ELRCTROCHEMICAL TREATMENT AND RECYCLING OF PULP AND PAPER MILL WASTEWATER

Ph.D. THESIS

by

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ROORKEE – 247 667 (INDIA)
August, 2014

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A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
of

DOCTOR OF PHILOSOPHY
in
ENVIRONMENTAL ENGINEERING

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this thesis entitled **"Electrochemical Treatment and Recycling of Pulp and Paper Mill Wastewater"** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Paper Technology, Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out at Department of Paper Technology during the period from August, 2008 to July, 2014 under the supervision of Dr. Satish Kumar, Professor, and Dr. Chhaya Sharma, Associate Professor, Department of Paper Technology, Indian Institute of Technology Roorkee, Roorkee, India.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(RAJNI SHARMA)

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

(Satish Kumar)
Supervisor

(Chhaya Sahrma)
Supervisor

Date: /08/2014

Dedicated to

MY PARENTS

ABSTRACT

The pulp and paper industry is among one of the largest sources, which discharge enormous quantity of pollutants including gaseous, liquid, and solid waste into the environment. Despite these, it is also the third largest consumer of fresh water after primary metals and the chemical industries. Higher consumption of water is one of the key environmental concerns in paper industry, since it produces a large volume of wastewater as well. The wastewater from paper industry contains a significant amount of organic matter, with low biodegradability, high color, AOX and toxicity values. Various wastewater pollutants, including toxic organic compounds at a high concentration, are difficult to treat with conventional treatment processes. Hence, treatment technologies require continuous advancements in order to meet the rigorous discharge standards and to improve the cost effectiveness of the processes. The electrochemical (EC) method is a treatment process that can be a promise as an effective treatment alternative for high strength organic wastewater containing toxic substance.

The pulp and paper mill wastewater from primary and secondary clarifier was characterized in terms of environmental parameters; COD, TOC, BOD, color, solids, Cl^- and AOX. The electrochemical (EC) treatment using stainless steel anode was used to treat the present effluent. Optimization of the process variables i.e., initial pH of the wastewater, current density (CD), treatment time (t), and initial organic load, for the treatment of paper mill wastewater by EC was carried out. This was done in terms of COD and color removal efficiency. The removal efficiency for other parameters such as BOD, TOC, AOX, and chlorophenols were determined under optimized conditions. Both primary and secondary clarifier wastewater was subjected to electrochemical treatment under the optimized conditions. The electrochemical treatment method was found to be efficient for the color removal. BOD_5/COD ratio of the effluents improved after the treatment to a significant extent. The biodegradability of the effluent improved substantially after the EC treatment, indicating the easy removal of pollutants by biological process. The generated sludge was characterised for various physico-chemical parameters.

The results on detection and quantitative determination of various chlorophenols in the combined pulp and paper mill effluent are reported. The GCMS analysis of both primary and secondary clarifier effluents samples leads to the identification of 20 low molecular weight chlorophenolic compounds in primary clarifier effluent and 18 compounds in the secondary clarifier wastewater in various concentrations. Six types of chlorophenolics compounds i.e., chlorophenols, chloroguaiacols, chlorocatechols, chlorovaillin, chlorosyringols and chlorosyringaldehyde, were identified in the effluent. The results indicate that, among the total compounds detected, the higher contribution to the chlorophenols comes from di-substituted compounds in the paper mill effluent. The effectiveness and performance of the stainless electrodes for the degradation of chlorophenols is also examined. In case of chlorophenols, monochlorophenols were oxidized to the maximum extent followed by di- and trichlorophenols. For chlorophenol treatment, 68.7 % organic removal was achieved after 2h on stainless steel anode at current density of 15 A/cm^2 for primary clarifier effluent and 85.3 % removal was achieved in secondary clarifier effluent. Analysis with the High Performance Liquid chromatography (HPLC) revealed many intermediate products during the EC process, from aromatic compounds to aliphatic acids, which were oxidized by SS electrode. Based on the EC degradation performance and the HPLC results, the treated samples were also analyzed on GC-MS for the qualitative and quantitative analysis of the chloro-organic intermediates.

The EC treated secondary clarifier wastewater was used as wash water to study the recycling of this wastewater in pulping and bleaching sections of paper mill. The pulp was bleached to 84% ISO target brightness using DEpD bleach sequence in the laboratory. D and E_P, refer to chlorine dioxide and H_2O_2 reinforced NaOH extraction stages, respectively. For DEpD sequence a Kappa Factor of 0.28 was found to be optimum for attaining the target brightness (84% ISO). The two DEpD sequences were done in parallel using fresh water (DEpD) as well as EC treated water (RC_DEpD) for washing to achieve the target brightness. The two bleaching sequences were compared in terms of bleach chemical demand, pulp brightness, and change in bleach chemical dose to get the same target brightness. The generated bleach effluent was characterized for environmental load. A higher COD and color was generated in RC_DEpD sequence as compared to DEpD as a higher kappa factor of 0.29 (RC_DEpD) was required to achieve the same target brightness (84% ISO). There was no effect of wastewater recycling on pulp and paper properties i.e. viscosity, tear, tensile, and burst indexes.

ACKNOWLEDGEMENT

This thesis arose in part out of research work that has been done since I came to IIT Roorkee. By that time, I have worked with a great number of people whose contribution in assorted ways to the research and the making of the thesis deserved special mention. It is a pleasure to convey my gratitude to them all in my humble acknowledgment.

First of all I am highly obliged to the Almighty God for his wonderful care for me. In the next place I would like to record my gratitude to Prof. Satish Kumar and Dr. Chhaya Sharma for their supervision, advice, and guidance from the very early stage of this research as well as giving me extraordinary experiences throughout the work. Above all and the most needed, they provided me immense encouragement and support in various ways.

I convey my special thanks to Dr. Vivek Kumar my supervisor for his guidance, support and advice at all stages of my work. I would like to thank Prof. Y.S. Negi, Professor-In-charge, Department of Paper Technlogy (DPT), for giving me the opportunity to work in the department. I am very much thankful to my Students Research Committee members Prof. Anil Kumar (Prof. & Head, Department of Chemistry) and Dr. S.P. Singh for their invaluable suggestions and encouragement throughout my work. I would like to thank all the staff in DPT, IITR for all their support for the completeion of this research work. I would like to express my sincere thanks to Ministry of Human Resource Development GOI (MHRD) and IIT Roorkee, India for providing funding during my research work.

Collective and individual acknowledgments are also owed to my colleagues and friends at Environmental Laorartory, DPT, IITR whose presence perpetually refreshed, helpful, and memorable. Many thanks go in particular to Dr. Parveen Kumar for helping me during my research work and thesis writing, to Dr. Shiv Kumar, Ashutosh, Chhotu Ram, Raisa, Anushree,Vivek and Dushyant for giving me such a pleasant time when working together with them since I knew them in IITR.

Thanks Ankita, Suman, Indu, Anshu, Luxmi, Pawan Rekha for creating such a great friendship. It is pleasure to mention for sharing various thoughts during the “evening tea” with small chit chats at Indira Bhawan hostel. I wish to express my hearty gratitude to my dear friends who have been always with me during ups and downs, and they are Divya Abrol, Deepika Tiwari and Ashish Bais.

Where would I be without my family? My parents deserve special mention for their inseparable support and prayers. My mother, Mrs. Shobha Sharma and my very caring papa, Mr. B.K. Sharma in the first place are the persons who put the fundaments of my learning character, are those who sincerely raised me with their caring and gentle love. It’s really a pleasure to acknowledge my very caring and loving mother-in–law Mrs. Renuka Nagpure, for always appreciating and patiently encouraging me for completing my thesis. My very dear and sweet little sister Mini Sharma, thanks a lot for being supportive and caring sibling and I really appreciate your valuable advices. I thank my sister and brother-in-law Jyoti di and Vijay jijaji for their invaluable blessings and delightful love. Thanks Vijay Nagpure and Neha Nagpure, my dear brother and sister-in-law, for always being there to support me and their caring attitude was appreciable.

Words fail me to express my appreciation to my loving husband and a very good friend Dr. Ajay Nagpure, whose dedication and persistent confidence in me, has taken the load off my shoulder. I owe him for being unselfishly supportive, without his support, I would not be here at IITR. I am so thankful to him for his patience throughout my stay at IITR.

Last but not the least, I wish to thank to critics of mine as they made me more alert and creative towards my ambitions. Finally, I would like to thank everybody who was important to the successful realization of thesis, as well as expressing my apology that I could not mention.

Rajni Sharma

TABLE OF CONTENTS

CHAPTER 2: MATERIALS AND METHODS 29-48

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

AOPs	Advanced Oxidation Processes
AOX	Adsorbabale Organic Halides
BI	Biodegradability Index
BDD	Boron doped diamond efficiency
BOD	Biochemical Oxygen Demand
C	Chlorination stage
CC	Chlorocatechols
CED	Cupriethylenediamine
CG	Chloroguaiacols
COD	Chemical Oxygen Demand
CP	Chlorophenols
CS	Chlorosyringol
CSA	Chlorosyringaldehyde
CV	Cyclic voltammetry
D	Chlorine dioxide stage
DCP	Dichlorophenols
DTA	Derivative thermal analysis
DTG	Differential thermo gravimetric analysis
E	Alkaline extraction stage
ECF	Elemental chlorine free
EDAX	Energy dispersive X-ray analysis
EE	Extraction efficiency
EOX	Extractable organic halides
Eo	Oxygen (O_2) reinforced extraction stage
Ep	Peroxide (H_2O_2) reinforced extraction stage
FE-SEM	Field emission scanning electron microscope
FID	Flame ionization detector
GC-MS	Gas chromatography-mass spectroscopy
HPLC	High pressure liquid chromatography

KF	Kappa factor
LSV	Linear Sweep Voltametery
m/z	Mass/charge ratio
MCP	Monochlorophenols
O	Oxygen delignification stage
O.D.	Oven dried
PCP	Pentchlorophenol
POPs	Persistent organic compounds
RF	Response factor
RT	Retention time
TCD	Total chlorine demand
TCF	Total chlorine free
TCP	Tri-chlorophenols
Tet-CP	Tetrachlorophenols
TOC	Total organic carbon
TGA	Thermal Gravimetric Analysis
XRD	X-ray diffraction
Cl^-	chloride ion
Fe^{2+}	ferrous ion
Fe^{3+}	ferric ion
$^{\bullet}OH$	hydroxyl radical
OH^-	hydroxyl ion
H^+	hydrogen ion
$Fe(OH)_2$	ferrous hydroxide
$Fe(OH)_3$	ferric hydroxide

PUBLICATIONS

Peer-reviewed research papers (Published/accepted)

1. **Rajni Sharma**, Satish Kumar, Chhaya Sharma, "Mechanism of the anodic oxidation of Chlorophenolics in pulp and paper industry effluent using stainless steel electrodes, Environmental Science and Pollution Research (ESPR), Springer **(Accepted)**
2. **Rajni Sharma**, Satish Kumar, Chhaya Sharma, "Influence of Operational Parameters on Electro coagulation Process in Pulp and Paper Mill Effluent Treatment" Environment Engineering and Management Journal (EEMJ), Vol. 13 (2): 289-296 (2013)
3. **Rajni Sharma**, Satish Kumar, Chhaya Sharma, Tertiary Treatment Option for Pulp and Paper Mill Wastewater to Achieve Effluent Recycling", Indian Pulp and Paper Technical Association Journal (IPPTA), Vol. 23 (4): 155-159, (2011).

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Chapter 1

INTRODUCTION

1.1. PULP AND PAPER INDUSTRY

The pulp and paper industry has been considered one of the world’s growing sector which depends on the natural resources including forest fiber, water and energy. The global paper and paperboard production is dominated by North America (25%), Europe (30%) and Asia (particularly China).North America has historically been the top producer and consumer of paper and paperboard globally, but with the recent rapid economic growth in Asia, these two regions currently rank as the number one and two global producers of paper and packaging [1,2]. Paper demand is unequally distributed as 22% of the world’s population in USA, Europe and Japan consume 72% of the global paper. The global demand is anticipated to grow by 3% yearly, reaching an expected value of 490 million tonnes by 2010, with a significant increase in Asia and Eastern Europe [2]. The Indian paper industry is one of the oldest industrial sector and it accounts for 1.6% of global paper and paperboard manufacture. The operating capacity of the industry currently stands at 12.75 million tons and it is prepared to grow at the rate of 8% per annum and 15 million tonnes in 2015 [1,3,4].

The socio-economic importance of paper has its own value to the country's development as it is directly related to the industrial and economic growth of the country. The per capita consumption of paper in India is still low, at around 10 kg, which is well below the global average of 55 kg. In fact, consumption in India is set to double by 2020, from the current level of 12 million tonne [5]. India has 600 paper mills. The country’s paper is mainly manufactured from hardwood and bamboo fiber (40%) followed by agro waste (30%) and recycled fiber (30%) [3]. Being a fiber deficient country, two third of the raw materials comes from non-wood sources. This includes agro residues like wheat straw, rice straw, bagasse, bamboo etc. A common raw material used by industries in the country is wheat straw, bagasse and waste paper; approximately 35% are based on chemical pulp, 44% on recycled fiber and 21% on agro-residues [6].

The paper manufacture involve two major processes: pulping and bleaching. The pulping process involves the degradation of lignin from the wood and removal of soluble fractions from the plant tissue producing unbleached pulp. The unbleached pulp consists of 80-90% cellulose content, 10-15% hemicellulose and 2.5-4% residual lignin content. The residual lignin in the pulp is accountable for the color and photo yellowing of the paper [7]. The bleaching of pulp is done to achieve the desirable brightness of the pulp [8]. The bleaching is done in a continuous sequence of different stages with in-between washing of pulp. The first stage is either chlorination (Cstage) or chlorine dioxide (Dstage) in which Cl_2 or ClO_2 is used to delignify the pulp followed by alkaline extraction stage (Estage) where alkali (NaOH) and oxygen (O_2) or hydrogen peroxide (H_2O_2) are used for the removal of alkali soluble lignin content. The subsequent stages like peroxide (Pstage, Hstage and Dstatge) increases the pulp brightness by removing the chromophoric groups of the lignin [9]. The Indian paper mills are broadly grouped into three categories, i.e., large (>100 tonnes per day, medium (30-100 tonnes per day) and small (<30 tonnes per day) [10]. Large mills (wood and bamboo based), use chemical recovery, while smaller mills (agro based) with no chemical recovery are extremely polluting.

In developed countries, the mills have reduced their pollution discharge below the prescribed limit by adopting the modern technologies for pulping and bleaching of pulp. The Indian mills are still using the conventional bleaching sequences like CEH, CEHH and CEpHH and use elemental chlorine (Cl_2) for bleaching because of techno-economic reasons. Thus the bleaching plant become the major source of environmental pollution releasing high biological oxygen demand (BOD), chemical oxygen demand (COD), adsorbabale organic halides (AOX) and color loads. Nowadays few Indian mills have shifted from conventional bleach sequence to elemental chlorine free sequences like OD/CEpD, ODED, ODEopD etc to reduce the effluent color and pollution loads. Apart from the pollution, there is a growing water scarcity and deterioration in water quality in many parts of India. Thus, reduced fresh water availability, declining water quality and environmental pollution are the major issues to deal in country like India [6, 11]

1.2. PULP AND PAPER MILL WASTEWATER CHARACTERISTICS

Pulp and paper industry generates a huge quantity of wastewater from various process of paper manufacture. The major sources of pollution are wood preparation, pulping, pulp washing, bleaching and coating operations. Bleaching section is one the major contributor to the color, organic matter and toxicity [12-15]. The wastewater is discharged at the rate of 20-250 m^3/t of O.D. pulp. The generated effluents, based on raw materials used and employed production process, commonly have a high COD and a low biodegradability (defined as the ratio of BOD_5/COD) and more than 200–300 different organic compounds and approximately 700 organic and inorganic compounds [16]. Such compounds may include non-biodegradable organic materials, adsorbable organic halogens (AOX), color, phenolic compounds, etc. [17], depending upon the applied pulping process, additives, and the amount of water consumed. It is characterized by high BOD (10-40 kg/t of O.D. pulp), COD (20-200 kg/t of O.D. pulp), suspended solids (10-50 kg/t of O.D. pulp), AOX (0-4 kg/t of O.D. pulp), color, toxicity and high concentration of nutrients (nitrogen and phosphorus) which causes eutrophication in receiving water bodies. The main source of nutrients comes from raw material (wood) [18, 19]. Bleach plant alone accounts for 60-70% of BOD and 80-90% of color loads of the entire paper mill having chemical recovery systems [20]. The 90% of the color in bleach plant wastewater comes for first two beaching stages, out of which E stage individually accounts for 70-80% of the color [21]. The color in the wastewater is mainly due to the lignin content and also associated with wood extractives and chlorinated organics formed during beaching [22, 23]. The use of chlorine in pulp bleaching results in the formation of various chlorinated organics in the wastewater like chlorophenolics, chloro-resins and fatty acids, which are collectively estimated as AOX [24, 25]. Chloro-organics are toxic and tend to persist in nature, because 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 [26].

1.2.1. Formation of chlorinated compounds

Chlorophenolic compounds are generated by the lignin degradation products during pulp bleaching by chlorination process [27, 28]. It is well established that a series of various chlorophenols are formed during bleaching process. The nature and extent of formation of chloro-organics are determined by the residual lignin content in the pulp and the type of bleaching chemicals used. The conventional kraft pulp bleaching by chlorination produces 5.4-9.0 kg/t of chlorinated compounds per ton of bleached pulp. Approximately 300 different compounds in pulp and paper industries effluents have been identified and about 200 of these are chlorinated organic compounds [29]. The chloro-organic present in the spent bleach liquor was first characterized by Lindstrom and Nordin in 1976 [30]. Since then a large amount of literature has been reported for the identification of chlorophenolics from softwood [31], grasses [32, 33], and agro-residues [34]. Only few studies has been conducted for the characterization of chloro-organics in Indian hardwoods [35-37]

1.2.2. Toxicity of pulp and paper mill wastewater

The toxicity of pulp and paper mill effluent mainly depends on the total organically bound chlorine, extractive content of the raw material and to the extent of extractives removal by different processes [38]. The chlorinated compounds present in pulp and paper industry effluents have known to exhibit acute, chronic and some mutagenic toxicity to aquatic life. Various studies conducted in developed countries reveal that the low molecular weight (LMW-20%) chlorinated compounds are the major contributors to toxicity and mutagenicity. It is because of the fact that, high molecular weight compounds (HMW-80%) are biologically inactive due to their inability to penetrate the cell membranes of living organisms, while LMW compounds, are hydrophilic and can be easily metabolized. However, the past studies conducted, indicate that, these high molecular weight chloro compounds may also break down to smaller more biologically active compounds and can cause long-term toxic effects to the recipients [38, 40]. The chlorinated compounds present in the E stage bleaching effluent are more toxic and contribute more than 90% to acute toxicity [41]. The chlorophenolics i.e., trichlorophenol (TCP), tri and tetra chloroguaiacols (CG), in particular may accumulate in fish and are responsible for acute toxicity. The chlorophenolics biodegradability rates decreases with increase in the chlorination [27]. Among the chlorinated organics, the dioxins and dibenzofurans are toxic in nature. The prominent among the dioxins are 2,3,7,8 tetra chloro dibenzo dioxin (TCDD) and 2,3,7,8 tetra chloro dibenzo furan (TCDF). Dioxins are highly lipophilic and bioaccumulative compounds. 2,4- dichlorophenol (2,4-DCP), 2,4,5-trichlorophenols (2,4,5-TCP), pentachlorophenols (PCP) and chloroform are carcinogenic, whereas chlorocatechols are highly mutagenic [42].

