

Estimation and Removal of Chlorophenolic Compounds from Paper Mill Waste Water by Electrochemical Treatment

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Abstract—A number of toxic chlorophenolic compounds are formed during pulp bleaching. The nature and concentration of these chlorophenolic compounds largely depends upon the amount and nature of bleaching chemicals used. These compounds are highly recalcitrant and difficult to remove but are partially removed by the biochemical treatment processes adopted by the paper industry. Identification and estimation of these chlorophenolic compounds has been carried out in the primary and secondary clarified effluents from the paper mill by GCMS. Twenty-six chlorophenolic compounds have been identified and estimated in paper mill waste waters. Electrochemical treatment is an efficient method for oxidation of pollutants and has successfully been used to treat textile and oil waste water. Electrochemical treatment using less expensive anode material, stainless steel electrodes has been tried to study their removal. The electrochemical assembly comprised a DC power supply, a magnetic stirrer and stainless steel (316 L) electrode. The optimization of operating conditions has been carried out and treatment has been performed under optimized treatment conditions. Results indicate that 68.7% and 83.8% of chlorophenolic compounds are removed during 2 h of electrochemical treatment from primary and secondary clarified effluent respectively. Further, there is a reduction of 65.1, 60 and 92.6% of COD, AOX and color, respectively for primary clarified and 83.8%, 75.9% and 96.8% of COD, AOX and color, respectively for secondary clarified effluent. EC treatment has also been found to increase significantly the biodegradability index of wastewater because of conversion of non-biodegradable fraction into biodegradable fraction. Thus, electrochemical treatment is an efficient method for the degradation of chlorophenolic compounds, removal of color, AOX and other recalcitrant organic matter present in paper mill waste water.

Keywords—Chlorophenolics, effluent, electrochemical treatment, wastewater.

I. INTRODUCTION

THE chlorophenolics are formed during the chlorination stage (C stage) of pulp bleaching and these get solubilized in the first extraction stage (E stage) [1]. Chlorinated phenolic are found in bleach plant effluent [2]. Biochemical treatment processes are adopted by the paper industry to remove these compounds. These chemicals are highly recalcitrant and difficult to remove from the environment as their half-life in water can be 3.5 months to several years in organic sediments [3].

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Electrochemical (EC) technology is one of the emerging processes that attracted attention of many researchers in past few years [4], [5]. Toxic phenolic compounds can be effectively oxidized by the electrochemical process using electric current with various features like simplicity, compact structure and operation [6]. This technique is an efficient method for the oxidation of the pollutants, where the oxidants are generated *in situ* by electro oxidation at anode, generally made up of iron and aluminum. The electrochemical process has already been successfully used to treat the wastewater from textile [7] and oils [8]. The effectiveness of the process depends on the type of electrode used. The traditional electrodes like graphite and nickel show poor efficiency towards organic removal. Dimensionally stable anodes (DSA) are highly expensive [9] and not very effective for phenols. In this study, a less expensive anode material, stainless steel, is used for the treatment of paper industry wastewater. SS electrodes consumes less electrode material (longer service life) and also produced less amounts of sludge, and the operating cost is about 0.7 times less as compared to Fe electrodes [10].

II. EXPERIMENTAL PROCEDURE

A. Reagents and Effluent Samples

Chlorophenols were obtained from Aldrich, Milwaukee, USA and Helix Biotech, Richmond, BC, Canada. Solvents, viz., *n*-hexane, acetone, methanol used were of HPLC grade. Diethyl ether and ethanol, both were of LR grade. Analytical grade acetic anhydride was used after double distillation. Stock standard solutions of chlorophenolics (20-30 mg/L) were prepared in acetone/water (10:90). The wastewater samples were collected from the primary and secondary clarifier effluent outlet of an integrated paper mill located in India. The mill uses OCEpHH bleach sequence and activated sludge process for treatment.

B. Treatment Assembly

The electrochemical assembly used for the treatment of wastewater included a direct current power supply, a magnetic stirrer, four stainless steel (316 L) electrodes; two anodes and two cathodes and an undivided electrochemical reactor. The EC reactor was a 1000 mL beaker filled with the waste water. The two SS electrode plates with a dimension of 50 cm² each were used as anode. The electrodes were positioned vertically and parallel to each other in a mono polar arrangement (a pair of anodes and a pair of cathodes).

The parallel arrangement is chosen in order to lower the potential difference between the electrodes, because it leads to the lower energy consumption. The gap distance between the two electrode plates was kept constant at 1 cm because, less than 1cm spacing prevents the movement of the electrolyte in the system, thus affecting the removal efficiency. A digital multi meter is used to read the current and voltage values of the circuit. All the treatment experiments were carried out in batch mode.

