that for a given time, the removal efficiency increased signi?cantly with increased current density. This is attributed to the fact that at high current, the amount of aluminum oxidized increased, resulting in a greater amount of precipitation. The percentage of COD removal for the Al electrode was higher than that for the SS electrode.

The Al electrode revealed a tendency for steadiness after 374 A/cm^2. However, in the case of the SS electrode, a fast removal up to 362 A/cm^2 and then gradually slowing removal was observed. At higher current densities, the supply of aluminum ions was generated rapidly compared to the coagulation process, resulting in a decrease in removal efficiency calculated on an equivalent aluminum basis. In addition, the faster removal of aluminum hydroxide from solution by flotation leads to a reduction in the probability of collision between the pollutant and coagulant.

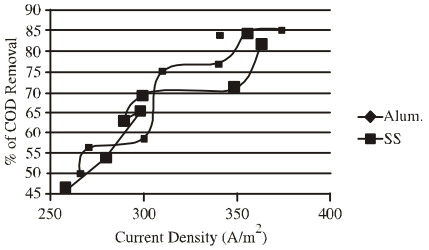


Fig. 5. Effect of current density on COD removal.

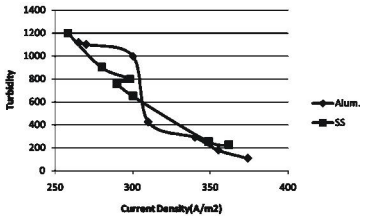


Fig. 6. Effect of current density on Turbidity.

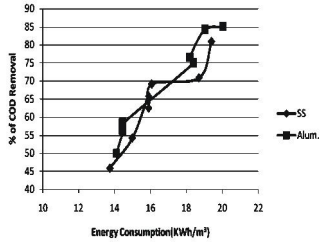


Fig. 7. Effect of Energy Consumption on COD removal.

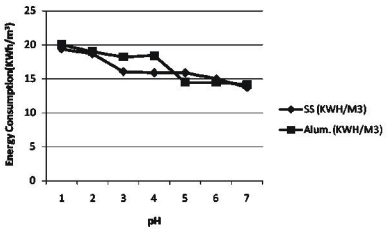


Fig. 8. Effect of Energy Consumption on pH.

Table 2: Treatment efficiencies achieved through Electro-chemical treatment of bleach effluents at different pH values.

pH	*Current Density*		*COD (mg/l)*		*Turbidity (JTU)*	
	SS Electrode	*Alum. Electrode*	*SS Electrode*	*Alum. Electrode*	*SS Electrode*	*Alum. Electrode*
2.	362	374	460	360	224	108
3.	349	355	700	380	250	180
4.	300	340	740	560	650	290
5.	290	310	900	600	760	425
6.	298	300	820	1000	800	1000
7.	280	270	1100	1050	900	1100
8.	258	265	1300	1200	1200	1120
Untreated Effluent			2400		137	

Both the electrodes showed similar behavior for COD removal at low current densities. The results are given in Fig. 11. The efficiency of COD removal (80%) was found at approximately 374 A/cm^2. A very small decrease with increasing current density was observed. When organic pollutants in effluents were treated by electrochemical methods, COD removal increased with increasing current intensity.

C. Effect of Energy consumption

The results obtained are plotted in Figs. 7-8. Fig. 7 depicts the COD removal efficiency as a function of Energy Consumption. The percentage of COD removal ups to approximately 20.03 KWh/m^3 was for the Al and 19.39 KWh/m^3 was for SS electrodes. Fig.8 depicts the value of energy consumption of at different pH. At 2 pH the energy consumption was 20 KWh/m^3 *i.e.* in acidic medium the energy consumption was maximum.

Table 3: Effect of Electrode Mass Consumption and Energy Consumption on COD and Turbidity removal at different pH.

pH	*Energy Consumption (KWh/m^3) (grams)*		*Electrode Mass Consumption*	
	SS Elec	*Alum Elec*	*SS Elec*	*Alum Elec*
2	19.39	20.03	0.910	0.941
3	18.69	19.01	0.878	0.893
5	15.89	18.39	0.729	0.863
6	15.89	14.46	0.746	0.679
7	14.99	14.46	0.704	0.679
8	13.74	14.01	0.645	0.662
Untreated effluent				

D. Effect of Electrode Mass Consumption

The results obtained are plotted in Figs. 9-11. Fig. 9 depicts the COD removal efficiency as a function of Electrode Mass Consumption. The percentage of COD removal ups to approximately 0.941 gm was for the Al and 0.910 gm was for SS electrodes. Fig.10 depicts the Turbidity removal efficiency as a function of Electrode Mass Consumption. The Turbidity removal ups to approximately 108 JTU was for the Al and 224 JTU was for SS electrodes.Fig. 11 depict the Electrode Mass Consumption as a function of pH.