1.3. POLLUTION ABATEMENT IN PAPER MILLS

The water pollution abatement in pulp and paper mills can be achieved by two approaches: in-plant modification or end-pipe treatment (wastewater treatment).

1.3.1. In-plant Modification

The in-plant modification can be done by various process modifications in pulping and bleaching sections like extended delignification which leads to the reduction in pulp lignin content before bleaching. This leads to the reduction in bleach chemical dose to achieve the target brightness and also reduces the generation of chloro-organic [43].

1.3.1.1. Oxygen delignification

O_2 delignification is another approach which is normally used as the first stage of bleaching by all modern mills these days, followed by ECF and TCF bleaching, which subsequently reduce the pollution discharge from the bleaching section [44]. O_2 delignification is being utilized by almost all the paper mills in developed countries to further decrease the unbleached pulp kappa number before bleaching. This process decreases the kappa number by 40-50% and AOX generation by 60-70% [45] The O_2 delignification results in considerable decrease in effluent load generation. The partial closure of fiber line is also possible by recycle of the O_2 stage effluent to chemical recovery [46, 47].

1.3.1.2. ECF and TCF bleaching

ECF and TCF bleaching are other options for reducing the environmental impact of pulp mills. Mostly, ClO_2 has been utilized as a dilignifying agent for pulp bleaching due to its high selectivity and significant decrease in the AOX generation [48, 49]. Presently, the ECF bleaching is a dominant technology for high brightness commercial chemical pulp production. About 75% of the world’s bleached chemical pulp is manufactured by ECF bleaching [50-52]. Oxygen based bleaching reagents such as oxygen (O_2), peroxide (H_2O_2), and ozone (O_3) are used in TCF bleaching. The combined application of O_2 and $O_{3,}$ before ECF bleaching results in the high quality brightness pulp, which needs small or no Cl_2 and ClO_2 bleaching. Ozone (O_3) is a potential alternative to Cl_2 and ClO_2, which reduces AOX generation significantly [53].

1.3.1.3. Peroxide reinforced alkaline extraction

Peroxide (H_2O_2) reinforced alkaline extraction has found an important role in ECF and TCF bleaching sequences for chemical pulps in addition to the mechanical pulp bleaching [54, 55]. H_2O_2 has been applied as a primary chemical in bleaching stage as well as in Estage with NaOH [56]. The use of peroxide in extraction stage (Ep) is increasing considerably for bleaching process that requires only 0.3-0.5% H_2O_2 [57]. Ep also increases delignification and pulp brightness and decreases the active chlorine demand in subsequent bleaching stages hence leads to the reduction in cost and environmental load [53].

1.3.1.4. Enzyme pre-treatment of pulp

Enzyme pre-treatment can also be another option for lignin removal by biological means and is called bio-bleaching. It is a cost effective and eco-friendly means of pre-bleaching [58, 59]. Xylanase and laccase enzymes from different origins, has been investigated as a potential agent for bio-bleaching of kraft pulp [81]. Xylanase hydrolyze xylan layer present in the plant cell wall and influence the structural integrity and facilitate the lignin removal during the succeeding bleaching stages. Laccase directly and specially act on lignin and oxidize it to make more soluble. Laccase attack primarily the phenolic groups by simultaneous reduction of O_2 and H_2O_2, through phenoxy radical formation as intermediate [62].

1.3.1.5. Chlorination (C) stage modification

The pulp bleaching with chlorine results in the generation of toxic compounds in the effluent [37]. The replacement of ClO_2 for elemental Cl_2 as a bleaching agent is gaining extensive application, because of its beneficial impacts on pulp and paper effluent quality. Chlorination stage modification at Cstage is also a good option, practiced by some mills in India [43]. It results in the low AOX generation at Cstage. In this process elemental chlorine (Cl_2) is replaced by ClO_2. Besides AOX reduction, it also improves the pulp brightness and viscosity of the pulp.

1.3.1.6. Improved pulp washing

Improved pulp washing aims to remove most of the soluble impurities as possible from the pulp using small amount of fresh water [62]. The modern eucalyptus kraft pulp bleach plants equipped with state-of-art washing equipment produce pulp by bleaching and generate COD as low as 5 kg/t of O.D. pulp. Washing of the pulp effects the pulp properties and consequently the paper produced from it [63, 64]. While poor washing of brown stock and post oxygen washing in older mills results in higher COD generation of 20-30 kg/t of O.D. pulp and resin carryover along with pulp [65]. Thus, improved pulp washing can decrease the required bleach chemical dose and leads to the subsequent decrease in the cost and decrease in chlorinated organic compounds formation [43]. Improved washing practices combined with the decrease in fresh water consumption can reduce the volume of effluent generated, which leads to the decreased size of effluent treatment plants and cost [64].

1.3.1.7. Internal water reuse

The paper industry is one of the major users of water, ranking about third among all the industries in the quantity of water used. Wastewater recycling can also be done to reduce the effluent volume and fresh water consumption in the paper mills [67]. However the water usage in the mills per tonne of paper produced has decreased in recent years as a result of conservation measures, which involve; the reuse of diluted black liquor for liquor makeup in the kraft process, the use of cooling water from turpentine condensers and condensate from digester blow-down in the kraft process, the reuse of white waters from deckers to thin fresh stock in cleaning, the treatment of paper machine water to re-use in the wet end system and many other such measures. These measures leads to the less fresh water consumption and corresponding wastewater generation will also be lower.

1.3.2. Wastewater treatment

Wastewater treatment is a process in which the pollutants in wastewater are partially removed and partially changed by decomposition from highly complex to simpler form. Conventional wastewater treatment consists of a combination of physical, chemical, and biological processes to remove solids, organic matter and, sometimes, nutrients from wastewater. Different degrees of treatment, in order of increase the treatment level, are preliminary, primary, secondary, and tertiary and/or advanced wastewater treatment [65, 66]. Biological treatment, such as the activated sludge process, is normally the cheapest and simplest technology used by many paper industries in India to remove organics waste. However, chlorinated phenols are often recalcitrant and cannot be removed by biological systems. Two separate reports showed that wastewaters containing 200 mg/L or more of 2- MCP could not be effectively treated at biological treatment facilities. So, an alternate treatment technology is required to make these compounds more biodegradable, less toxic, or towards complete oxidation to CO_2 and H_2O.

With increasing stringent effluent discharge standards and increasing environmental awareness, there is an urgent need to adopt advanced treatment systems such as advance oxidation processes (AOPs). AOPs can be broadly defined as aqueous phase oxidation methods based on the very reactive oxidizing species i.e., (primarily but not exclusively) hydroxyl radicals ($OH^\bullet$) for the degradation of organic compounds [68]. AOP's are $OH^\bullet$ radicals are reactive electrophilic species (2.33 V oxidation potential), hence cause degradation of organic compounds [69]. These include the generation of $OH^\bullet$ radicals and are very effective at initiating the oxidation of the target compounds by attacking the C-H bonds or addition at unsaturated and aromatic centers. Various AOP's are attempted to degrade organic toxicants like ozonation, fenton oxidation, homogenous and heterogeneous photocatalysis based on near UV or solar irradiation, electrochemical oxidation and wet air oxidation (WAO), etc. [70, 71]. Depending on the quality of the effluent AOP's can be applied independently or as a pre or post-treatment step for enhancing the biodegradability of the effluent. AOP's are still expensive to operate owing to usage of expensive chemical like H_2O_2 and increased energy consumption in case of photocatalysis and ozonation. WAO is expensive in terms of installation cost, as special construction material may be needed to withstand increased corrosion. High electrical energy, installation cost and chemical consumption are the common problems hampering its industrial application. However the AOP's can be optimized for its efficient use and industrial application [68].

Among the various AOPs, electrochemical technology is one of the emerging processes that attracted attention of many researchers in past few years. Research has shown that EC is effective and has been used for water purification [72]. Electrochemical technologies have attracted a great attention and research because of their versatility, which makes the treatment of liquids and solids possible, and their environmental compatibility and simplicity. In electrochemical treatment, the main reagent is the electron, which is a ‘‘clean reagent’’ [73]. Over the past few years, there has been growing interest in electrochemical treatment application in potable and industrial effluent having high concentration of recalcitrant pollutants. The application of electrochemical methods for the removal of organic pollutants has advantages as compared with chemical or biological methods. Chemical oxidation methods can be used for the decomposition of many organic pollutants that require large amount of expensive chemical reagents. Biological and electrochemical methods have little or no harmful effects on the environment, because these techniques do not involve the use of harmful reagents. Legislators and industry also favor waste treatment without the use of added chemicals. The US EPA classified “electro-mitigation” as the only *in-situ* method that can be applied to low permeability clays and silty soils [24]. Electrochemical reactions are more or less independent of the condition of the wastewater and can continue as long as a current is supplied to the electrode [74].

1.4. ELECTROCHEMICAL TREATMENT

Electrochemistry is a clean, powerful and versatile method for the destruction of pollutants in wastewater. Electrochemical methods certainly involve two processes: oxidation and reduction, oxidation, which takes place at the positive electrode (anode) and reduction which occurs at the negative electrode (cathode). Therefore, electrolysis can be applied to contaminants that are capable of undergoing either oxidation or reduction; provided that one of these reactions is possible. Electrochemical technologies have the advantage that the electrode processes involve only the removal (oxidation) or addition (reduction) of electrons [75]. It can also be applied to convert the toxic and recalcitrant pollutants to biodegradable organic compounds, which can be removed by biological treatment, required after the electrochemical oxidation [76]. Electrochemical treatment process is the combination of oxidation, flocculation and flotation.

1.4.1. Electrode selection

In electrochemical process, the electrode selection is an important factor which decides the overall performance and mechanism of the treatment process. Based on the electrode material, the mechanism pathway of the electrochemical process can be electrocoagulation (EC) or electro-oxidation (EO). The electrode materials mostly used in the EC method are aluminum or iron metal, other metal electrodes like stainless steel, titanium, copper, zinc, etc. are also used. The best electrode material which can be used in the electrochemical method must have high electrochemical activity for aromatic ring opening and low electrochemical activity for further oxidation [76].

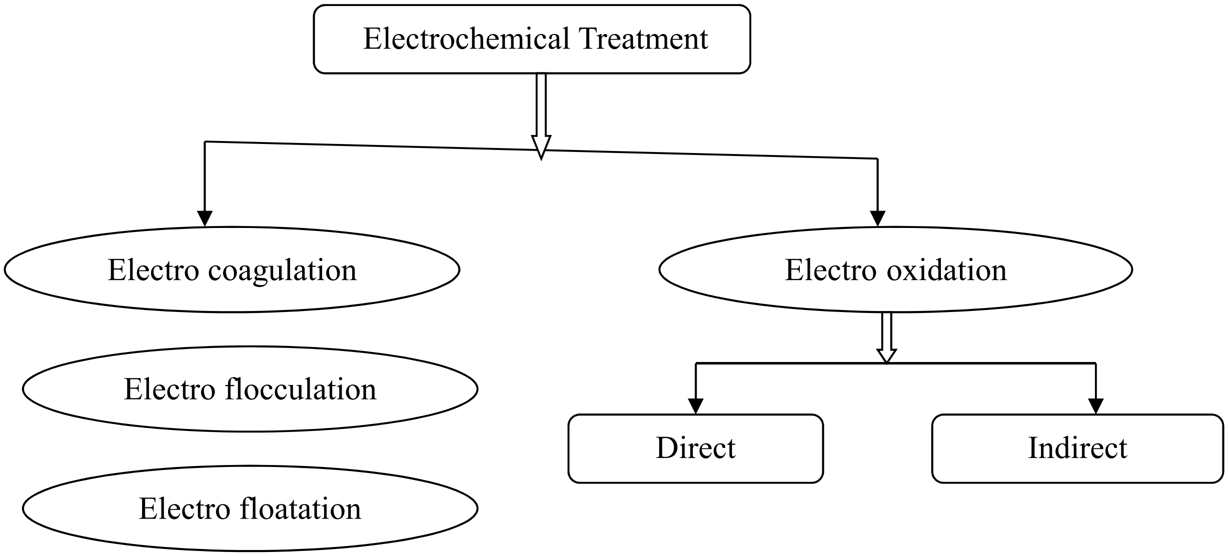

Figure 1.1: Mechanisms of electrochemical treatment process

1.4.2. Mechanism of the process

(a) Electro-coagulation, Electro-flocculation, Electro-flotation

Electrocoagulation involves the generation of coagulants *in-situ* by the action of electric current on iron or aluminum electrode. In this process, the metal ion is generated at the anode with simultaneous release of hydrogen gas at cathode [77]. These Al^{3+} or Fe^{2+} metal ions generated in the reaction are very efficient coagulants for particulates flocculating. The hydrolyzed aluminum ions can form large networks of Al–O–Al–OH that can chemically adsorb pollutants [78]. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials. This released gas help in the floatation of flocculated particles out of the water. This process is called electro flocculation [79].

(b) Electro-oxidation

The electro-oxidation reactions mainly occur at the anode, which contributes to the conversion and/or the oxidation of the organic pollutants. Generally, the pollutants are degraded through the two pathways; direct or indirect oxidation mechanism. The direct oxidation occurs at the surface of the anode through the generation of physically adsorbed ‘‘active oxygen’’ (adsorbed hydroxyl radicals, $^{\bullet}OH$). This mechanism is proposed by [76]. It is an efficient method for the degradation of pollutants, it does not require any additional chemicals and with no tendency to produce secondary pollution. In the case of indirect oxidation the intermediates (e.g., ozone, hydrogen peroxide, and hypochlorite are generated anodically to destroy the pollutants [80, 81].

1.5. LITERATURE REVIEW OF ELECTROCHEMICAL TREATMENT

Electrochemical treatment has been successfully utilized for the treatment of various industrial wastewaters and specifically for pulp and paper industry wastewater, either singly or in combination of other physiochemical or biological methods. A review of work done during the last few years in the field of electrochemical treatment for different industrial wastewaters and pulp and paper industry wastewater is presented in Table 1.1 and 1.2 respectively.

Recent research has demonstrated that electrochemical technologies can be applied to the treatment wide range of pollutants. Chen in 2004 has published an extensive review on the development, design and application of electrochemical technology such as electro-deposition, for metal recovery, electrocoagulation and electro-floatation for removal of suspended solids, colloids etc., and electro-oxidation for removal of organic compounds [82]. However, the effectiveness of EC wastewater treatment depends on the type and properties of the anode material used for treatment [83]. Other DSA coating materials, such as PbO_2 and SnO_2, have been introduced to improve the performance of treatment performance. The coating techniques still need to be modified to improve the quality of the coating surface for better wastewater treatment performance and more cost-effective application [83]

The electrochemical process has already been successfully used to treat the heavy metal containing waste for metal recovery [84, 85], dye containing wastewater from textile industry [86, 87]. Wastewater from restaurant [88] and oil containing waste [89] has also been treated successfully with good removal efficiencies. Organic pollutants such as phenol and chlrophenols were also studies and presented by many researchers [90, 91, 92, 93]. Traditional electrodes, such as graphite and nickel, are not applicable for organic degradation [75]. The commonly used RuO_2 and IrO_2 coating surface does not show high reactivity for organic oxidation [94].

Phenol oxidation could stop with the formation of products such as maleic acid at the Pt anode [90]. However, complete phenol degradation could be brought by the PbO_2 electrodes [95]. Therefore, the oxidation pathway of aromatic chemicals on different anodes remains a subject matter for further investigation. A review on the electro-oxidation processes (i.e. electrochemical, electro-Fenton, photoelectro-Fenton, photoelectrochemical, and electrochemical peroxidation) was published by Bashir et al, 2012 about the effectiveness and mechanism of electro-oxidation processes employed for the treatment of stabilized landfill leachate [96]. The removal of coliform bacteria from landfill leachate by use of Electro-Fenton oxidation was also presented by Aziz et al, 2013 [97]. Applications of the EC treatment for textile wastewaters have also been done by various workers. Electrochemical treatments of textile dye-containing solutions or wastewaters samples have been conducted on a laboratory scale and significant removal of organic substances and color was reported under varying operating conditions [86, 98]. Electrochemical treatment has been widely attempted for the purification and recycling of industrial wastewaters. It has been found to be efficient for color removal and effluent recycling in textile industry [99] and turbidity removal for recycling in tissue paper industry [100].

The application of electrochemical treatment for the remediation of pulp and paper industry has tried way back in 1991 by Comnenellis and Pulgarin for the removal of phenols using Pt cylinder as anode [86]. The generation of hydroxyl radical and removal of phenols by chemical oxidation have been investigated. Springer et al., in 1995 used mild steel as sacrificial electrode to remove 90% of color and toxicity from bleach kraft effluent [101]. Bejankiwar et al., in 2005 used stainless steel anode for the oxidation of 1,2-dichloroethane (DCA) and found to be efficient for its removal [102]. It was concluded that, the removal of DCA is independent of its initial concentration and it follows first order kinetics. Lignin and phenols are the major components of paper industry as it leads to the color and chloroorganics generation. So, it has been a subject matter of great interest to researchers for the remediation of paper industry effluent. Ugurlu et al., in 2008 compared Fe and Al electrode for lignin and phenol removal and got good results with both Fe (92% lignin removal, 93% of phenol reduction) and Al electrodes (lignin 80% and phenol 98%) [103]. Patel et al., used graphite electrode for the degradation of pentachlorophenol (PCP), color and COD reduction. Small scale paper industries do not have recovery system and hence their wastewater is highly polluted. Electrochemical treatment is proved to be efficient even for high COD wastewaters [104]. Zaid and Bellakhlal in 2009, treated black liquor using Fe and Al, and have reported, 98% reduction in COD, 92% reduction in color and 92% reduction in polyphenols [105]. Pulp and paper industry effluent was effectively treated using iron and mild steel electrodes [106]. Turbidity of tissue paper mill effluent was removed by passing 0.6 A direct current through Al plates and the water could be recycled [100]. Sridhar et al. used Fe plates for the treatment of bleach plant effluent [107]. 4-CP (1-5 mM) was effectively oxidized by vitreous carbon electrode by cyclic voltammetry (CV) technique by Duan et al in 2013 [93]. The coated electrodes are found to be efficient in the removal of phenols by successful oxidation of 2-4-DCP and PCP in separate studies [108, 109]. They used Ti/SnO_2-Sb electrodes and found their degradation followed pseudo-first-order kinetics. Shao et al., in 2014 found electrochemical treatment as an efficient method to enhance the biodegradability of the pulp and paper mill effluent containing lignin, by using Ti/Sb-SnO_2 and Ti/PbO_2 anodes [110]. The recycled paper wastewater was effectively treated by electrochemical peroxidation method (Fe-H_2O_2) having high COD values of 4300 mgL^{-1} to get 95.7% reduction. Further research is still going on in the direction of electrochemical treatment, especially for making it acceptable in industrial application. Electrode selection is also an important issue, which has been extensively studied and still continues to be the subject of interest.