C. Optimization of Operational Parameters

Optimal parameters for the treatment of paper mill wastewater were determined using an electrochemical assembly, wherein a 250 ml of wastewater sample was taken in an electrochemical vessel. The investigations were carried out to study the effect of varying current density, pH, treatment time and organic load. After treatment, the wastewater samples were then kept for 1 h for the settling of the sludge and the supernatant was collected and analyzed for pH, COD and color.

The physicochemical analysis of the wastewater samples was performed before and after the electrochemical treatment. The various environmental parameters namely COD (Chemical Oxygen Demand), BOD₅ (Biochemical oxygen demand), color, AOX (adsorbable organic halides), TOC (Total organic carbon), solids etc., were measured by standard methods.

D. GC-MS Conditions

The analysis of chlorophenolic compounds in the paper industry effluent sample was performed by gas chromatography mass spectroscopy (GC-MS). Samples were extracted and derivatized for the GC-MS analysis. The chlorophenolic compounds were converted to readily volatilized acetyl derivatives. The quantitative analysis of chlorophenolic compounds were carried out with the help of calibration curve and extraction efficiency (EF) of the detected compound. The details of the procedures followed are from our earlier publication [1]. 1 μ L of acetyl derivative, taken from the hexane layer by a syringe, was injected into GC capillary column TR-5(30 m x 0.25 mm, 0.25 μ m) by an auto sampler (AI 3000) and GC-MS analysis was carried out using a Trace GC Ultra-DSQ (Thermo Electron Corporation, Massachusetts) GCMS. The samples were injected in the splitless mode (1 min). The operating conditions for GC-MS are: Ionising energy 70eV, Scan range (m/z) 42 to 336, Scan speed (amu/sec) 216.7, Fore pressure (mTorr) 38 to 45, Ion source temp. 200°C.

III. RESULTS AND DISCUSSION

A. Optimization of Electrochemical Treatment Parameters

The paper industry primary clarifier (PC) and secondary clarifier (SC) effluent was used for the optimization studies of electrochemical treatment. The parameters were studied by changing one parameter and other parameters were kept constant. The COD and color of the effluent is used to optimize the operational parameters of the EC treatment

process. From this study the optimum treatment conditions arrived at are pH 7.0, CD 15 A/m² and treatment time 2h. The behavior of PC effluent was also found similar to the SC effluent, except the removal efficiency decreases with increased organic load at the same conditions. The optimum conditions for SC effluent were taken, the same as for PC effluent treatment.

B. Effluent Characterization

The grab samples of primary and secondary effluent were collected and average values of three samples of different parameters are summarized in Table I. The primary effluent is having around four times higher pollutant load, as compared to the secondary effluent. As can be seen from the Table I that for PC effluent the reduction of recalcitrant organic pollutants (AOX and chlorophenolics) is not very significant, which indicates low biodegradability of the organics present. On the other hand, the BOD₅ reduction is quite significant i.e., about 93%, indicating a good efficiency of activated sludge process leading to the low BOD₅/COD ratio of 0.07 for secondary effluent, as compared to 0.22 for primary effluent. The industrial effluent varies in characteristics because of several parameters which are difficult to control.

C. Effluent Treatment

1. COD Removal

EC treatment gives 65.1% COD reduction in PC effluent and 83.8% reduction in SC effluent (Table II). Removal of COD of PC effluent with varying time show a good COD reduction (65%) in 2h of treatment after that the removal becomes somewhat constant. EC treatment converts the higher functional groups of the organic matter to more easily degradable forms during the initial period, and the rest are recalcitrant organic compounds whose degradation is slower in nature. Trapido et al., has shown that the number of chlorine atoms in the aromatic ring facilitates the dechlorination step and the degradation is faster [11].

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2. BOD₅ Removal

EC process gives BOD₅ reduction of 58.5% in PC effluent and 35% in SC effluent (Table II). This behavior is quite different from other Parameters like COD and color. SC effluent contains much higher proportions of recalcitrant compounds which are difficult to oxidize. BOD₅ reduction with time has also been studied in order to see the biodegradability of the PC effluent (Fig. 1). BOD₅ reduction is not very significant (12%) until 1.5 h of treatment but increases with treatment time to 35% and then becomes

constant. Conversion of non-biodegradable fraction into the biodegradable fraction leads to the increase in BOD₅ values.