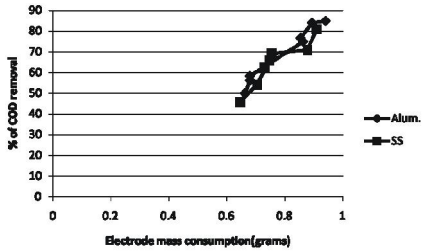


Fig. 9. Effect of Electrode mass Consumption on COD removal.

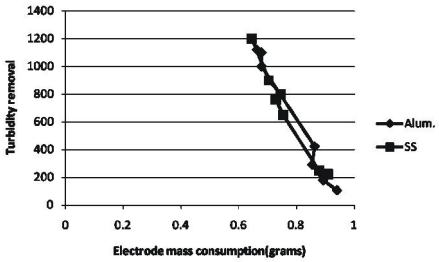


Fig. 10. Effect of Electrode mass Consumption on Turbidity removal.

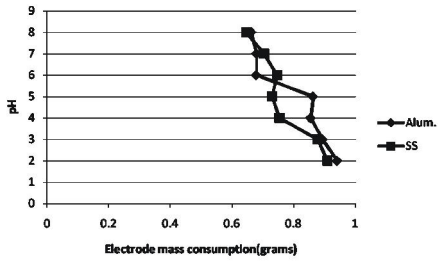


Fig. 11. Effect of Electrode mass Consumption on pH.

E. Effect of retention time

Electrochemical process involves two stages which are destabilization and aggregation. The first stage is usually short, whereas the second stage is relatively long. The effect of retention time (*t*) on treatment efficiency was carried out by fix pH value and fix voltage. In the Electrochemical process, metal ions as destabilization agent are produced at the anode through electrochemical reactions.

The effect of retention time on the current density was shown in Fig. 12. The effect of retention time on the COD removal was shown in Fig. 14. Fig. 13 shows the relationship between the Energy Consumption and time. An increase in time from 5 to 35 min causes a decreased in current density from 450 to 316 at Alum and 400-300 at SS electrode. Decrease in Energy Consumption from 24.10 to 16.09 kWh/m^3 at alum and 21.42 to 16.06 kWh/m^3 at SS.

This shows that retention time is very important parameter due to affecting the economic applicability of electrochemical process in treatment of the black liquor.

Table 4: Effect of Energy Consumption and Current Density on removal of COD at different Time interval.

Time (mins)	COD (mg/L) Initial COD=2400		Energy Consumption (KWh/m^3)		Current Density (A/m^2)	
	Alum Elec.	SS Elec.	Alum Elec	SS Elec.	Alum Elec	SS Elec.
5	980	1020	24.10	21.42	450	400
10	440	540	22.75	20.88	425	390
15	280	360	21.42	19.99	400	373.3
20	280	320	19.99	18.74	373.3	350
25	260	300	19.81	19.09	370	356.6
30	260	280	16.42	16.95	306.6	316.6
35	260	280	16.06	16.06	316.6	300

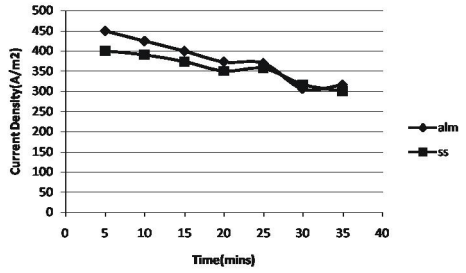


Fig. 12. Effect of Time on Current Density.

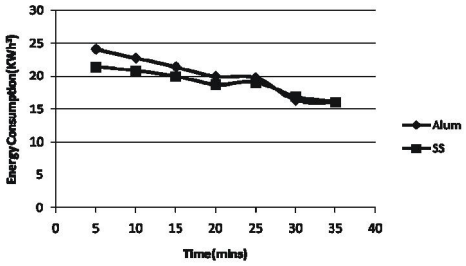


Fig. 13. Effect of Time on Energy Consumption.

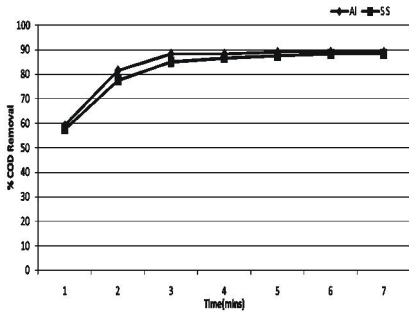


Fig. 14. Effect of Time on % COD removal.