Table 1.1: Literature review of electrochemical treatment used for treatment of different types of wastewater using different anodes

S.No.	Pollutants removal	Application areas	Remarks	Reference
1.	Heavy metals	Metal Industry	Metal recovery	[84,85,105]
2.	Oil containing wastewater	Petro-chemical industry	Removal of oil and grease	[94]
3.	Nitrate	Domestic, agricultural & industry	-	[115]
4.	Tannery wastewaters	Tannery industry	-	[72, 114]
5.	Dairy wastewaters	Dairy industry	Oil-grease	[116]
6.	Restaurant Wastewater	Domestic effluent	Removal of oil, grease, detergent etc.	[88]
7.	Pentachlorophenol	Polluted clay soils	-	[117]
8.	Landfill leachates	Polluted soil	Coliform bacteria removal	[96, 97]
9.	Dye containing wastewaters	Textile industry	Color removal, effluent recycling	[86, 98, 99, 118, 119]
10.	Tissue paper industry	Paper industry	Turbidity removal and effluent recycling	[100]

Table 1.2: Literature review of electrochemical treatment of pulp and paper industry application

Pollutants removal	**Anode**	**Treatment conditions**	**Remarks**	**References**
Phenol wastewater	Pt cylinder	150 g/dm^3 Na_2SO_4 $^+$ phenol, pH- 12.5	Phenol degradation by chemical oxidation and eletro-generated hydroxyl radicals	[90]
Bleach kraft effluent	Mild steel	pH-6, I-1 A, Temp.- 50^{o}C	Color removal 90% and toxicity decreased to a smaller degree	[101]
Phenol degradation	Ti/SnO_2-Sb, Ti/RuO_2, and Pt.	CD-20 mA/cm^2 V- 4.6 V,	Intermediate products include benzoquinone and organic acids, and oxidized rapidly by the Ti/SnO2-Sb anode	[83]
1,2-dichloroethane (DCA)	Stainless steel (304 L)	-	SS is efficient for removal of DCA and independent of initial concentration till 25–100 mg/L TOC. TOC removal followed zero-order kinetics	[102]
Lignin and Phenol	Al & Fe	V-12 V, CD-77.1 mA/m^2, t- 2min	Fe electrode (92% lignin, 93% phenol, 80% BOD & 55% COD), Al electrode (80% lignin, 98% phenol, 70% BOD and 75% COD)	[73]
Chlorophenols (PCP)	Graphite	CD-6 mAcm^{-2}, 1000 mgL^{-1}, pH- 9.3, t-2h	>90% color and COD reduction	[120]
Black liquor	Fe & Al	pH-7, CD-14 mA/cm^2, t-50 min	COD 98%, polyphenol 92% & 99% color	[105]
Pulp and paper mill effluent	Iron plates	pH-7.58, CD- 20.7 A/m^2, t-30-45 min	Color-97.0%, COD- 87.8%, BOD_5-91.2%, TSS- 89.8%, TDS- 37.5%	[106]

Pollutants removal	**Anode**	**Treatment conditions**	**Remarks**	**References**
Pulp and paper mill wastewater	Mild steel	pH-7.3, CD-112.9 A/m^2, t-6.9 min	Biodegradability Index increased (0.11 to 0.46) and COD-55% and Color -87% reduction	[121]
Tissue paper wastewater	Al plates	Direct current of 0-6 A	Turbidity 92%, EC treated water is of acceptable quality for reuse in tissue paper industry	[100]
Pulp & paper mill bleach effluent	Iron plates	pH-7, CD- 15 mA/cm^2	-	[108]
4-Chlorophenol	Vitreous carbon electrode	pH (pH 0.4-12.0), 1–5 mM of 4-CP, temp. 25 and 85 ◦C by CV technique	4-CP can oxidized more easily in alkaline medium than acidic and neutral mediums,	[93]
2,4-dichlorophenol	Ti/SnO2-Sb electrode	CD 2–40 mA/cm^2, pH 3–11, initial concentration of CP 5–200 mg/L t- 20 min	99.9% of 2,4-DCP removal and the reaction followed pseudo first-order kinetics	[108]
Pentachlorophenol (PCP)	Ti/SnO2–Sb	PCP (5–1000 mg L^{-1}), pH (3.0–11.0) & CD (5–40 mA/cm^2)	Degradation of PCP over Ti/SnO2–Sb electrodes follows pseudo-first-order kinetics	[109]
Paper recycling plant wastewater	Fe-H_2O_2 (electro-fenton process)	pH-4, CD- 5 mA/cm^2, t-30 min,	COD reduction from initial level of 4300 mg/L to 106 mg/L (95.7% removal)	[112]

1.6. PROBLEM STATEMENT

The pulp and paper industry is highly polluting and capital intensive industry. Water pollution is one of the major concerns of pulp and paper industry due to toxicity of the wastewater generated [26]. It is also a heavy water user and hence the corresponding wastewater generation is also high. There are several sources of water pollution from the paper industry while bleaching section is the most significant source. The bleaching section is the main contributor to the color, organic matter and toxicity. The use of chlorine and chlorine based chemicals for pulp bleaching generates a variety of chlorophenolic compounds originating from chlorination of residual lignin [26, 110]. Studies indicate that, some of these chlorophenolics are toxic, mutagenic and resistant to biodegradation [27]. The pulp and paper industries generally employ two stages of treatment for the generated wastewater; primary (physico-chemical treatment) and secondary (biological treatment). The secondary treatment processes for pulp and paper effluents are lagooning, biofilters, activated sludge and anaerobic treatment [65, 111, 112]. These conventional processes are also not efficient for the degradation of many of the the recalcitrant organic matter (chlorophenolic compounds) and color reduction is also low. Recently, several physical and chemical processes have been extensively studied, for colour removal in paper mill effluents, These include rapid filtration through soil, ultrafiltration, ion-exchange, lime precipitation, some bleach plant modifications such as such as peroxide addition during extraction and the replacement of chlorine by chlorine dioxide, and sorption on hypo-and alum-sludge, activated carbon etc. However, the problem remains unsolved, since lignin undergoes a spatial rather than chemical change and thus persists though in a different forms, even after treatment. Hence, paper mills are looking up in adopting some alternative treatment processes like advanced oxidation methods [113]. Over the past few years, there has been growing interest in the application of electrochemical treatment in potable and industrial effluent having high concentration of recalcitrant pollutants and for color removal. The application of electrochemical methods for the removal of organic pollutants has advantages over chemical or biological methods [74]. Electrochemical method has also been tried and found efficient for effluent recycling, in textile industry (color removal) and tissue paper industry (turbidity removal) [99, 100].

The present work aims to evaluate the performance of electrochemical treatment process, using stainless steel electrodes, for the removal of color and recalcitrant compounds in pulp and paper mill wastewater. To try the EC treatment as an advanced method for the treatment of secondary clarifier effluent and look at the possibility of recycling of the EC treated water in pulping and bleaching sections of the mill.

1.6.1.Objectives of this study

Looking at the advantages of electrochemical treatment, this treatment was chosen for the present study. The objectives of the present study are:

1. To evaluate the performance of electrochemical treatment (EC) process for removal of recalcitrant organic compounds and color from pulp and paper mill wastewater using stainless steel electrode.
2. To identify the intermediates formed during the EC treatment of chlorophenols and to look at possible degradation mechanism.
3. To evaluate the impact of using EC treated water as wash water for washing of unbleached and bleached pulp. The impact of recycling can be evaluated by comparing the bleach sequences in terms of;
    - Bleach chemical consumption
    - Environmental load generation like COD, color, AOX etc.
    - Mechanical strength properties of paper

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Chapter 2

MATERIALS AND METHODS

2.1. REAGENTS AND CHEMICALS

All the reagents and chemicals used were of analytical grade and used without further purification. The standard reference compounds of chlorophenols (CP) were obtained from Aldrich, Milwaukee, WI, USA. Chloroguaiacols (CG), chlorovanillin (CV), Chlorocatechols (CC), chlorosyringaldehyde (CSA) and chlorosyringol (CS) were purchased from Helix Biotech, Richmond, BC, Canada. All the other chemicals used were of the highest purity commercially available. Solvents, viz., *n*-hexane, acetone, methyl tertiary butyl ether (MTBE), methanol used were of HPLC grade, diethyl ether and ethanol, both 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 pH of the pulp and the aqueous solutions was adjusted with 1M H_2SO_4 or NaOH solutions. Sodium chlorite ($NaClO_2$) solution was used for the *in-situ* generation of chlorine dioxide for D stage bleaching. NaOH solution and hydrogen peroxide (Fisher Scientific, SQ grade) were used in alkaline extraction (E_P stage) of pulp.

2.2. PULP SAMPLES

The unbleached and unwashed mixed hardwood (Eucalyptus: Popular, 70:30) kraft pulp after the blow tank was procured from an integrated paper mill in India. The pulp was then washed, air dried and stored in air tight polyethylene bags for further use in bleaching experiments. The pulp was bleached to a target brightness of 84% ISO following DEpD bleach sequence under controlled laboratory conditions. The effluent from the individual stage was collected for further characterization.

2.3. EFFLUENT SAMPLES

The wastewater samples used in the study were collected from the primary and secondary clarifier effluent outlet of an integrated pulp and paper mill located in India. The mill uses OCEpHH bleach sequence. The major fraction of biodegradable organic compounds has been treated in activated sludge process at ETP of the mill leaving behind mostly non-biodegradable organic compounds.

2.3.1. Electrochemical Wastewater Treatment

2.3.1.1.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 (Figure 2.1). The EC reactor was a 1000 mL beaker filled with the waste water. The two SS electrode plates with a dimension of 50 cm^2 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) [1].

The parallel arrangement is chosen in order to lower the potential difference between the electrodes because it leads to the lower energy consumption [2]. 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 [3]. 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.

2.3.1.2.Optimization of operational parameters

Optimal parameters for the treatment of pulp and paper mill wastewater were determined using an electrochemical assembly, wherein 250 ml of wastewater sample was taken in an electrochemical vessel. The investigations were carried out to study the effects 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.

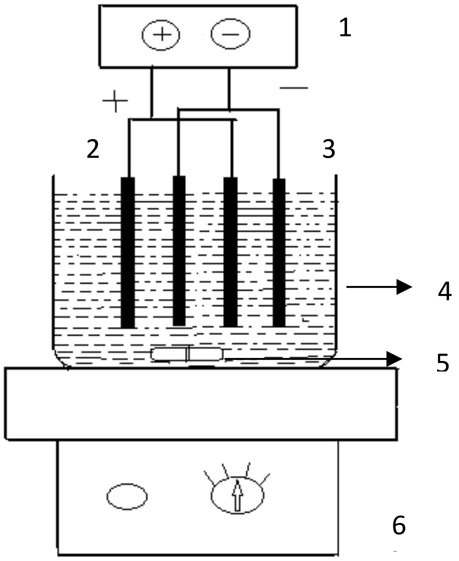


Figure 2.1: Schematic diagram of the experimental set up: (1) D.C. Power supply, (2) Anode, (3) Cathode, (4) Reaction vessel, (5) Magnetic bead, (6) Magnetic Stirrer

2.4. ANALYTICAL METHODS

The physicochemical analysis of the wastewater samples was performed before and after the electrochemical treatment, using standard test methods for analysis of water and wastewater [4].

2.4.1. Color Measurement

2.4.1.1. Preparation of standard color solution

250 mg metallic Pt (99.99% pure) was dissolved in hot aqua regia. This solution was heated to dryness to remove excess of HNO_3 (as oxides of nitrogen) by the repeated evaporation and addition of fresh portions of concentrated HCl. The residue was dissolved in distilled water along with 500 mg of crystallized $CoCl_2.6H_2O$ (equivalent to 125 mg Co) and 5 ml of concentrated HCl. The total volume of the solution was made up to 100 ml with distilled water to yield a standard solution of 2500 parts-Co color units (mg/L) [5].

2.4.1.2.Color measurement

Standard solutions of 50, 100, 250, 500, 750, 1000, 1500, and 2000 Pt-Co units were prepared by diluting 0.5, 1.0, 2.5, 5.0, 7.5, 10, 15, and 20 ml of standard stock solution to 25 ml in a volumetric flask. Absorbance of different standard solutions (Table 2.1) was determined at 465 nm on UV/Visible double beam spectrophotometer and calibration curve was plotted as shown in Figure 2.2. This curve was used to determine the color of the effluent. The pH of the effluent was adjusted to 7.6 and centrifuged for 5 min at 1500 rpm to remove suspended particles. Then the absorbance of the solution was measured at 465 nm and color concentration was calculated from the calibration curve.

Table 2.1: Absorbance of standard color solutions

S. No.	Concentration (Pt-Co units)	Absorbance
1.	50	0.012
2.	100	0.027
3.	250	0.066
4.	500	0.125
5.	750	0.198
6.	1000	0.264
7.	1500	0.382
8.	2000	0.510
9.	2500	0.660

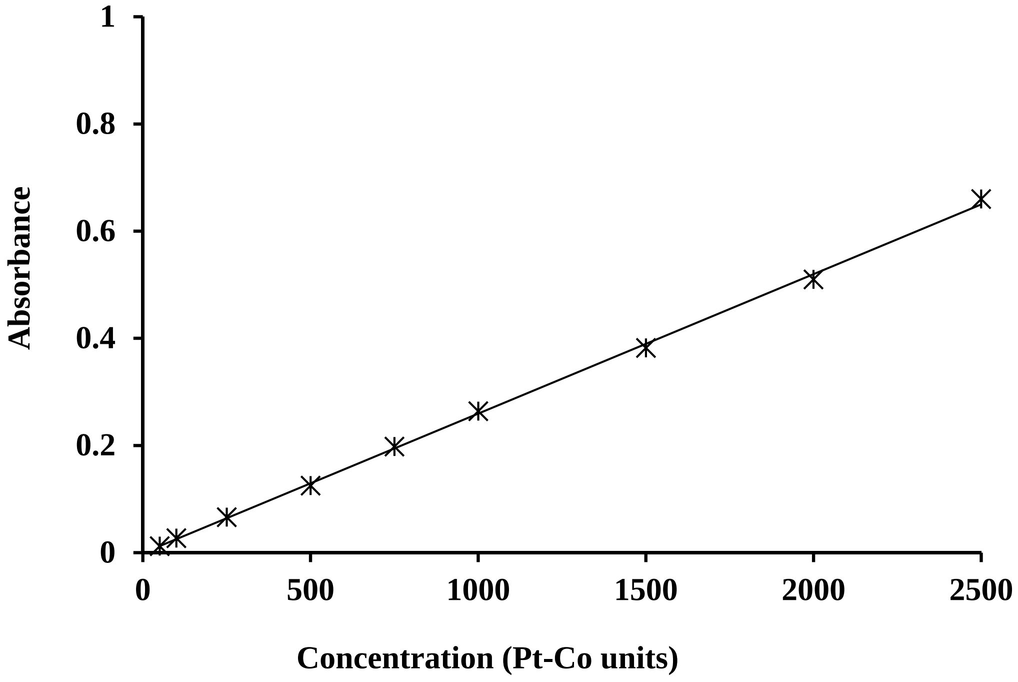


Figure 2.2: Calibration curve used for effluent color estimation

2.4.2. High performance liquid chromatography (HPLC) study

High performance liquid chromatography, HPLC (Figure 2.3) was used to determine the concentrations of chlorophenols and the intermediate organics of the EC degradation process. The intermediates included aromatic compounds of benzoquinone, hydroquinone and catechol and aliphatic acids i.e.; maleic acid, fumaric acid, succinic acid, malonic acid, oxalic acid and acetic acid. The HPLC (Shimadzu LC-20 AD) equipped with a diode array detector (Shimadzu SPD-M 20A) was used at working wavelengths from 190 to 400 nm. For analysis of phenol, aliphatic acids and other aromatic compounds, a capillary column C18 H 5 μm (250 × 4.6 mm) was used. Acetonitrile/water = 60:40 (V/V) was used as the mobile phase at a flow rate of 1 ml/min under room temperature for phenols and aliphatic compounds.

For analysis of aliphatic acids the column C18 H 5 μm (250 × 4.6 mm) was chosen. NaH_2PO_4 (0.25 mM) solution adjusted to pH 2.7 with H_3PO_4, was used as the mobile phase at a flow rate of 0.5 ml/min for aliphatic acids. Before each analysis, the sample was filtered through a 0.2-μm membrane syringe filter (Millex-LCR) in the ambient environment. The sample injection volume was 10 μl.

2.4.3. Gas Chromatography Mass Spectroscopy (GCMS) study

The qualitative and quantitative analysis of chlorophenolic compounds in the paper industry effluent sample was performed by gas chromatography mass spectroscopy (GC-MS) shown in Figure 2.4. Samples were extracted and derivatized for the GC-MS analysis. The chlorophenolic compounds were then converted to readily volatilized acetyl derivatives prior to GC-MS analysis. For quantitative analyses, the response factors (RF) and extraction efficiencies (EF) of various compounds were determined.

2.4.3.1.Extraction and Derivatization of chlorophenolic compounds

The chlorophenol extraction was done by simple modification of the procedure suggested by Lindstrom and Nordin (1976) [6]. The untreated, treated and bleaching effluent samples (1L) were adjusted to pH 2 with dilute H_2SO_4, followed by extraction with 400 mL of 90:10 diethyl ether/acetone for 48 h with intermittent shaking. The emulsion formed in the ether layer was broken by using a heat gun. A schematic flow sheet of detailed procedure followed for the chlorophenol extraction and derivatization is presented in Figure 2.6.