3. Color Removal

The dark brown color of the paper mill effluent is due to the presence of lignin and its derivatives that are released from the substrate during the bleaching process. The electrochemical treatment method was found to be highly efficient for color removal. Color reduction was 92.6% and 96.8% in PC and SC effluent respectively (Table II). The effect of treatment time on the color reduction of PC effluent is shown in Fig. 1. Significant removal of color (75.3%) takes place during 1h of treatment. Lignin is the major color causing agent in the paper mill effluent and its degradation starts at early stages of the treatment process. Thus, EC treatment may be good option for the paper industry.

During the EC treatment there is a fast increase in the color during the initial period (15-30 min) of electrolysis. The solution is transparent and gradually becomes darker and more opaque as the reaction progresses. This may be due to fast generation of Fe (II) and Fe (III) species at the beginning which have forest green to yellow-brown color [12]. The color disappears gradually as the generated Fe ions mostly combine with the pollutant species and form settleable sludge.

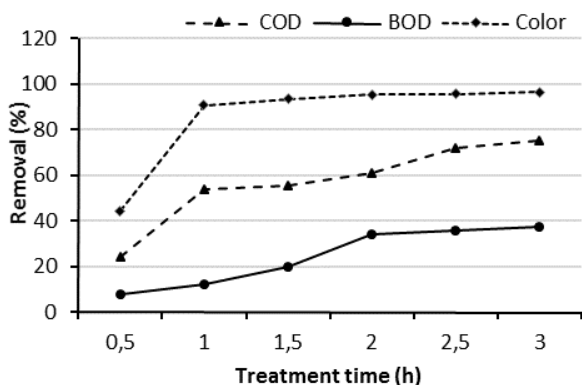


Fig. 1 Reduction in COD, color and BOD₅ in PC effluent

4. TOC Removal

A noticeable removal of TOC was observed for both primary and secondary effluents, probably due to the degradation of the biodegradable components (Table II). It was found that the TOC removal at 2h for PC effluent is 44.5% and 37.7% in SC effluent. The removal of TOC with time was studied in PC effluent. The results are presented in Fig. 2. In the initial 1h, the TOC removal was not so significant (only 10-12%), but increased substantially in 2h of treatment and reached to 44.5%.

5. AOX Removal

AOX can be efficiently degraded using electrochemical oxidation and can reduce more than 60% and 75.9% AOX from PC and SC effluent respectively (Table II). Faster AOX removal takes place mostly in first hour of treatment (Fig. 2). Fast adsorption or degradation of higher molecular weight compounds into smaller ones and further slow destruction of

these low molecular compounds further [13] take place.

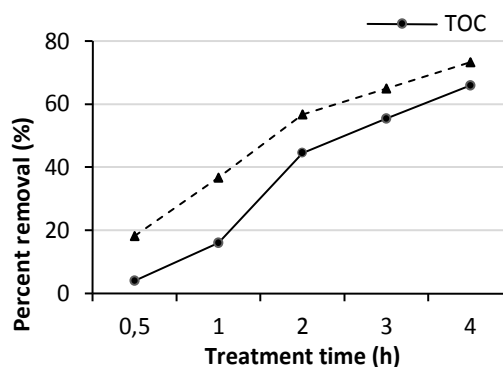


Fig. 2 Reduction in AOX and TOC in PC effluent

6. Solids Removal

The removal of both TDS (Total dissolved solids) and TSS (Total suspended solids) was studied with time for PC effluent (Fig. 3). There is a 27.5% removal of TDS and 51.4% removal in TSS was achieved in PC effluent under the optimized condition of treatment (Table II) and for secondary effluent the reduction is 11.4% and 42.6% in TDS and TSS, respectively. The removal in the case of TDS is not as good as found in the case of TSS and other pollutants. This is because the dissolved solids also consist of calcium, chlorides, nitrate, phosphorus, iron, sulfur, and other ions particles and their removal is slower, as compared to organic matter.

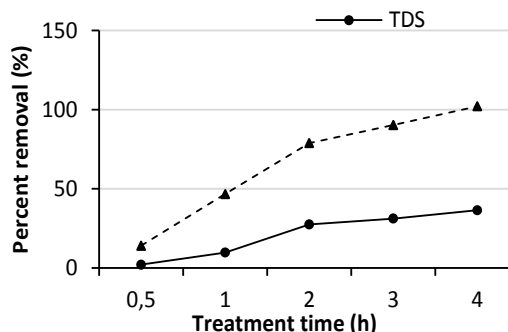


Fig. 3 Reduction in solids (TDS and TSS)

