Electrochemical Treatment of Pulp and Paper Effluent using $RuO_2/TiO_2/Ti$ Electrode

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Abstract

The issue of electrochemical treatment of pulp and paper effluent is addressed. Increasing importance for environmental standards calls for genuine treatments methodologies for industrial effluents. Pulp and paper effluent is one such hazardous material that requires proper treatment. In this work, results of electrochemical treatment method of pulp and paper mill effluent with the principal aim of eliminating COD is discussed. $RuO_2/TiO_2/Ti$ and stainless steel are used as anode and cathode respectively. Experiments were conducted to examine the effect of operating parameters such as current density, concentration of mediator and flow rate on COD removal efficiency. The effluent treatment was done in batch reactor and the best conditions are optimized. The results of the experiments provide emphatic evidence for the best compatibility of electrochemical treatment methods for effluent treatment and further it is established that this does not produce any secondary pollution.

INTRODUCTION

Environmental pollution control is the concern of the day. Nearly 5 million chemicals are synthesized in the world catering to various purposes in the last 40 years, out of which 50000 to 70000 chemicals are used extensively in millions of different commercial products without the availability of proper toxicological information on most of them. Polluted water is the primary concerns of environmentalists. Consequently, some important chemicals producing taste and odour in water are iron, Mn, Cl_2, phenol, H_2S etc. Many industries use very large volumes of water-94% of which is used for condensing, cooling and boiler feed. Only 0.2% is incorporated into industrial products.

Pulp and paper effluent

In India there are about 22 integrated mills (wood based) and about 360 small mills (agro and waste paper based). The pollution loads from small pulp and paper mills are very high as 'the black liquor is discharged into effluent stream directly since there is not feasible chemical recovery system. The black liquor of such mills is highly coloured due to the presence lignin and its degradation products. The highly water intensive liquid waste from the pulp and paper industry is generated from 2 different sections, namely, pulping process and paper machine unit. The liquid waste generated from pulping section, popularly known as black liquor mainly consists of organic as well as inorganic dissolved salts.

Effluent treatment methods

Table 1 shows the currently available treatment methods of organic, inorganic and microbiological pollutants in air, water and soil.

It is to be noted that electrochemical treatment had been traditionally applied only to treat inorganic pollutants. Nevertheless, advancements in the field has lead to the application of electrochemical methods even for organic and to an extent, for microorganisms too.

Table 1: Current methods for pollutant treatment

| Organic	Inorganic	Microorganism
Incineration & Pyrolysis Air stripping Carbon adsorption Microbial treatment	Precipitation/coagulation Membrane separation Distillation Chemical treatment Electrochemical treament Microbial treatment	Incineration High-energy ()- irradiation Filtration Carbon adsorption Direct UV irradiation Ozonation Chlorination

EXPERIMENTAL

The cell setup is shown in Fig (1). The reactor (or) cell is a cylindrical glass container, closed with a lid, which helps to fit the electrodes at a position to maintain the constant distance between them. Noble metal oxide MOx (RuO_2) coated on Titanium mesh served as working electrode and stainless steel as counter electrode. The dimensions of the electrodes for all the conditions are, 7.7cm x 4.6 cm. Reference electrode is calomel electrode, which is connected to the cell through the salt bridge, for which provision is made on the lid. The lid is so designed as to facilitate the sample collection. Stirring is done with the magnetic stirrer. The electrical energy for the system is available from the regulated power supply. The reactor was charged with different volume of the effluent, for the present study undivided cell is used. The effluent is taken as such for the electrolysis. The experiment is conducted under galvanostatic condition in the batch reactor fixing the current density. The experiment is repeated for three different holdups such as 200 ml, 400ml, and 600ml. For each holdup volume, the experiments were carried out at, two different current densities 2.5 and 5.0 A/dm^2 and different mediator concentration like 1,2,3,4,5,6 and 9GPL. The electrode area, which is exposed to the effluent, does not vary with the volume of the effluent taken. The current passing through the electrodes depend on electrode area, especially anode area. The total quantity of electricity (q) is kept constant at 5.0 Ah for each experiment. The cell voltage, anode potential and cathode potentials are noted down periodically. The samples from the electrolytic cell are collected for each one-hour period and is kept at acidic condition and analyzed for COD.

Influence of supporting electrolyte (NaCl) on COD removal:

Anode : Catalytic anode $(RuO_2/TiO_2/Ti)$

Cathode : Stainless Steel
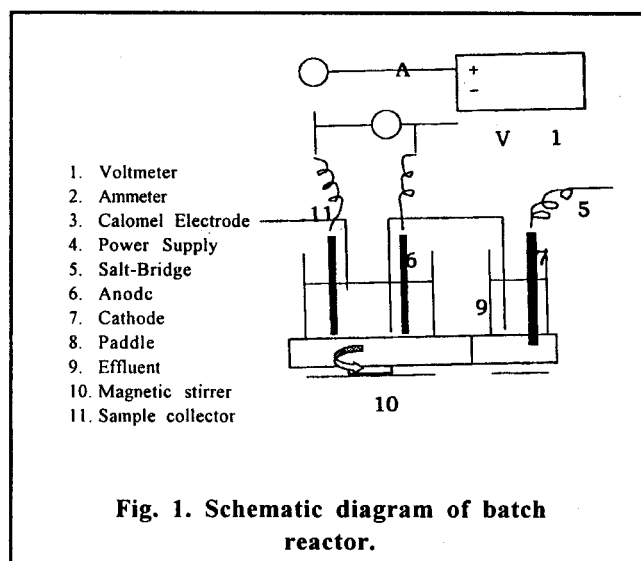
RESULTS AND DISCUSSION