After 48 h, the whole ethereal extract of the effluent sample was transferred into another separating funnel and shaken with 5 mL of $NaHCO_3$ (0.5 M) solution to remove acidic impurities. Then the ether layer was shaken with 5 mL of NaOH (0.5 M) solution for the chlorophenols extraction. The aqueous NaOH layer, containing chlorophenols, was separated and washed with 10 mL of fresh diethyl ether to remove the neutral impurities. The remaining aqueous NaOH layer was derivatized for injection into GC-MS.

After the liquid-liquid extraction of the 1 L the effluent sample around 4 mL effluent extract is obtained. The total effluent extract (4 mL) is taken and diluted to 4.5 mL using distilled water. This diluted sample was taken in a PTFE lined screw capped glass tube, 0.5 mL of Na_2HPO_4 (0.5 M) buffer solution was added to the glass tube and shaken for 2 min. Then 0.5 mL of acetic anhydride was added for derivatization of chlorophenolics and tube was shaken for 5 minutes. The acylation was done with acetic anhydride based on procedure suggested by Abrahamsson and Xie in 1973 [7]. The acetyl derivatives of chlorophenolics were extracted with 1 mL of n-hexane. The mixture was shaken for 3 min and 1 μL of acetyl derivative, taken from the hexane layer by a syringe, was injected into GC column by an auto sampler (AI 3000, Thermo Electron Corporation), for the identification and quantitative analysis of chlorophenolics [8].

Figure 2.3: High Performance Liquid Chromatography (Shimadzu LC-20 AD)

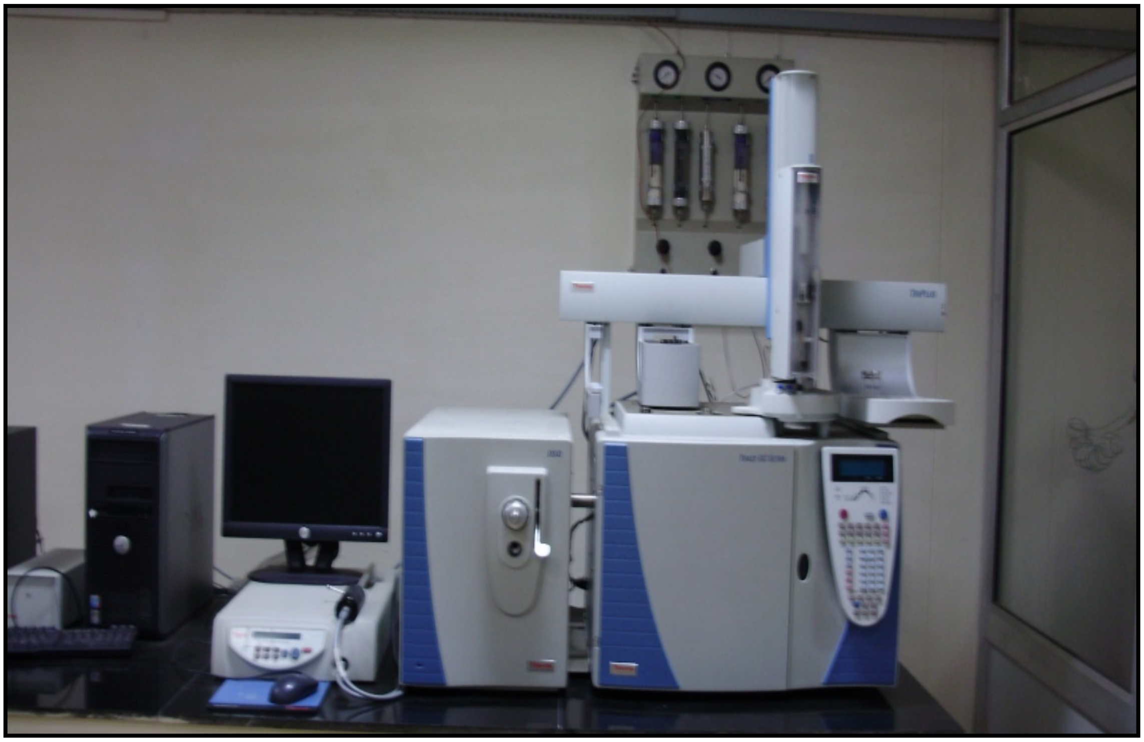


Figure 2.4: Gas Chromatograph Mass Spectroscope (Trace GC Ultra-DSQ, Thermo Electron Corporation, Waltham, Massachusetts)

Figure 2.5: AOX analyzer (Dextar AOX analyzer, Thermo Electron Corporation)

2.4.3.2.GC-MS conditions

GC-MS analysis was carried out using a Trace GC Ultra-DSQ, Thermo Electron Corporation, Waltham, Massachusetts, equipped with a capillary column TR-5 (30 m x 0.25 mm I.D. with 0.25 µm film thicknesses) containing 5% phenyl methyl polysiloxane was for the chromatographic separation of the target compound. The target compounds in the effluents were first identified by qualitative analysis by matching their mass spectrum with the National Institute of Standards and Technology library (NIST). Once the compounds were identified the calibration curves of the identified compounds were prepared in the concentration range of interest for the quantitative analysis. Temperature programmed for the GC-FID analysis was kept at 45°C for 1 minute and increased to 280°C at the rate of 6°C per minute, keeping the final temperature for 25 minutes.

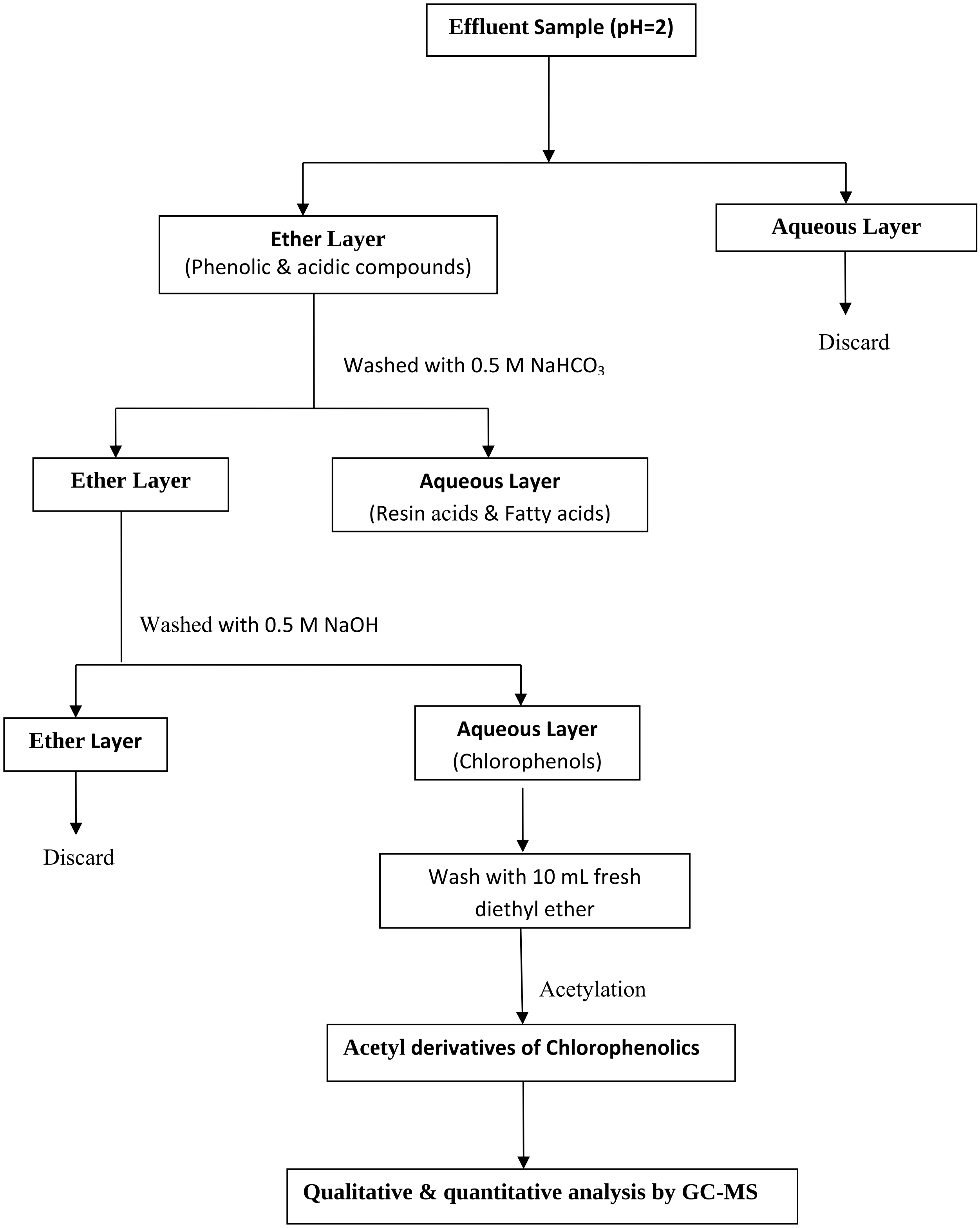


Figure 2.6: Schematic diagram for the extraction of chlorophenolic compounds from effluent

Injector, mass transfer line, and ion source temperatures were set at 210 °C, 280 °C, and 200 °C, respectively. The helium (He) is used as the carrier gas, at a flow rate of 1 mL/min. MS was operated in the electron impact ionization (EI) mode with an ionizing energy of 70 eV and an emission current of 100 µA. Full scan data were obtained by scanning from 42-336 m/z at a scan speed of 216.7 amu/sec (0.7241 scans per second) and pressure 38-45 mTorr. Target compounds in the samples were first identified by matching their mass spectrum with that of NIST library. Once the main peaks were identified, the standard solutions of identified target compounds were injected into GC-MS system in order to determine their retention times (RT). The samples were injected in the splitless mode (1 min). The operating conditions for GC-MS is given in Table 2.2.

Table 2.2: GC-MS conditions for the analysis of chlorophenolic compounds

Gas Chromatography		**Mass Spectrometer**	
Parameter	**Condition**	**Parameter**	**Condition**
Column	Capillary column TR-5	Ionising energy (eV)	70 eV
Column dimension	30 m x 0.25 mm I.D.	Scan range (m/z)	42 to 336
Detector	Mass Spectrometer		
Film thickness	0.25 µm	Scan speed (amu/sec)	216.7
Sample injection volume	1 µL	Fore pressure (mTorr)	38 to 45
Carrier gas (Flow rate)	Helium (1mL/min)	Ion source temperature (°C)	200
Injector temperature (°C)	45 for 1 min	-	-
Column temperature (°C)	45 to 280 @ 6°C min^{-1} 280 for 25 min^{-1}	-	-

2.4.3.3.Quantitative analysis of chlorophenolic compounds

The quantitative analysis of chlorophenolic compounds were carried out with the help calibration curve and extraction efficiency of the detected compound. Standard solutions of chlorophenols were prepared in acetone: water (10:90) solution and injected at different concentrations. The calibration curves of the pure standard compounds were drawn by measuring their peak areas.

The extraction efficiency was determined by taking 1mL of standard solution of each pure chlorophenolic compound and diluted to 1 L with distilled water. The pH of the solution was adjusted to 2.0. The above solution was then extracted and derivatized by the above mentioned procedure (section 2.4.3.1.), 1 μL of the derivatized sample was injected into the GC-MS. The peak areas of the injected standards were determined in order to find out the quantity present in the sample.

The extraction efficiency (EE %) was determined by following formula;

$$Extraction\ efficiency\ (EE\ \%) = \frac{Quantity\ in\ the\ extracted\ sample}{Quantity\ in\ the\ non\ extracted\ sample} \times 100 \tag{2.1}$$

The response factor was estimated by taking 1 mL of standard solution of chlorophenol, which was then derivatized for converting into its the methyl esters (0.5 μL) were injected into GC column. The area of the peak was recorded and RF was calculated from the expression;

$$RF = \frac{Area\ of\ the\ peak}{Wt.\ of\ the\ sample\ injected\ (pg)} \tag{2.2}$$

2.4.4. Other water quality parameters

The *pH* of the test sample was measured using a bench scale *pH* meter. The color of the sample was measured by using a UV-VIS double beam spectrophotometer (Analytical Jena SPEKOL 2000), chemical oxygen demand (COD) by using a COD reactor (Thermoreaktor CR 2010) according to closed reflux method and AOX analysis by using an AOX analyzer Dextar AOX analyzer, Thermo Electron Corporation (Figure 2.5). The TOC was measured by a TOC analyser (Shimandzu TOC-V CNS analyzer), based on combustion-infrared method. The sample was also analyzed for inorganic contents like Cl^-, Ca^+, K^+, Na^+ and Fe^+ ions using ICP-OMS (Teledyne Leeman Labs Prodigy SPEC)

2.4.5. Electrochemical treatment

The percent removal efficiencies were determined by the equation 2.3

$$E\ (\%) = \frac{C_o - C_t}{C_o} \times 100 \qquad (2.3)$$

Where E is efficiency (%), C_t is Concentration of the pollutants at time t (mgL^{-1}) and Co is the Initial concentraion (mgL^{-1}) and the current density of the process was determined by following expression;

$$CD = \frac{Current\ applied(I)}{Area\ \ (A)} \qquad (2.4)$$

Where CD is current density applied (Am^{-2}), I is current applied in ampere and A is area of the electrode (m^{2}).

The relative standard deviation (RSD) of the removal effeciencies was calculated by using equation 2.5

$$RSD\ (\%) = \frac{S(x)}{x} \times 100 \qquad (2.5)$$

Where $S_{(x)}$ is the standard deviation and x is the arithmetic mean.

The Electrical energy consumption for EC treatment process was determined. The amount of energy consumption was calculated using equation 2.6 [9, 10].

$$\mathrm{EE}\ (\frac{\mathrm{kWh}}{m3}) = \frac{\mathrm{VIt}}{Treated\ volume\ (L)} \qquad (2.6)$$

Where; V= applied voltage (V), I= current (A), t= electrolysis time (h), v= volume of sample (L)

2.5. SLUDGE CHARACTERIZATION

2.5.1. Sludge settling characteristics

The settling characteristic of the EC generated sludge was determined by the most common parameter, sludge volume index (SVI). SVI is defined as the volume occupied by 1g of slurry after 30 minutes of settling. It can be calculated by;

$$SVI = \frac{H_{30}}{H_o S_o} \times 100 \tag{2.7}$$

Where H_{30} is the height of the sludge after 30 min of settling, H_o is the initial height of the slurry and S_o is the initial concentration of the solids in the slurry.

2.5.2. Physico-chemical characterization of sludge

The sludge obtained from the EC treatment of the wastewater was characterized for various physico-chemicals as well as environmental parameters in order to suggest a proper disposal of the same. The environmental parameters like pH, COD, BOD, BOD_5/COD ratio, total solid content and organic/inorganic ratio has been determined by the different methods and instruments used are outlined in section 2.4.4. Elemental content is done by CNHS analyzer (Thermo Scientific flash 2000). Fourier Transform Infrared (FTIR) spectrophotometer (Perkin Elmer 1720 X) was used to determine the functional groups in the sludge.

2.5.3. THERMAL ANALYSIS

The sludge sample was analyzed by thermal gravimetric analysis (TGA) to monitor the weight loss and nature of thermal reactions (exothermic/endothermic) occurring during the burning of the sludge. A Thermo gravimetric (TG) EXSTAR TG/DTA 6300 was used for this purpose. The TG, DTG and DTA traces were obtained from this instrument. The procedure and conditions used for thermo-analytical experiments are as follows; the sample was evaporated at 100 °C and 10-15 mg of the sample was transferred to the TGA cell. The temperature was raised to 1200 °C at the rate of 10 °C min^{-1}, using air as the carrier gas with air flow rate of 200 ml min^{-1}. The derivative thermal analysis (DTG) measurement conditions were; sensitivity: ±1000 mV, balance type: horizontal differential; thermocouple: Pt, Pt-Rh (13%), heating rate: 0.01- 100 K min^{-1}.

2.6. PULP BLEACHING EXPERIMENTS

2.6.1. Pulp washing

Both unbleached and bleached pulp was washed with the EC treated (recycled) water to study the recycling potential of the EC treated wastewater. The Buchner funnel was used for washing of the pulp and fixed volume of water (700 mL/100 g of pulp) was used in all the experiments.

The unbleached pulp (after blow tank), was washed separately with tap water and then recycled water on a Buchner funnel. Parallel bleaching experiments were performed on both the pulps (recycled water washed and tap water washed) using same bleaching conditions to compare the pulp brightness and paper properties of both pulps.

2.6.2. Bleach liquor analysis

A solution of bleach liquor (40 g/L $NaClO_2$ solution) was prepared in distilled water. The strength of $NaClO_2$ solution (as active chlorine aCl^-), was determined by titrating it with standard 0.1 N $Na_2S_2O_3$ solution using starch (0.5%) as an indicator. 10 mL of diluted bleach liquor was taken, 10 mL KI (10%) and 10 mL acetic acid (10%) were added and the resulting solution was titrated against standard 0.1 N $Na_2S_2O_3$ solution. The solution turned from blue to colorless indicating its end point. The strength of the bleach liquor was calculated using the following expression;

$$Strength\ of\ bleach\ liquor\ (g/L) = Normality\ of\ bleach\ liquor\ \times 35.5 \qquad (2.8)$$

2.6.3. Bleaching of pulp

The bleaching was performed on 100 g O.D. unbleached pulp. The target brightness of 84% ISO was achieved by bleaching sequence DEpD bleaching sequence. All the bleaching experiments were performed in a polyethylene bag. The experimental conditions used for bleaching are given in Table 2.3. The kappa number, the total chlorine demand (TCD) was calculated using the formula in Equation 2.9.

$$TCD\ (\%\ a\ Cl^{-}) = Kappa\ no.\times Kappa\ factor \tag{2.9}$$

70% of the total chlorine demand was given in the first D_1 stage and the remaining 30% in D_2 stage.

2.6.4. Residual chlorine analysis

100 mL of spent bleach liquor was titrated against standard 0.01 N $Na_2S_2O_3$ solutions using the same procedure that was followed for the analysis of bleach liquor [11].