7. Biodegradability Index (BOD₅/COD Ratio)

The biodegradability index increase with EC treatment time and reaches a value of 0.50 after 120 min (2h) of treatment indicating that the effluent is now easily biodegradable. There is a fast increase in the BOD₅/COD ratio till 90 min (1.5h) of treatment and after that there is a slow increase in the ratio. Generation of strong oxidizing agents in the initial hours of the EC leads to the oxidation of the organic matter present in the wastewater. The long chain organic matter such as lignin may get converted into lower molecular weight components. This step will not only considerably reduce the COD component, but also increases BOD₅ resulting in an increase in BI of the sample. Thus, this technique can be used as a pre-treatment step for conventional biological wastewater treatment. Considerable reduction reactor volume or residence

time of the existing aerated biological treatment system can be expected by giving such a small electrochemical pre-treatment.

D. Chlorophenols

1. Estimation in Effluent

The total chlorophenolics concentration in primary and secondary clarifier effluent was $44.06\mu\text{gL}^{-1}$ and $21.65\mu\text{gL}^{-1}$ respectively (Table III). The symbols used for describing chlorophenols in the discussion refer to CP (chloro phenol), CC (chloro catechol), CG (chloro guaiacol), CV (chloro vanilin), CSA (chloro syringaldehyde), M(mono), D(di), T (tri), Tet (tetra); P (penta). Among all the identified compounds it was found that CP and CG are the major components, whereas CS, CV and CC are detected in trace quantities. It has been found that 2, 4, 5-TCP and 4, 5-DCG are the major identified compounds. 4-CG, 2,4-DCP, 3-CP, 2,5-DCP, 3,4,5-TCG and 2,3,6-TCP are present in significant quantities and all the other chlorophenols are present in trace quantities.

TABLE I
CHARACTERISTICS OF PAPER MILL WASTEWATER

Parameters (Unit)	PC effluent	SC effluent
pH	6.9±0.3	7.6±0.2
COD (mgL ⁻¹)	1096.5±98	263.6±90
TOC (mgL ⁻¹)	293.8±4.0	95.96±10
BOD ₅ (mgL ⁻¹)	250±12	18±3.0
BOD ₅ /COD ratio	0.22±0.01	0.07±0.01
Color (Pt-Co units)	1827.5±210	745±100
TDS (mgL ⁻¹)	2414±26	1963±10
TSS (mgL ⁻¹)	181±20	20±8.0
AOX (mgL ⁻¹)	14.3±0.57	6.3±0.40
Chloride (Cl ⁻) ions (mgL ⁻¹)	400±20	320±26
Sulphate ions SO ₄ ²⁻ (mgL ⁻¹)	316±10	210±20

2. Removal from Secondary Clarifier (SC) Effluent

The removal of individual chlorophenolic compounds are given in Table III. Under optimum conditions 83.6% of chlorophenolics get removed from SC effluent by EC treatment. The removal of most of the compounds was from 30-100%. Compounds like 4-CP, 2,3,5-TCP, 2,4,6-TCP, 2,3,4-TCP, 4 CG, 4,5-DCG, 4,6-DCG, 3,4,5-TCG, 5,6-DCV and Tet-CC are completely removed or are not detected. 2, 4,5-TCP was removed almost completely up to 91.2% followed by 3,4,6-TCG (87.2%), 3-CP (86.5%) and 3,5-DCC (78.8%). The rest of the compounds were removed up to 30-62% only. 2,6-DCP, 2,5-DCP, 2, 4-DCP and 3,6-DCC are removed only 31.6%, 45.1%, 60.9% and 62.0% respectively. It may be due to the formation of these low molecular weight compounds from the degradation of high molecular weight compounds in the system because mostly *ortho*- and *para*-chlorinated phenols were encountered during the electrochemical conversions [14]. TCS was removed by 63.9%, followed by Tet-CG which was removed by 45.9% (Table III). The group-wise removal of chlorophenolics is TCS (63.9%) followed by CP (79.4%), CC (85.2%), CG (94.1%) and CV (100%).