The removal of COD from the effluent by anodic oxidation method was studied using Ruthenium oxide coated on Titanium electrode acted as anode and stainless steel acted as cathode under various experimental conditions in order to find out the optimum condition on COD removal. The result obtained from the COD analysis for different mediator (NaCl) concentrations, current

1. Voltmeter
2. Ammeter
3. Calomel Electrode
4. Power Supply
5. Salt-Bridge
6. Anode
7. Cathode
8. Paddle
9. Effluent
10. Magnetic stirrer
11. Sample collector

Fig. 1. Schematic diagram of batch reactor.

Total quantity of electricity : 5 Ah Volume : 200 ml

Table 2 : (CD : 25A/dm²)

S.No.	NaCl Conce. Gm/lit	C.V. Volts	COD PPM		Percentage Reduction of COD	P.C. kWh/kg COD	Temp.ºC	Rate Constant Cm/sec *104
			I	F				
1	1	10.89	1446	723	50.00	169.45	46	4.37
2	2	8.35	1687	723	57.14	97.46	42	5.03
3	3	7.5	1687	723	57.14	87.52	41	5.38
4.	4	6.11	1446	482	66.67	71.30	41	5.59
5.	5	5.13	1422	474	66.67	60.88	40	5.59

Table 3: (CD : 5A/dm²)

S.No.	NaCl Conce. Gm/lit	C.V. Volts	COD PPM		Percentage Reduction of COD	P.C. kWh/kg COD	Temp.ºC	Rate Constant Cm/sec *104
			I	F				
1	5	9.17	1180	236	80.00	218.56	48	10
2	6	7.48	1652	236	85.71	118.85	47	9.3
3	7	7.02	1750	250	85.71	105.30	47	5.85
4.	9	6.64	2000	500	75.00	99.60	49	3.52

Table 4: (Variable Volume) : NaCl concentration : 5gpl

S.No.	Reactor Volume ml	C.V. Volts	COD PPM		Percentage Reduction of COD	P.C. kWh/kg COD	Temp.ºC	Rate Constant Cm/sec *104
			I	F				
1	200	5.13	1422	474	66.67	60.88	40	5.59
2	300	7.12	1750	750	57.14	40.05	38	10.60
3	600	6.92	1500	750	50.00	34.63	38	13.33

densities and volume of the electrolyte are presented in the tables 2, 3 and 4

Effect of Mediator Concentration (NaCl) on COD Removal:

The effect of NaCl concentration on the two different current densities such as 2.5 A/dm² and 5 A/dm² is shown in tables. It was observed from the tables that the percentage of COD reduction increased in both current densities with the increase of NaCl concentration from 1gpl to 7gpl, the COD reduction decreased. This may be due to generation of ClO_3^- ions formed by the excess OCl^- ion concentration in the electrolyte i.e., this side reaction hinders the main oxidation step.

Effect of current density on COD removal

Regarding the effect of current densities it was observed from the tables that maximum of 67% of COD was removed in 2.5 A/dm² at 5gpl NaCl concentration. By increasing the current density to 5A/dm² the COD removal also increased to 86% at 6gpl of NaCl concentration and also temperature of the effluent increased rapidly. Due to increase in temperature, experiment conducted at the current density of 5A/dm² was terminated. At current density of 5A/dm² the cell voltage was also high. Due to this high voltage, the temperature rises very fastly.

Effect of reactor holdup on COD removal

The reactor holdup has an effect on the COD reduction, which is clear from the final COD values. Experiments were conducted for current density of 2.5 A/dm² in batch reactor for reactor volume of 200ml, 400ml and 600ml respectively. The total quantity of electricity was fixed by considering the current passed rate, the duration of electrolysis and not upon the reactor holdup. The reactor hold up increases as the percentage COD removal decreases. (Tables 2-4.) A decrease in the power consumption is noticed when the reactor holdup increases.

Effect of power consumption on COD removal

The power consumption in kWh /kg of COD removal was calculated and shown in Tables 2-4 Power consumption decreases with increase in the sodium chloride concentration and reactor holdup. Mainly reactor holdup increases with decreasing the power consumption.

Effect of temperature on COD removal

Generally reactor holdup increases with decrease in reaction temperature for a particular current density. At low current density temperature is not a deciding factor for reaction.

CONCLUSION

The pulp and paper industry effluent was treated in the batch reactor. Excellent result is obtained for the sodium chloride concentration of 5 gpl, reactor volume of 200ml and current density of 2.5 A/dm².

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