2.6.5. Chlorine dioxide (D) stage

For chlorine dioxide bleaching stage, the disintegrated pulp was diluted with distilled water and the pH of the pulp is adjusted between pH 3 to 4, using 1M H_2SO_4 and NaOH solutions. The required quantity of bleach liquor ($NaClO_2$) was added into the polythene bag and mixed properly to maintain 10 % consistency. The bleaching was performed in a water bath at 70 °C for 3 h with intermitted mixing. After the completion of bleaching, the pulp was washed on a Buchner funnel with distilled water and recycled water as per the case. The washed filtrate was collected for characterization. The parameters like end pH, COD, BOD, color AOX and chlorophenols were determined.

Table 2.3: Bleaching conditions for different DEpD bleaching sequences

Parameter	**D_1EpD_2**			***RC_D_1EpD_2**		
	D_1	**Ep**	**D_2**	**D_1**	**Ep**	**D_2**
Kappa no.		16			16	
Kappa factor		0.28			0.29	
Total aCl^- (%)		4.48			4.64	
Bleach chemical (% aCl^-)**	3.14	----	1.34	3.25	----	1.39
Residual aCl^-	Nil	----	0.04	Nil	----	0.03
NaOH (%)	----	0.7	----	----	0.7	----
H_2O_2 (%)	----	0.3	----	----	0.3	----
Consistency (%)	10	10	10	10	10	10
End pH	3.4	11.5	3.3	3.4	11.5	3.3
Temperature (°C)	70	70	70	70	70	70
Time (min)	180	90	180	180	90	180
Brightness (% ISO)		84			84	

* RC_D_1EpD_2 is the bleach sequence washed with the treated water (recycled)

** Bleaching chemical dose expressed as percent (%) of OD pulp

2.6.6. Strength of hydrogen peroxide

The strength of H_2O_2 solution was estimated for the extraction stage. 10 mL H_2O_2 solution was diluted to 250 mL in a volumetric flask. 10 mL KI (10%), 10 mL H_2SO_4 (4N), and 1 mL ammonium molybdate (1%) were added to 5 mL of this solution and the resulting solution was titrated against standard 0.1 N $Na_2S_2O_3$ solution using starch (0.5%) as an indicator [12]. The end point was blue to colorless. Strength of H_2O_2 solution was calculated using the following formula:

$$Strength\ of\ H_2O_2\ (g/L) = Normality\ of\ H_2O_2 solution \times 34 \tag{2.10}$$

2.6.7. Peroxide reinforced alkaline Extraction (Ep) stage

The peroxide reinforced alkaline extraction was done with 0.3% H_2O_2 on O.D. pulp basis. The H_2O_2 is added to the pulp suspension along with the alkali (NaOH) and mixed with the pulp to give 10% consistency in a polyethylene bag. The extraction was done in a water bath at 70 °C temperature for 90 min with intermitted mixing. After the extraction, the pulp was washed and effluent was collected for characterization. The parameters like end pH, COD, BOD, color AOX and chlorophenols were determined.

2.6. PULP CHARACTERIZATION

2.6.1. Brightness measurement

The brightness of the bleached pulp was measured on a TECHNIBRITE ERIC 950 from Technibrite Corporation, USA. The various test methods used for preparation and characterization of the pulp and paper hand sheets are listed in Table 2.4. The photographic view of pulp tear tester, tensile tester, and burst tester is shown in Figure 2.7 (a-c).

2.6.2. Viscosity measurement

The viscosity of the bleached and unbleached pulp was measured using a capillary viscometer with 1M cupriethylenediamine (CED) solution following TAPPI test method (T 230 om-99) (Table 2.4). The viscometer constant was determined using glycerol solution of known specific gravity and viscosity. The constant thus obtained was used for further viscosity calculations. The 0.25 g O.D pulp sample was taken into a 50 mL dissolving bottle containing 2-3 copper beads. 25 mL of distilled water was added to the bottle, capped, gently shaken for dispersing the pulp and left for 2 min. Then 25 mL of CED solution was also added to the pulp suspension and air purged by passing nitrogen stream for 1 min. The bottle was capped and shaken until the fibers are completely dissolved (about 15 min). After shaking, bottle was kept for 2 min to allow the solution to degas. The viscometer was placed in a constant temperature bath at 25±0.1 °C for attaining constant temperature. The measuring leg of the viscometer was filled by suction up to the upper mark. Then the solution was allowed to drain down. The efflux time was determined by measuring the time required for the meniscus to pass between the two marks. The efflux time measurement was repeated and the pulp viscosity was calculated by using the following formula;

$$V = C \times t \times d \tag{2.11}$$

Where V is viscosity of CED solution at 25 °C (cP), C is the viscometer constant found by calibration, t is the average efflux time (seconds) and d is the density of the pulp solution ($g/cm^3 = 1.052$)

2.6.3. Sheet preparation

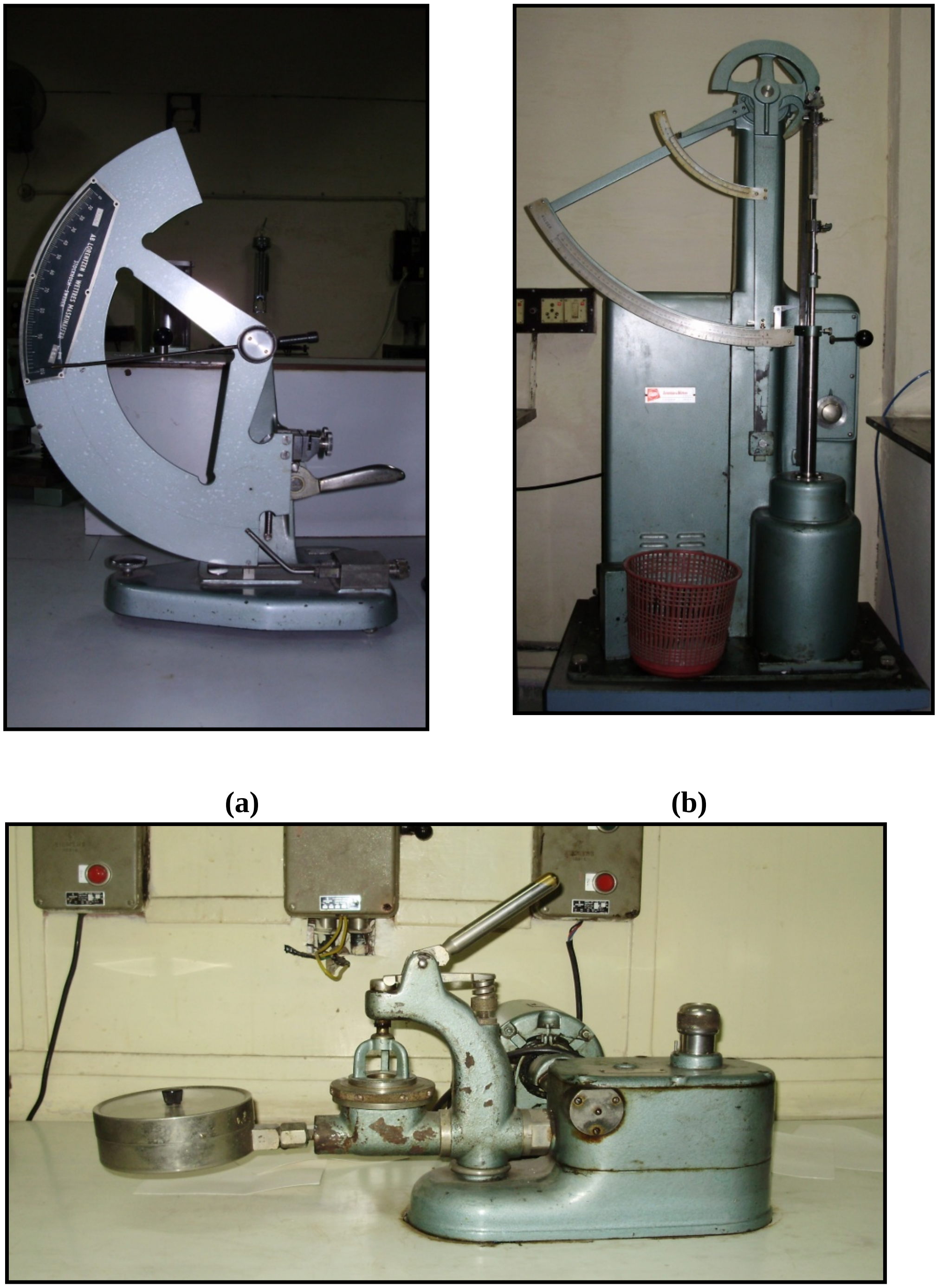
The disintegrated pulp samples were taken and 1 % consistency was maintained. This suspension is then transferred to a Buchner funnel to drain the water through the 22 mesh size plastic mesh, to make a 5 g O.D. sheet. The wet pulp sheet was picked with the help of blotting paper and pressed using a hydraulic press. The sheet was then air dried for 24 h and used for brightness measurement. The same sheet was cut into small pieces to measure the viscosity of the pulp.

2.6.4. Effluent characterization

The wash filtrate after washing of the bleached pulp was collected and stored at 4°C for characterization. The bleaching effluent from different stages and treated effluent after recycling was characterized for various environmental parameters like end pH, COD, BOD, color AOX and chlorophenols were determined.

Table 2.4: Test methods for preparation and characterization of pulp and paper sheets

Test No.	Description
SCAN C 18 : 65	Disintegration of chemical pulp for testing
T 248 sp - oo	Laboratory beating of pulp (PFI mill method)
T 205 sp - 95	Forming hand sheets for physical tests of pulp
T 218 sp - 97	Forming hand sheets for reflectance testing of pulp (buchner funnel procedure)
T 227 om - 99	Freeness of pulp (canadian standard method)
T 410 om - 98	Grammage of paper and paperboard (weight per unit area)
T 230 om - 99	Viscosity of pulp (capillary viscometer method)
T 236 om - 99	Kappa number of pulp
T 403 om - 97	Bursting strength of paper
T 404 cm - 92	Tensile breaking length and elongation of paper and paperboard (using pendulum type tester)
T 414 om - 98	Internal tearing resistance of paper (elmendorf-type method)
ISO Standard 2469	Brightness of pulp
T 610 sp - 97	Preparation of indicators and standard solutions



(a) (b)

(c)

Figure 2.7: Photographic views of (a) Tear tester, (b) Tensile tester, and (c) Burst tester

2.7. REFERENCES

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Chapter 3

EFFLUENT TREATMENT STUDIES

3.1. INTRODUCTION

The pulp and paper industry is one of the most important industries in India, but the environmental problems associated with it are numerous and extensively documented by various researchers [1-3]. There are several sources of water pollution existing in the industry while bleaching section is the most significant source. The use of chlorine and chlorine based chemicals for pulp bleaching generates variety of chlorinated phenolic compounds originating from the chlorination of residual lignin, in the bleach plant effluent. High Chemical Oxygen Demand (COD), presence of organic halides, lignin and its derivatives, etc. in effluents are the main components which are responsible for the degrading quality of receiving streams [4].

Pulp and paper industries generally employ two stages of treatment for the generated wastewater; primary (physico-chemical treatment) and secondary (biological treatment). These conventional processes involve physical and biological techniques with modest COD reduction, marginal color reduction and incomplete degradation of the recalcitrant organic matter (chlorophenolic compounds) [5]. Hence, paper mills are looking up adopting some alternative treatment processes. In this context, the electrochemical treatment can be one possible method to overcome these disadvantages. The electrochemical technology and its application in water and wastewater treatment have received worldwide attention in the past recent years, due to its advantages that include high removal efficiency, compact treatment facility, low land area requirement and complete mineralisation of a wide range of pollutants [6-8]. This technique is an efficient method for the oxidation of the pollutants, where the oxidants are generated in situ by electro oxidation at the anode which depends on the type of electrode material. The electrochemical process has already been successfully used to treat the waste containing heavy metal for metal recovery [9-11], dye containing wastewater from textile industry [12-14], waste water from restaurant [15] and oil containing waste [16] with good removal efficiencies.

3.2. PRINCIPLE OF ELECTROCHEMICAL REMEDIATION

During the electrochemical process, pollutant degradation/removal takes place by two mechanisms, namely; electro-oxidation and electro-coagulation. The electro-oxidation reactions mainly occur at the anode, which contributes to the conversion and/or the oxidation of the organic pollutants. Generally, the pollutants are degraded through the two pathways; direct or indirect oxidation mechanism. The direct oxidation occurs at the surface of the anode through the generation of physically adsorbed ‘‘active oxygen’’ (adsorbed hydroxyl radicals, $^{\bullet}OH$). This mechanism is proposed by [17]. It is an efficient method for the degradation of pollutants, it does not require any additional chemicals and with no tendency to produce secondary pollution. In the case of indirect oxidation the intermediates (e.g., hydroxyl radicals, ozone, hydrogen peroxide, and hypochlorite are generated anodically to destroy the pollutants [18-19]. In addition, the process of electro coagulation also occurs during the electrochemical treatment. The electro coagulation involves the generation of coagulants in situ by dissolving the metal electrodes electrically. The materials used for the electrodes can be aluminum or iron. The electro coagulation mechanism involves the following reactions [20];

For aluminum anode: $Al - 3\ e^- \longrightarrow Al^{3+}$ (3.1)

Under alkaline conditions: $Al^{3+} + 3OH^- \longrightarrow Al\ (OH)_3$ (3.2)

Under acidic conditions: $Al^{3+} + 3\ H_2O \longrightarrow Al\ (OH)_3 + 3H^+$ (3.3)

For iron anode: $Fe - 2e^- \longrightarrow Fe^{2+}$ (3.4)

Under alkaline conditions: $Fe^{2+} + 2\ OH^- \longrightarrow Fe\ (OH)_2$ (3.5)

Under acidic conditions: $4\ Fe^{2+} + O_2 + 2\ H_2O \longrightarrow 4\ Fe^{3+} + 4OH^-$ (3.6)

In addition, there is oxygen evolution reaction:

$$2\ H_2O - 4\ e^- \longrightarrow O_2 + 4\ H^+ \qquad (3.7)$$

The reaction at the cathode is:

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^- \qquad (3.8)$$

The Al^{3+} or Fe^{3+} ions generated in the reaction are very efficient coagulants for particulates flocculating. The hydrolyzed aluminum ions can form large networks of Al–O–Al–OH that can chemically adsorb pollutants [21]. The ferric ions generated by electrochemical oxidation of iron electrode may form monomer ions and polymeric hydroxyl complexes, depending on the pH of the aqueous medium [22-23]. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials.

This chapter investigates the optimization of operational parameters and electrochemical degradation of pulp and paper mill effluent using stainless steel electrodes. Additionally sludge characterization studies have also been performed.

3.3. RESULTS AND DISCUSSION

3.3.1. 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 wastewater samples, of both primary and secondary clarifier, were characterized for various environmental parameters namely COD, BOD_5, color, TOC, solids etc., as per standard methods [24]. The COD and color of the effluent is used to optimize the operational parameters of EC treatment process.

3.3.1.1. Secondary Clarifier (SC) effluent optimization

(a) Effect of pH

To examine the effect of pH on electrochemical treatment (EC) process experiments were performed at varied pH (5.0-8.0) keeping the CD fixed at 15 A/m^2 and time duration of 2 h. The EC process with stainless steel shows better removal efficiency for both COD and color, especially near the neutral pH. The COD removal efficiency increased from pH 5.0 to 5.5, became nearly constant between pH 5.5 to 7.0 and decreased substantially with increase in pH up to 8.5 (Figure 3.1). This can be explained that the fact that the solubility of $Fe(OH)_3$ increases beyond pH 7 and results in the formation of solid $Fe(OH)^-$ which does not contribute to the COD reduction [12].

The color reduction efficiency decreased by small amount (87-84%) with increase in the pH value from 5.0 to 6.5 and increased from pH 7.5 to 8.5. The removal efficiency was highest at pH 7.0. For reduction in color levels, the initial *pH* of wastewater (pH 6.0-7.5) in the investigated range did not significantly affect the removal efficiency, the influence is pretty low (SD of ±2%) as shown in Figure 3.1**.** The removal efficiency goes down at acidic pH (<6) and alkaline pH (>8), which can be explained on the basis of above explanation given in case of COD. So, in this case keeping in mind the neutral pH (pH 7.0) of the wastewater of the pulp and paper mill, pH 7.0 is taken as an optimal value.

During the pH optimization experiments an observation was noticed that, when the effluent feed was acidic to neutral (pH 5-7.5), the pH of wastewater goes up after EC treatment. However it drops if the influent pH was in basic range (pH ≥ 8) as given in the Table 3.1. The increase in the pH value for the acidic or neutral influent is because of the production of hydroxyl ions at cathode (Eq. 3.8); this behavior is also stated by Boroski et al., 2008 [25]. However, the decrease of the pH value for alkaline effluent can be attributed to the formation of H^+ near anode (Eq. 3.3) [26]. It can be inferred that the electrochemical process acts as a buffer and leads to the neutralization of the effluent. This behavior of the process has the advantage that the effluent is appropriate for the direct disposal after the treatment. This characteristic of the EC process is very important for its application in the treatment of wastewater.

Table 3.1: pH change during electrochemical treatment

Initial pH	Final pH
5.0	7.0
5.5	7.2
6.0	7.4
6.5	7.6
7.0	7.9
7.5	8.2
8.0	7.7
8.5	7.5

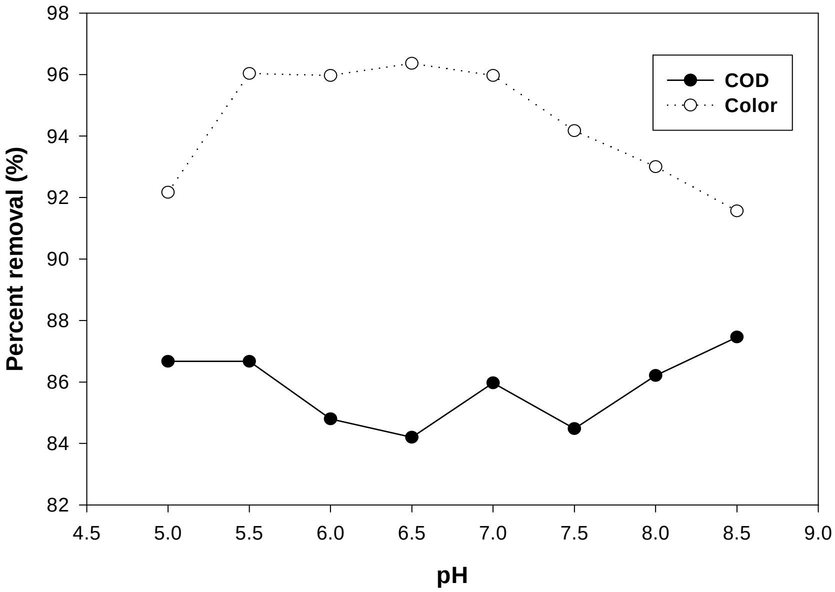

Figure 3.1: Removal of COD and color by EC treatment as a function of pH (CD- 15 A/m^2, t-2 h)

(b) Effect of current density

Current density (CD) at the anode in any electrochemical reactor is considered to be one of the important parameters as it strongly controls the rate of the reaction. Further, it determines the total efficiency and cost of the process. The changes in COD and color were measured as a function of current density (5-25 A/m^2). The experiments were performed at a *pH* of 7.5 and treatment time of 2 h. The results are shown in the Figure 3.2. The graph shows that, the percent removal of COD and color increases with increase in CD values upto 15 A/m^2 and then decreases upto 20 A/m^2. With the further increase in the CD value upto 25 A/m^2, COD reduction increases as color reduction reached a constant value. At a current density value of 15 A/m^2 an 80 % reduction in COD and 85 % reduction in color was observed. Therefore, the CD value of 15 A/m^2 was taken as the optimum condition for the treatment of pulp and paper mill wastewater, because any increase in applied current will lead to the higher energy consumption. Chen et al., 2000 have also observed increase in the removal efficiency with increase in current density [15]. It is ascribed to the fact that, at high current values the amount of iron oxidized is increased, resulting in a greater amount of precipitate formed and increased removal of pollutants. In addition, it was established by other workers that bubble density of gases increases and their bubble size decreases with increase in the current density, resulting in a greater upward flux and a faster removal of the pollutants and sludge formation [27].