TABLE II
EC TREATMENT UNDER THE OPTIMIZED CONDITIONS

S. No.	Parameters	Percent removal (%)	
		PC Effluent	SC Effluent
1.	COD	65.1	83.8
2.	BOD ₅	58.5	35.0
3.	Color	92.6	96.8
4.	TOC	44.5	37.7
5.	TDS	27.5	11.4
6.	TSS	51.4	42.6
7.	Cl ⁻	30.0	41.0
8.	SO ₄ ²⁻	65.8	60.0
8.	AOX	60.0	75.9
9.	Chlorophenols (Total)	68.7	83.8

TABLE III
CONCENTRATION AND REMOVAL OF CHOROPHENOLICS BY EC

Compound	PC effluent		SC Effluent	
	Conc (μgL ⁻¹)	Removal (%)	Conc (μgL ⁻¹)	Removal (%)
3-CP	1.04±0.50	100	0.39±0.23	86.5
4-CP	0.56±0.01	99.4	0.14±0.07	100.0
2,6-DCP	0.94±0.29	40.7	0.72±0.16	31.6
2,5-DCP	3.99±0.16	65.6	0.27±0.029	45.1
2,4-DCP	1.49±0.15	69.8	0.06±0.10	60.9
2,3-DCP	ND	ND	0.03±0.004	ND
3,4-DCP	0.10±0.02	100	ND	ND
4-CG	3.06±0.08	79.3	0.18±0.15	100.0
2,4,5-TCP	24.96±4.59	66.2	8.99±1.34	91.2
2,3,6-TCP	0.06±0.01	100	ND	ND
2,3,5-TCP	0.15±0.01	100	0.17±0.10	100.0
2,4,6-TCP	ND	ND	0.05±0.03	100.0
4,5-DCG	4.19±0.70	80.9	1.18±0.71	100.0
2,3,4-TCP	0.16±0.05	73.7	0.07±0.02	100.0
4,6-DCG	0.42±0.01	52.3	0.51±0.22	100.0
3,6-DCC	2.04±0.15	79.8	5.90±0.37	62.0
3,5-DCC	ND	ND	2.66±0.47	78.8
3,4,6-TCG	0.12±0.03	100	ND	87.2
3,4,5-TCG	0.05±0.01	54.5	0.05±0.01	100.0
4,5,6-TCG	0.11±0.01	ND	ND	ND
5,6-DCV	0.12±0.02	19.2	0.08±0.015	100.0
PCP	0.18±0.12	100	ND	ND
Tet-CG	0.19±0.09	28.5	ND	45.9
TCS	ND	69.6	ND	63.9
Tet-CC	ND	ND	0.20±0.14	100.0
2,6-DCSA	0.13±0.03	ND	ND	ND
Total	44.06±7.04	68.7	21.65±4.16	83.8

ND-Not detected.

The removal of TCP was highest (91.6%), followed by MCP (88.1%) and DCP (38.9%). The removal of high chlorinated chlorophenolics (TCP) was higher as compared to lower chlorinated chlorophenolics (MCP). This may be due to the higher negative charge on the highly chlorinated chlorophenolics. More the chlorine atoms, more will be the negative charge on the chlorophenolic compound in the wastewater, and this favors the coagulation process or is due to the degradation of higher molecular weight compounds to lower molecular weight compounds [15]. Removal of higher chlorinated chlorophenolics (TCP and TetCC) by EC also reduces the toxicity of paper mill wastewater, as these

compounds are more toxic in comparison to lower chlorinated chlorophenolics (MCP and DCP).

3. Removal from Primary Clarifier (PC) Effluent

The EC treatment removes 68.7% of chlorophenols. The results are presented in Table III. Concentration of most of the chlorophenolics is reduced by 50-100%. Compounds like 3-CP, 2, 3, 6-TCP, 2, 3, 5-TCP, 3, 4, 6-TCG and PCP are completely removed or concentration falls below the detection limit of the instrument. 4-CP (99.4%) is almost completely removed. 4, 5-DCG and 3, 6-DCC are reduced by 80%. 2,5-DCP, 2,4-DCP and 2,6-DCP are reduced by 65.6, 69.8 and 40.7% respectively. 4,6-DCG, 3,4,5-TCG and TetCG are reduced by 52.3% 54.5 and 28.5% respectively, whereas 5, 6-DCV is reduced only by 19.2%. The group-wise removal of chlorophenols is the CG (80.9%) followed by CC (79.8%), TCS (69.5%) and CP (68.9%) and CV (19.2%). Monochlorophenols (CP) are removed almost completely (99.7%), then TCP (66.6%) and DCP (58.5%). The percent removal in PC effluent is lower than SC effluent because of higher concentration.

IV. CONCLUSIONS

- 1) Electrochemical treatment is an efficient method for the degradation of recalcitrant organic matter.
- 2) It enhances the biodegradability of paper mill wastewater.
- 3) Toxic Chlorophenols and color removal is very good.
- 4) COD, TOC and BOD reduction is modest.

ACKNOWLEDGMENT

The research grant for this study provided by the Ministry of Human Resource and Development, Government of India is gratefully acknowledged.

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