F. Effect of Coagulant Dose

Results obtained from the electrochemical treatment experiments on the wastewater, after adding the electrolyte at different concentrations ranging from 0.2 g/l to 2 g/l, are shown in Table 5 and Fig. 12. The experiments were conducted by stainless steel and aluminum electrodes at pH 2. Duration of electro-chemical treatment was maintained at 15 minutes in all these experiments. The results indicate that Stainless steel electrodes are superior to aluminum electrodes and best treatment efficiencies were obtained at 0.8 g/l of electrolyte dose. At 0.8 g/l of electrolyte dose, with stainless steel electrodes COD was reduced by 70%.

Table 5: Treatment efficiencies achieved through electro-chemical treatment of bleach effluent at different electrolyte doses.

Dose of ($Al_2(SO)18H_2O$)(*g/l*) *Aluminium Sulphate*	*COD* (*mg/l*) (*St. Steel*)	*COD* (*mg/l*) (*Alu*)
0.2	1400	1300
0.4	1300	1200
0.6	960	840
0.8	720	672
1.0	720	880
1.2	750	900
1.4	750	900
1.6	770	950
1.8	790	950
2.0	790	950

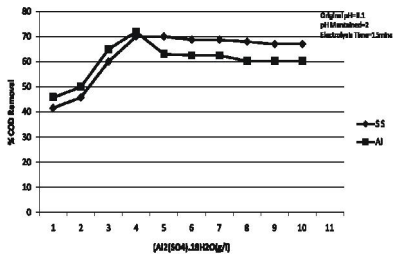


Fig. 15. Treatment efficiencies achieved through electro-chemical treatment of bleach effluent at different electrolyte dose.

Table 6: Treatment efficiencies achieved through electro-chemical treatment of bleach effluent.

S. No.	*Parameter*	*Untreated*	*Treated (Al)*
1.	pH	8.1	4.7
2.	COD (mg/l)	2400	360
3.	Turbidity	137	108
4.	TDS (mg/l)	4900	3500

CONCLUSIONS

The electro-coagulation and flocculation process was used to treat the wastewater from a bleach effluent from an integrated pulp and paper mill. Treatment was optimized for the operational variables such as electrode type, influent pH, and electrolyte dose and treatment time. Treatment efficiencies were assessed on the basis removal of turbidity, chemical oxygen demand (COD) and total solids from the effluents.

In case of bleach effluent, maximum removal efficiencies were found with Aluminum electrodes. Best results were obtained with aluminum electrodes at the voltage of 5V and at the pH of 2, for the electrolysis time of 15 minutes. Turbidity and COD of the first extraction stage effluent were removed by 76% and 85% respectively.

In respect to current density, there was an increase in COD removal by Al electrode with increase current density compared with the SS electrode. As expected, it appears that for a given time, the removal efficiency increased significantly with increased current density. This is attributed to the fact that at high current, the amount of aluminum oxidized increased, resulting in a greater amount of precipitation. The percentage of COD removal for the Al electrode was higher than that for the SS electrode. In case of Turbidity it ups to approximately 108 JTU was for the Al and 224 JTU was for SS electrodes.

Aluminum electrodes are preferred for this application. Under optimal value of process parameter (initial pH 2, t = 15 min and voltage = 5), COD removal reached at 85% .In addition Turbidity removal was obtained 76% and visually very clear following electrochemical treatment. Maximum current density was 374 A/m^2 at Al electrode.

The use of aluminum electrode will be a better choice, as compared to stainless steel or iron electrodes due to its role as scarified electrodes releasing of aluminum ions as coagulant. Amount of coagulants (*e.g.*, $Al_2SO_4.18H_2O$) may increase the conductivity of the solution and further enhance the efficiency of using electric energy to assist releasing aluminum ions as coagulating reagents. However, too much coagulant in the tested solution may lead to boiling of water without controlling power supply or treatment time.

The time dependence of COD removal by electrochemical process at fix pH is shown in Tables 6. It can be seen from the Tables that at 373.3 A/m^2 current densities and 19.99 KWh/m^3 energy consumption, the COD removal was 85% at fix pH value 2 and retention time 15 min.

The result of this study was showed (Table 3) that electrode mass consumption at electrical potential 5 V was 0.941gm at Alum and 0.910 gm at SS. It means that the electrode mass consumption was max. at aluminum electrode. It mean aluminum was better electrode than SS.

Power consumed was found to be high in cases of bleach effluent it was 20kWh/m^3.

In respect to power consumption, it was concluded that this technology is costly for wastewater treatment but for some of the difficult wastewaters for which the alternative technologies are not feasible, this technology may proves to be appropriate for treatment.

It is also concluded that if this technology is used in large scale, then it may be cheaper or less costly in comparison to the lab scale observations.

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