On further increasing the CD to 20 A/m^2, there is no substantial change in the percent reduction. This could be attributed to the adsorption of the lignin on the electrode surface that leads to the electrode passivation which decreases its activity [28].

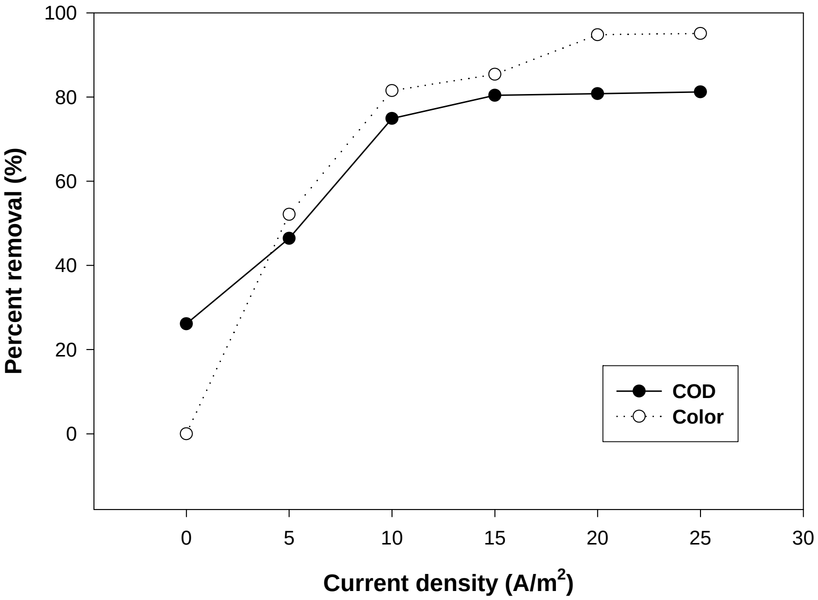

Figure 3.2: Removal of COD and color by EC treatment as a function of applied current density (pH-7.5, t-2h)

(c) Effect of treatment time

By keeping the *pH* and CD fixed at 7.5 and 15 A/m^2, respectively, the efficiencies of COD and color removal for the present effluent sample were tested at different treatment time (0.5 to 4.0 h). During the treatment process, it was observed that, the beginning of the run, the solution was transparent and which gradually becomes darker and more opaque as the reaction progresses. This increase in the color was due to the generation of Fe (II) and Fe (III) species which have forest green to yellow-brown in color. After about 0.5 h a significant reduction in color was observed (73%) and the value reached to 94% after 2 h of treatment (Figure 3.3). The color of Fe ion disappears gradually with the passage of time because the generated Fe ions mostly combined with the pollutant species and form settleable sludge [29].

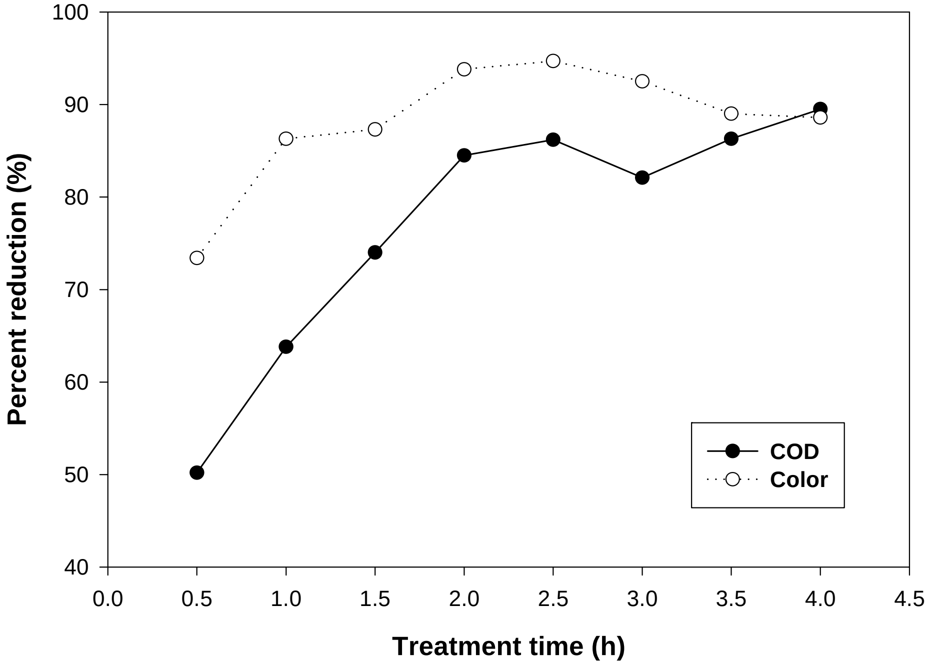

Figure 3.3: Removal of COD & color by EC as a function of treatment time (CD-15A/m^2, *pH*-7.5

A similar trend was observed in the case of COD removal. An increase in the EC time leads to the increase in the COD removal efficiency. A COD removal of 85 % was observed in about 2h, after that, the changes in COD become gradual, with the plot becoming constant after this point. Thereafter, the COD removal efficiency drops to 82 %, presumably due to the fact that a higher amounts of Fe (II) ions (contributes to the total COD component) are generated at longer electrolysis time which can react with the dissolved oxygen in the wastewater (Equation 3.9), leading to the lower oxygen in the treated wastewater. Therefore, 2 h is taken as the optimum time for the degradation of the organic matter in the present effluent sample. The above mentioned iron (II) production can be attributed to this reaction [28].

$$4\,Fe + O_2 + 10\,H_2O \rightarrow 4\,Fe(OH)_3 + 8H^+ \qquad (3.9)$$

(d) Initial organic load

The composition and pollutant load of the wastewater may vary widely under the industrial conditions. Therefore, the effect of initial organic load of the feed was investigated on the efficiency of the electrocoagulation method. Generally COD removal efficiency is dependent on the initial load of the wastewater and decreases with increasing initial organic load.

A comparison of relative COD and color removal from wastewater were carried out under the optimal treatment conditions discussed in section 3 (pH-7.0, applied CD-15 A/m^2, t-2h). It indicates that the removal efficiencies were decreased along with increase in the initial COD concentrations (from 157.3 mgL^{-1} to 1250.7 mgL^{-1}) (Figure 3.4). The maximum COD removal (87%) efficiency was observed for initial COD of 157.3 mgL^{-1}. At COD value of 222.5 mgL^{-1}, the ultimate COD concentration in treated effluents accounted for approximately 85.8% reduction of initial COD and above 500 mgL^{-1} COD, the removal is decreased substantially. At the highest initial COD concentration of 1250.7 mgL^{-1}, under the same experimental conditions, COD removal efficiency was the lowest (60.5 %). The same relationship was observed for the color, the lower the initial COD value of electro-coagulated effluents, the faster the rate of pollutant removal (COD and color). This behavior may be due to the fact that, Iron hydroxide produced during wastewater treatment by electro coagulation has good sorption properties and it destabilizes the negatively charged colloids responsible for turbidity and color, which are then adsorbed on its surface [30].

At lower initial COD levels, i.e., lower total pollutant load, the ratio between the number of pollutant molecules and the surface area of the adsorbent was lower, which increased the adsorption potential and improved treatment efficiency. Such behavior was also observed by Smoczyński and Załęska-Chróst (2002) [31].

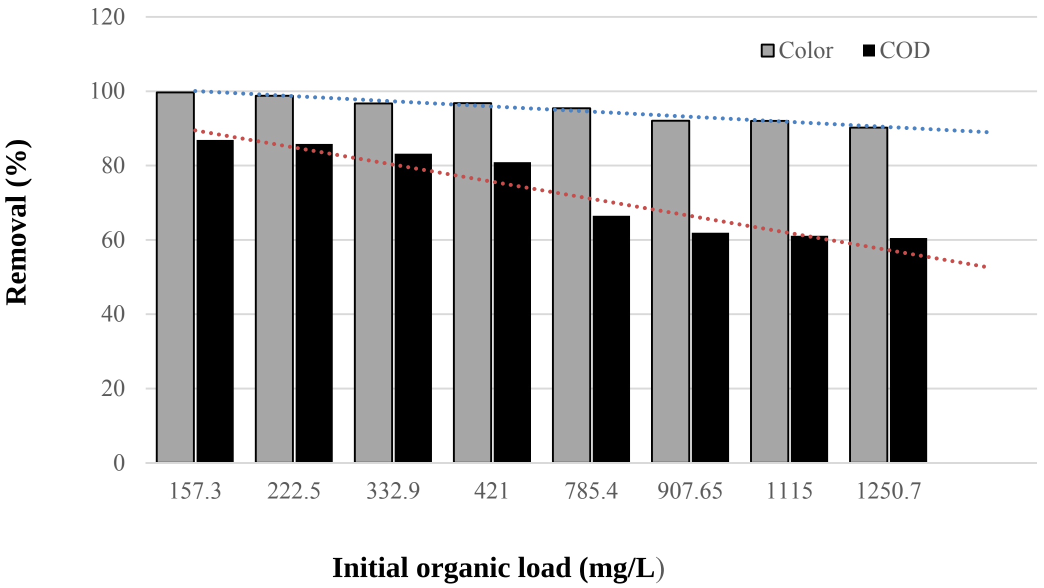

Figure 3.4: COD and color removal from wastewater for various initial organic loads under optimized conditions (CD-15A/m^2, *pH* 7.0, t-2h**)**

3.3.1.2. Primary clarifier (PC) effluent optimization

The initial organic load study clearly indicated that the efficiency of the electrochemical treatment method decreases with increasing organic load under the same operational conditions. Therefore the operational condition for primary clarified wastewater was also optimized for the pH, current density and treatment time.

(a) Effect of pH

The pH range of 5.0 to 8.5 was tested for PC effluent optimization, keeping the CD fixed at 15 A/m^2 and time duration of 2 h. The COD and removal efficiency increased from pH 5.0 to 5.5, became nearly constant between pH 5.5 to 7.0 and decreased substantially with increase in pH up to 8.5. The best removal efficiency of COD (65.0 %) and color (91.8 %) in the case of PC effluent was found at pH of 7.0 (Figure 3.5). So, pH 7.0 was taken as optimum in case of PC effluent. Figure 3.5 show the results for pH optimization.

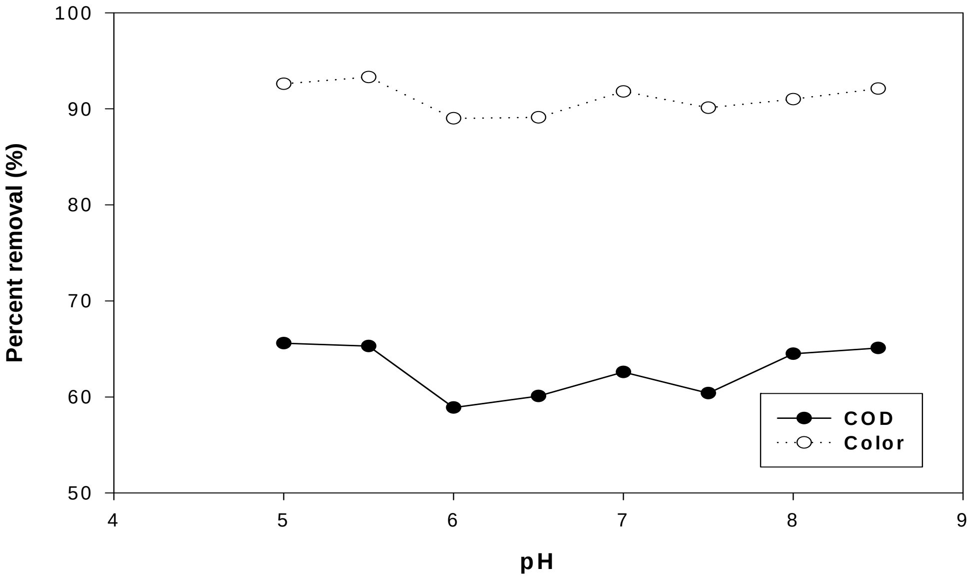

Figure 3.5: Removal of COD and color from PC effluent by EC treatment as a function of pH (CD- 15 A/m^2, t- 2 h)

(b) Effect of current density

The changes in COD and color were measured as a function of current density. The experiments were performed at a *pH* of 7.5 and treatment time of 2 h. The results are shown in the Figure 3.6. The graph shows that, the percent removal of COD and color increases with increase in CD values upto 15 A/m^2 and then decreases with the further increase in the CD value upto 25 A/m^2. At a current density value of 15 A/m^2, 60.9 % reduction in COD and 92.6 % reduction in color were observed. Therefore, the CD value of 15 A/m^2 was taken as the optimum condition for the treatment of PC effluent, because any increase in applied current will lead to the higher energy consumption [15].

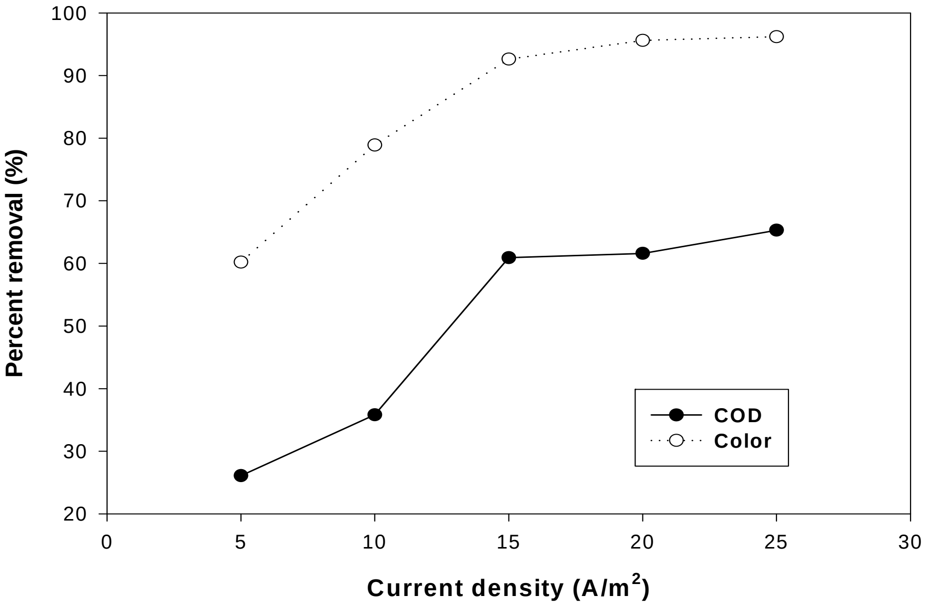

Figure 3.6: Removal of COD and color from PC effluent by EC treatment as a function of applied current density (*pH*-7.5, t-2h)

(c) Effect of treatment time

The treatment time studies were performed in the time range of 0.5 h to 5 h in case of PC effluent, the time is an important parameter for this study. The removal efficiencies for COD and color in 2 h was found appropriate for treatment because after increasing the time beyond 2h, there is no significant increase in the efficiency and further removal becomes slower, with the plot becoming constant after 3h. This may be due to the electrode passivation after this time. Although the removal efficiencies increases with increasing treatment time for higher organic load, but keeping in mind the energy consumption and cost, the 2 h is taken as optimum treatment time. This is found sufficient for the 65.2 % COD removal and 92.0 % color removal, which is significant for primary effluent treatment (Figure 3.7).

The behavior of PC effluent was also found similar to the SC effluent, except the removal efficiencies decreases with increased organic load at same conditions. So, the optimum conditions selected for PC effluent treatment are; pH 7.0, CD of 15 A/m^2 and treatment time of 2h.

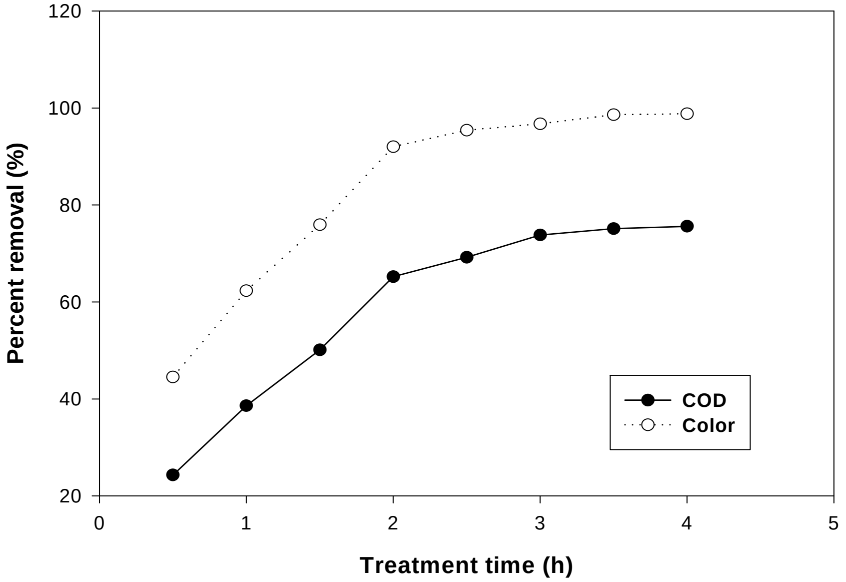

Figure 3.7: Removal of COD and color from PC effluent by EC treatment as a function of treatment time (*pH*-7.5, CD-15 A/m^2)

3.4. EFFLUENT TREATMENT

3.4.1. Effluent Characterization

The grab samples of primary and SC effluent were collected from an integrated pulp and paper mill and the average analytical values of different parameters are summarized in Table 3.2. The results are based on average values of three samples. The PC effluent was having around four times higher pollutant load as compared to the secondary discharge. As can be seen from the Tables 3.2 that recalcitrant organic pollutants (AOX and chlorophenolics) reduction is not very significant, which indicates low biodegradability of the organics present. On the other hand the BOD$_5$ reduction is quite significant i.e., about 93%, indicating a good efficiency of activated sludge process for biological waste, leading to the low BOD$_5$/COD ratio of 0.07 for secondary effluent as compared to 0.22 for primary effluent. The industrial effluent varies in characteristics, it is because in the industrial pulp production there are several parameters which are hard to control in the pipeline these are; (1) raw material type. Its quality, size, condition and age, (2) reactant (quality and quantity), (3) process parameters (time duration, temperature, pressure and others); and all the other conditions which are involved in large scale industrial production [32].

Table 3.2: Analytical characteristics of PC and SC pulp and paper mill wastewater

Parameters (Unit)	**Value ±SD**	
	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^{-1})ions (mgL^{-1})	400±20	320±26
Sulphate ions SO_4^{2-} (mgL^{-1})	316±10	210±20

3.4.2. Effluent treatment

3.4.2.1. COD removal

COD is the chemical oxygen demand of the organic and inorganic material dissolved in the effluent. The degradation of the dissolved organic matter present in the effluent sample was determined in terms of percent COD removal. 2 h of EC treatment leads to 65.1% COD reduction in PC effluent and 83.8% reduction in SC effluent (Table 3.3). EC treatment has a higher efficiency for SC effluent than the PC effluent (Figure 3.8). The reduction in COD values of PC effluent was studied with varying time and it was found that there is a good COD reduction (65%) in 2h of treatment after that the removal becomes somewhat constant. This is because of the fact that, the 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. This behavior agrees with results obtained by Trapido et al., 1997 reported that an increase in the number of chlorine atoms in the aromatic ring provides an increase in the degradation rate. Since the presence of chlorine facilitates the dechlorination step, and degradation is faster [33].

Table 3.3: Removal efficiencies by of 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

3.4.2.2. BOD_5 removal

EC process leads to 58.5% reduction in BOD_5 in PC effluent (Table 3.3). EC process gives BOD_5 reduction of 58.5% in PC effluent and 35% in SC effluent. This behavior is quite different from the behavior observed with other parameters like COD and color. This is because of the fact that SC effluent contains much higher proportions of recalcitrant compounds which are difficult to oxidize. Similarly, the BOD_5 reduction with time has also been studied in order to see the biodegradability of the PC effluent (Figure 3.8). It is seen that the percent BOD_5 reduction is not very significant (12%) till 1.5 h of treatment but increases with treatment time to 35% and then becomes constant. This is because of the conversion of non-biodegradable fraction (higher molecular weight compounds) into the biodegradable fraction (lower compounds), which leads to the increase in BOD_5 values [34].

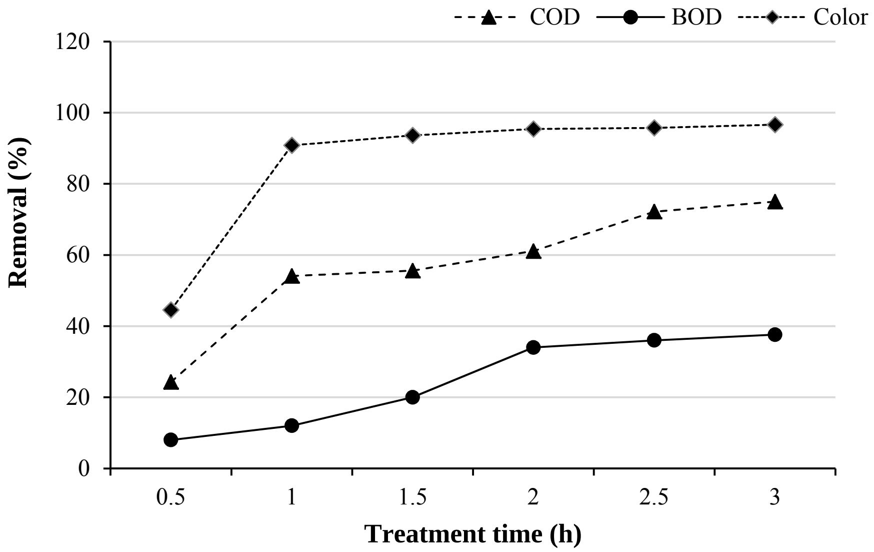

Figure 3.8: Reduction in COD, color and BOD_5 with treatment time in PC effluent

3.4.2.3. Color removal

The dark brown color of the pulp and paper mill effluent is due to the presence of lignin and its derivatives that are released from the substrate during bleaching process [35]. The electrochemical treatment method was found to be highly efficient for the color removal in pulp and paper mill effluent. The color reduction was 92.6% and 96.8% in primary and SC effluent respectively (Table 3.3). The effect of treatment time on the color reduction in PC effluent is shown in Figure 3.8. There is a significant proportion of color (75.3%) was removed in 1 h of treatment. It is because, the lignin is the major color causing agent in the paper mill effluent and its degradation starts at early stages of the treatment process [23, 36]. Therefore EC treatment may be better option for pulp and paper industry as it is facing a color removal problem.

During the process of treatment an interesting observation was found that, there was a fast increase in the color during the initial period (15-30 min) of electrolysis. At the beginning of the run, the solution was transparent and gradually becomes darker and more opaque as the reaction progresses. This color appearance is due to the Fe (II) and Fe (III) species generated at the beginning with fast rate, having forest green to yellow-brown in color [29]. The color of Fe ion disappears gradually with the passage of time because the generated Fe ions mostly combined with the pollutant species and form settleable sludge.

3.4.2.4. TOC removal

Total Organic Carbon (TOC) is the gross amount of carbon bound in the organic compounds in the wastewater. Suspended particulate, colloidal particles, BOD_5 and COD are all part of the TOC, and it has in some cases been possible to relate TOC to BOD_5 and COD values to measure pollution characteristics [37]. A noticeable removal of TOC was observed for both primary and secondary effluents, probably due to the degradation of the biodegradable components (Table 3.3). 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 Figure 3.9. In the initial 1h the TOC removal was not so significant (only 10-12 %), but increased substantially in 2h of treatment and reached 44.5%. It is due to the residual TOC in the sample after the EC treatment, suggests the formation and accumulation of organic intermediate products during the treatment process. The present behavior is similar to the phenol electrolysis [17, 38-40] where the aliphatic acid are believed to be the main intermediate products formed during the EC degradation of chlorophenols.

3.4.2.5. Adsorbable Organic Halides (AOX) removal

Effluent discharged from bleach plants, where chlorine-based chemicals are used; contain organically bound chlorine compounds such as dioxins and furans, measured as AOX [41]. It was found that adsorbable organic halides (AOX) can be efficiently degraded using electrochemical oxidation and can be reduced more than 60% from PC effluent and 75.9% from SC effluent (Table 3.3). The degradation of AOX with time in primary wastewater indicates that AOX removal takes place at a faster rate up to 1 h; it indicates that AOX reduction takes place mostly in first hour of treatment (Figure 3.9). This may be due to the fast adsorption or degradation of higher molecular weight compounds into smaller ones and a slow destruction of these low molecular compounds further [42].

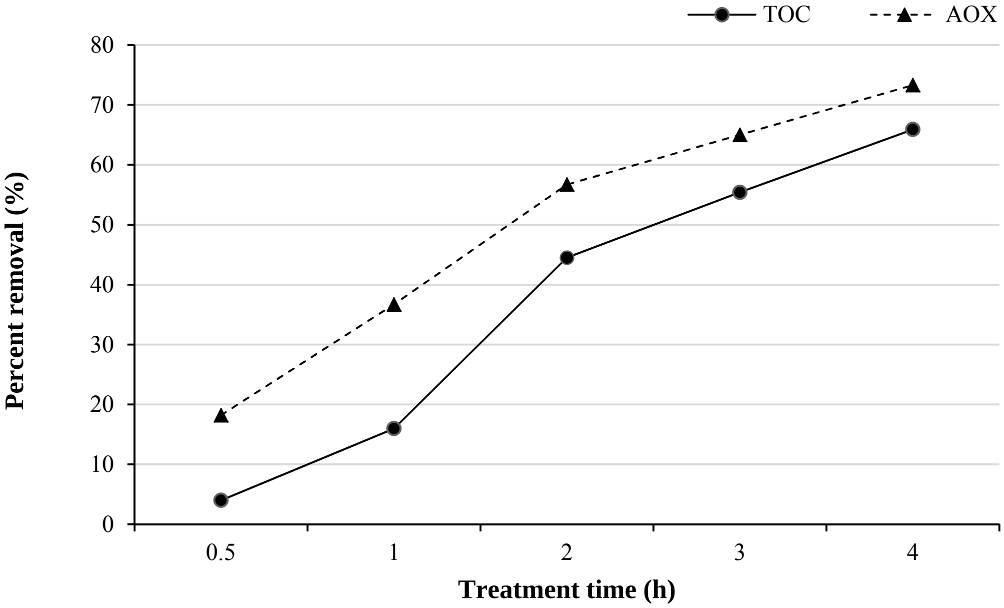

Figure 3.9: Reduction in AOX and TOC with treatment time in PC effluent

3.4.2.6. Solids removal

Total solids are total dissolved solids (TDS) plus total suspended (TDS) and settleable solids (SS) in water [43]. Total dissolved solid (TDS) is a measure of the combined content of all organic and inorganic substances contained in wastewater. Total Suspended Solid (TSS), is a parameter that describes the amount of emitted suspended solids (fibers, inorganic fillers, pigments etc.) within the wastewater. As long as concentration of TSS is kept low, there is no specific environmental problem connected to the emissions. It is however important to separate as much TSS as possible since it affects the biological treatment negatively and the solids can cause clogging problems in pipes and pumps [44]. The removal of both TDS and TSS was studied with time for PC effluent (Figure 3.10). 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 3.3). For secondary effluent the reduction is 11.4 % and 42.6 % in TDS and TSS respectively. Such behavior was also observed by Smoczyński, et al., 2002 [31]. 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 consist of calcium, chlorides, nitrate, phosphorus, iron, sulfur, and other ions particles and their removal is slower as compared to organic matter [43].

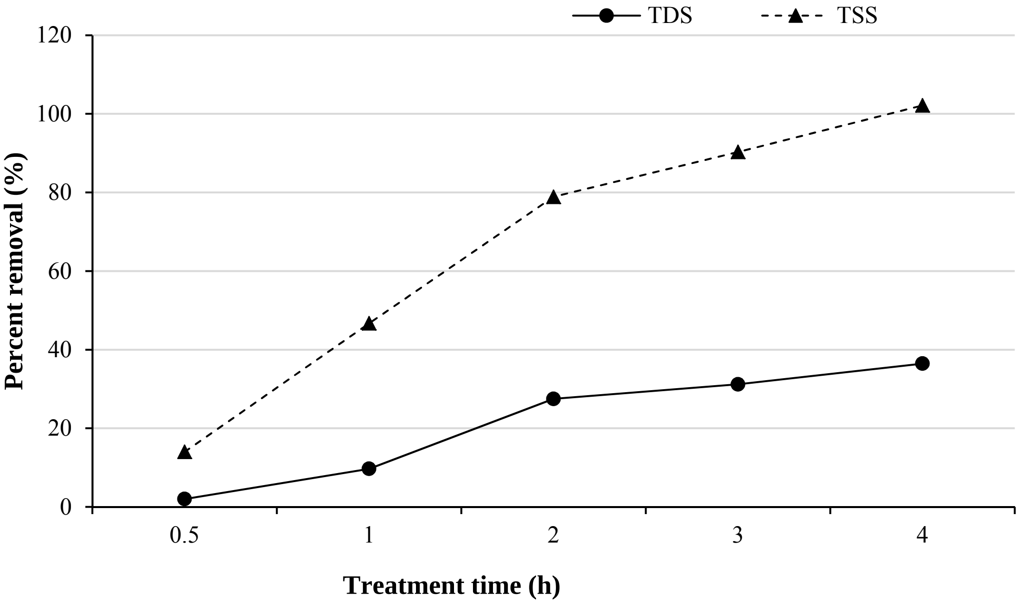

Figure 3.10: Reduction in solids (TDS and TSS) with treatment time

3.4.2.7. Biodegradability Index (BOD$_5$/COD ratio)

The BOD$_5$/COD ratio is a parameter of great importance for quantification of biodegradability of a contaminated effluent. A high ratio (>0.5) indicates good biodegradability as reported by Jamil et al., 2011 [41]. A ratio less than 0.3 is considered low, and corresponds to low biodegradability of the organic material present in the wastewater and indicates that the wastewater is not easily biodegradable [34]. The variation of BOD$_5$/COD ratio in PC effluent with varying treatment time is presented in Table 3.4**.** The biodegradability index increase with EC treatment time and reaches a value of 0.50 after 120 min (2h) of treatment which means that this effluent is now easily biodegradable; the similar results were also observed by Esplugas et al., in 2004 [45]. It is observed that, there is a fast increase in the BOD$_5$/COD ratio till 90 min (1.5h) of treatment and after that there is a slow increase in the ratio (Table 3.4). It may be due to the generation of strong oxidizing agents in the initial hours of the EC process mechanism of the process is given in Eq. 3.5 & 3.6, which leads to the oxidation of the organic matter present in the wastewater. In this process, the long chain organic matter such as lignin may get converted into lower molecular weight components. This step will not considerably reduce the COD component but increases BOD$_5$, resulting in an increase in BI of the sample [34].

Morais and Zamora in 2005, reported that samples with biodegradability index smaller than 0.3 are not appropriate for biological degradation [46]. According to Chamarro et al. 2001, for complete biodegradation, the effluent must present a biodegradability index of at least 0.40 [47]. Therefore using the EC treatment as a pre-treatment option, only 90 min can give a maximum enhancement of biodegradability (biodegradability index is improved from 0.22 to 0.45). These results are similar to earlier findings [32]. According to Kamali and Khodaparast 2014, Electrocoagulation and adsorption treatments can be efficiently employed to remove high molecular weight dissolved organic matters and they are considered a suitable option to be conducted prior to biological treatment (e.g., aerated lagoons) to reduce the color formation during such biological processes [49]. Thus, this technique could be used as a pre-treatment step for conventional biological wastewater treatment. Considerable reduction in the requirement of reactor volume or residence time of the existing aerated biological treatment system can be expected by giving such a small electrochemical pre-treatment.

Table 3.4: Biodegradability Index of PC effluent with treatment time

Treatment Time (min)	Biodegradability Index (BI)
0	0.22
30	0.27
60	0.40
90	0.45
120	0.50
150	0.52
180	0.60
210	0.62
240	0.68

3.4.3. Electrical energy consumption

Although EC processes have been shown to be efficient for the oxidation of recalcitrant pollutants, but it may require a substantial amount of electricity consumption for running the process [48]. Keeping in mind the above reason the electricity consumption for the EC treatment for pulp and paper mill wastewater has been determined. The amount of energy consumption was calculated using Equation 2.6 (Section 2.4.5) [50, 51]. The electrical energy (EE) consumed to treat 1 m^3 (KWh/m^3) of wastewater was calculated. The process has been used for the treatment of PC effluent and the corresponding COD removal (%) has been studied. The initial and final concentrations of COD (1115 mgL^{-1}) of the wastewater under optimized conditions of treatment (pH- 7.0, CD-15 A/m^2, Time- 2h), were considered for calculation. The energy consumption was found to be 0.9 KWh/m^3 for pulp and paper mill wastewater treatment. The electrical energy required to run the process has been considered for economic evaluation, the cost of the setup is low and it is not included in the operating cost. On comparing the cost with other AOP's and EC process by other workers, it is found that the electrical consumption is on the lower side under our optimized conditions with stainless steel electrodes (Table 3.5**).** Although, the cost of EC treatment under present conditions is lower than the other advance oxidation processes (AOP's) and even with the other workers, still it need to be optimized further and research is needed for large scale industrial application.

Table 3.5: Comparison of electrical energy consumption for EC process in various studies

Treatment process	**Electrode**	**Wastewater type**	**Treatment conditions**	**Electricity consumed (KWh/m^3)**	**Reference**
Electrocoagulation	Iron plates	Pulp and paper mill effluent	pH-7.58, CD- 20.7 A/m^2, Time- 30 min	1.2	[28]
Electrocoagulation	Aluminum	Pulp & paper mill bleach effluent	pH-7, CD- 15 mA/cm^2	10.1-12.9	[52]
Electrochemical	Iron and Stainless steel	Index reactive orange 84 and Textile wastewater	pH-7, CD-110 A/m^2 (SS) and 130 A/m^2 (Fe), Time- 40 min	SS-2.02 Fe-2.80	[53]
Electrochemical	Stainless steel (316 L)	Pulp and paper mill effluent	pH-7, CD-15 A/m^2, Time 2h	0.9	Present work

3.4.4. Sludge Characterization and disposal

Sludge characterization involves description of sludge behavior in treatment processes and disposal. Appropriate characterization methods facilitate understanding and prediction of sludge properties. Table 3.6 shows the physico-chemical characteristics of the sludge generated by the electrocoagulation treatment of pulp and paper mill wastewater. The amount of sludge produced was also less as indicated in the Table 3.6, 1.05 g/L of sludge was produced on the dry weight basis. The earlier studies also indicated stainless steel consumes less material and produced less amount of sludge as compared to iron electrodes [53]. The organic inorganics in the sludge was 40:60 ratios, indicating a higher amount of inorganics present in the sludge. The inorganic component mainly contains iron as also indicated by the EDX results of sludge (Table 3.7), which is 16.35 by weight percent.

Table 3.6: Physico-chemical characteristics of the sludge generated by EC treatment

Parameters	**Value**
pH	6.91±0.06
Color	Greenish dark brown
Moisture content (%)	10-11±2
Sludge formation (gL^{-1})	1.05
COD (mgL^{-1})	6080±92
BOD_5 (mgL^{-1})	1600±20
BOD_5/COD ratio	0.26±0.05
SVI ($mL\ g^{-1}$)	280.5±10
Organic/Inorganic ratio	40:60

3.4.4.1. FTIR spectral analysis

The surface chemistry of the sludge obtained after EC treatment was studied using the FTIR spectroscopy. The presence of different functional groups in the sludge shows that in the electrostatic interaction between flocs and cations played an important role in the removal of colloids during coagulation process. The FTIR spectra of the dried EC sludge (Figure 3.11) displays a broad band at 3403 cm^{-1} due to O-H stretching of either water or hydroxyl group present in the wastewater. This shows the presence of both the free and hydrogen bonded OH groups and the O–H stretching of the polymeric compounds on the sludge interface. The characteristic methyl group C–H stretching bands have appeared in the region of 2930 cm^{-1} (asymmetric stretching) and 2850 cm^{-1} (symmetric stretching) [54]. The presence of aromatic ring (C=C) is evidenced by the presence of bands in the regions of 1621-1400cm^{-1} indicating the ring stretching. The bands of the out-of-plane bending vibrations of aromatic compounds are strong and characteristic of the number of hydrogen atoms in the ring. Wen et al., 2006 also showed the presence of prominent stretching band of the carbonyl group of terephthalic acid at 1687cm^{-1} in Fe (OH)$_3$ flocs [55].

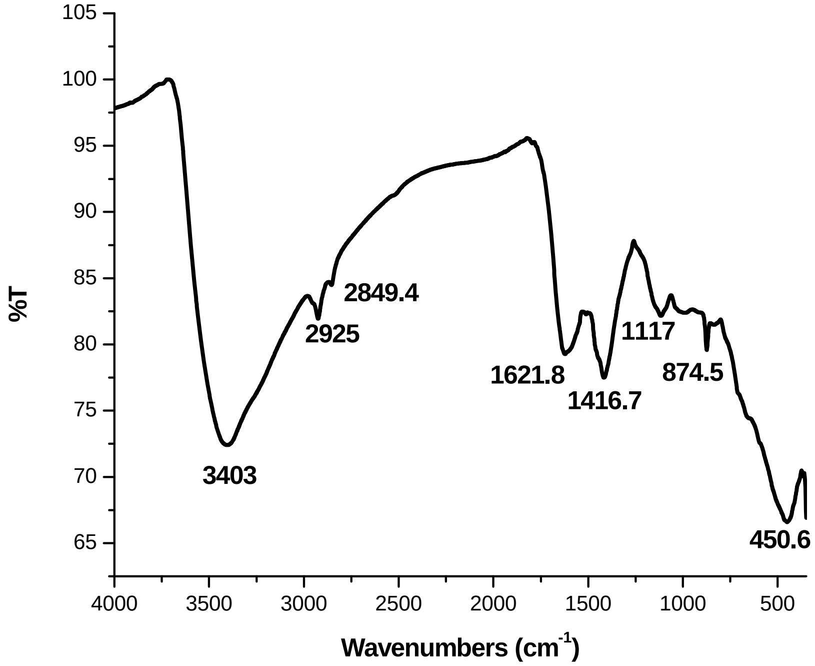

Fig. 3.11: FTIR spectra of EC sludge

In addition, region found in the 1117cm^{-1} shows the presence of esters (aromatic C–O stretching). There are characteristic infrared bands between the regions 800-400 cm^{-1}. This absorption region is the “finger print” region of EC sludge spectra and identified as the bands of organic halogen compounds (C-X stretching) [54] indicating the chloride and chlorophenols removal in the present sample. From the FTIR analysis, it is confirmed that the components of pulp and paper mill wastewater get attached to coagulants through some inherent complex chemical phenomenon, which results in the removal of same COD of the wastewater by these inorganic coagulants.

3.4.4.2. TGA, DTGA and DTA of the sludge

The thermo gravimetric analysis (TGA), differential thermo gravimetric analysis (DTGA) and derivative thermal analysis (DTA) for the EC precipitated sludge is shown in Figure 3.12. The removal of species at these temperatures is reflected in the TGA trace. The rate of weight loss as shown by DTG reaches a maximum value in the second stage, where the combustion of volatiles takes place exothermically as indicated by DTA.

The nature of TGA traces shows, the dehydration of the sample up to the 80-100 ºC losing about 10% of its weight. The degradation of lignin (organic content) and other such components can be easily seen till 200-300 ºC and losing around 20-23% mass of its initial mass. Between the short span of 200 and 399 ºC the residue oxidizes and loses about 15.1% of its weight. The organic matter oxidation seems to be complete at 400 ºC leaving behind the 67.4 % of inorganic content of the sludge. The weight loss at T_{max} (289 ºC) is 169 $\mu g\ min^{-1}$. The oxidation of sludge is found to be consistent and exothermic in nature with the heat evolution of 2.2 J/mg of organic matter burned with an exothermic peak at 293 ºC.

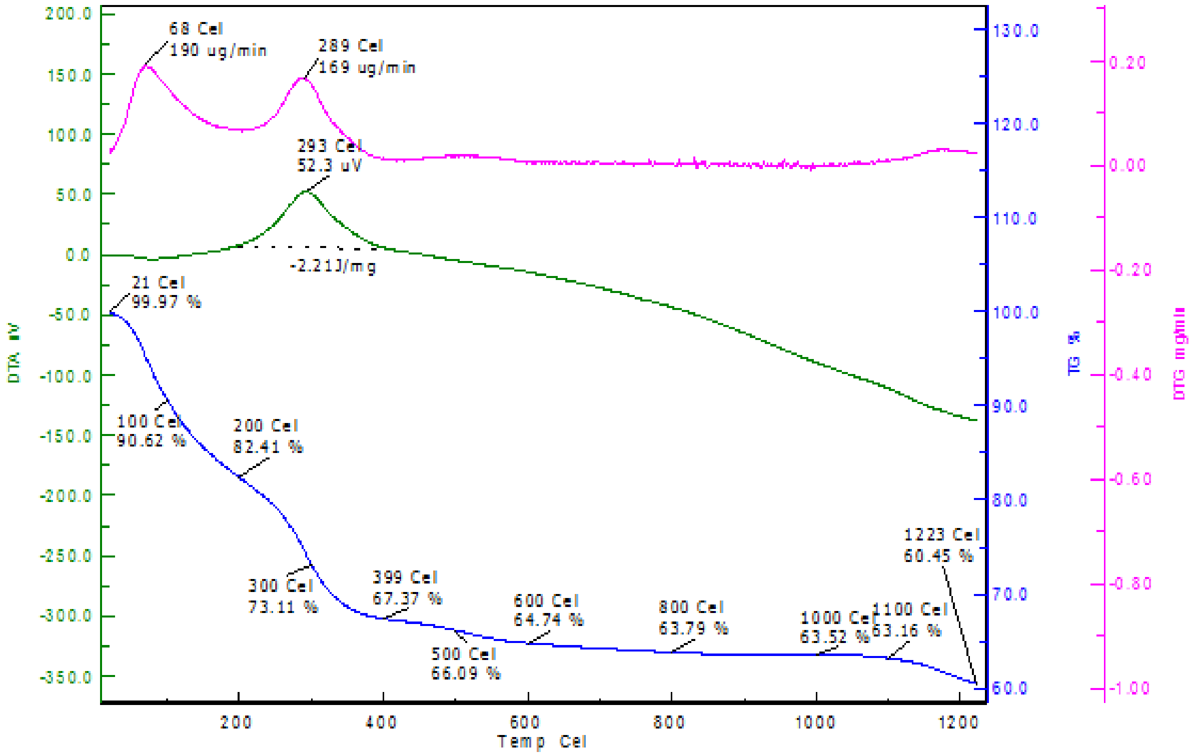

Figure: 3.12: DTA–DTG–TG plots of EC generated sludge

3.4.4.3. SEM micrographs and EDAX analysis

From the SEM micrographs (Figure 3.13a and b). It is clear that the flocs produced after the treatment of wastewater with EC are hard and sturdy with the colloidal particles entrapped in it, indicating the sweep flocculation for the colloidal particles in the wastewater mixture. Nearly spherical particles of size between 75 to 125 nm are observed. These are in the agglomerated form due to the high surface energy.

EDX analysis was done to find element composition in SS generated sludge [56]. The presence of elements is confirmed by the EDX analysis, which indicates that carbon, oxygen, sodium, calcium, silica and iron are present in the sludge in different weight percent. Among various elements, carbon content in was found to be higher and it indicates the COD removal during the process (Table 3.7)**.** This information confirms that once the organic matter is destabilized, it can be separated from the wastewater. It also confirms that, the iron generated during the electrolysis combine with the pollutants and form insoluble complexes.

Table 3.7: Characteristics of cathode scratch using EDX

Elements	**Wt %**
C	27.23
O	14.69
Fe	16.35
Na	4.38
Ca	4.17
Si	1.93
Cl	3.65

3.4.4.4. Sludge disposal

According to the chemical and structural characterization of the EC sludge, it can be confirmed that it is a non-hazardous solid waste. It is apparent that characterization is necessary for integrated assessment of the environmental risk for disposal or use of EC sludge. TGA/DTA analysis give qualitative and quantitative results regarding thermal degradation nature, energy content of the sludge which can help in deciding its possible usage as fuel in boilers and furnaces.

Potential applications for this pulp and paper treated EC sludge can also be used in cement production. The manufacture of portland cement typically involves mixing, heating and grinding raw materials. The primary input materials are limestone, clay, sand, gypsum and coal (fuel). There is significant scope to utilize non-primary raw materials which has already been exploited by cement manufacturers [57]. As can be seen in Table 3.7, that the sludge contains a substantial amount of Iron (Fe), so it could be a strong ingredient when mixed with the construction material like cement.

3.4.4.5. Cathode scratch characterization

During electrolysis, a white scaly deposition occurs on the cathode. The deposited material was scratched and characterized by FE-SEM and EDX to check if there is any toxic material formed and deposited on cathode after experiments. The FE-SEM image is shown in Figure 3.15a and b**.** Chemical composition of cathode scratch is given in Table 3.8 and EDAX spectra in Figure

3.16. Among various elements, calcium was found to be the dominant followed by oxygen, carbon and traces of iron and no toxic material was found in the scratch. It indicates that calcium from wastewater get deposited on cathode.

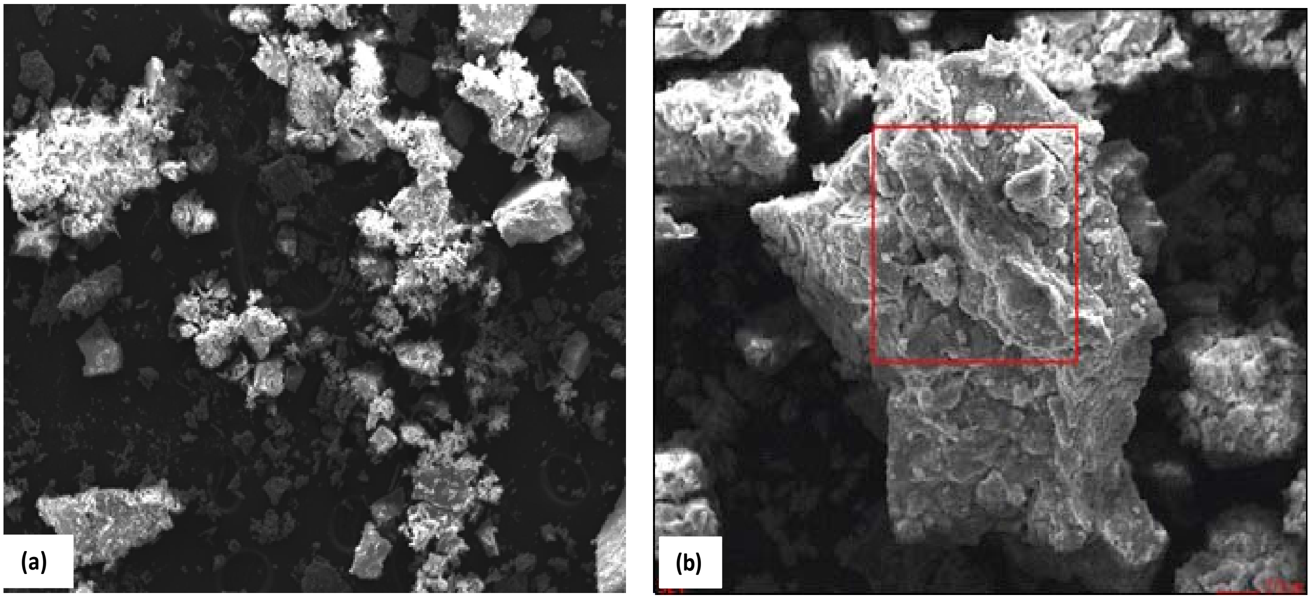

Figure 3.13: SEM micrograph of dried EC sludge at (a) 500X, (b) 1000X

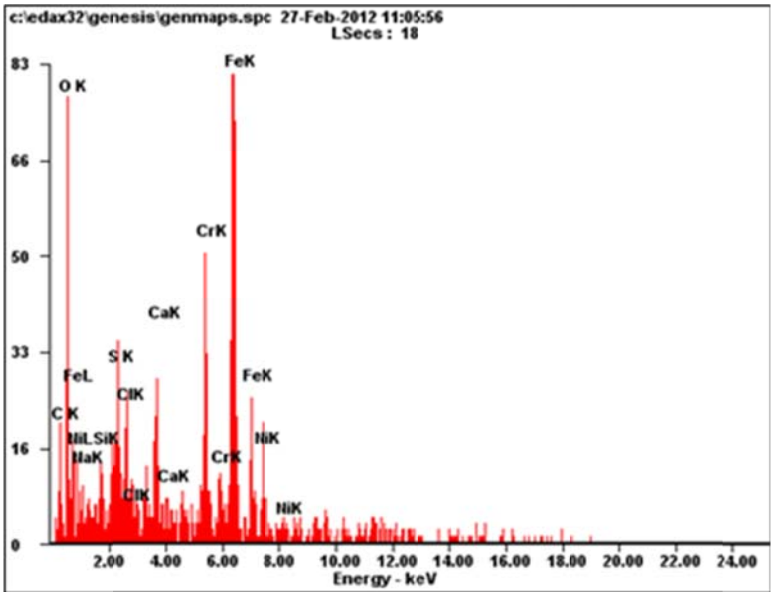

Figure 3.14: EDX spectra of dried EC sludge

Table 3.8: Characteristics of cathode scratch using EDAX

Elements	Wt %
Ca	66.92
C	13.08
O	17.35
Fe	02.65

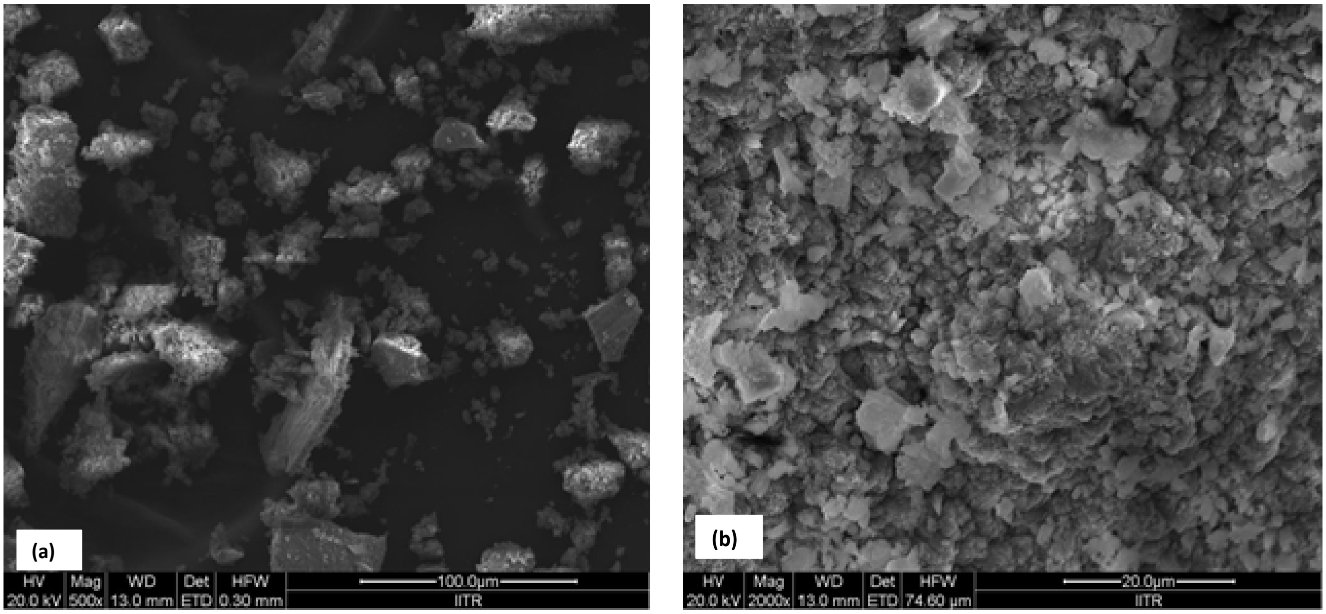

Figure 3.15: SEM micrograph of cathode scratch at (a) 500X, (b) 1000X

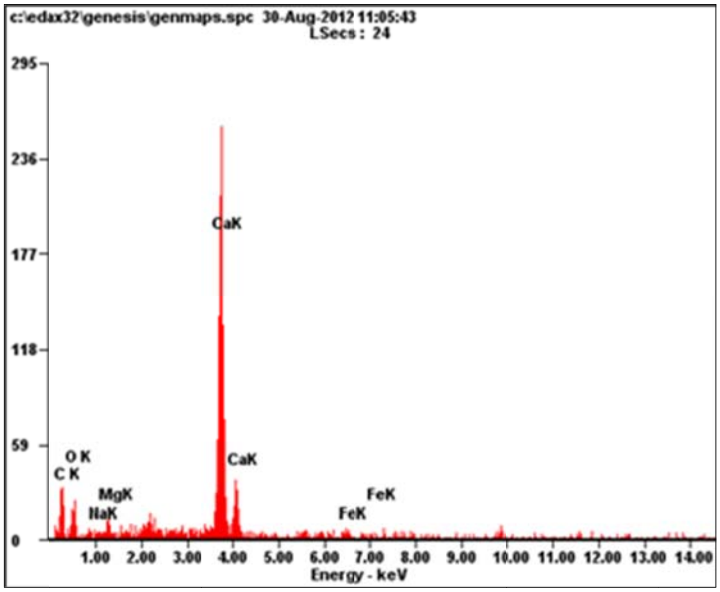

Figure 3.16: EDX spectra of cathode scratch

3.5. MAJOR FINDINGS

- The behavior of PC effluent towards EC treatment was found similar to the SC effluent, except the removal efficiencies decreases with increased organic load at same conditions. So, the optimum conditions selected for PC effluent treatment are; pH 7.0, CD of 15 A/m^2 and treatment time of 2h.
- EC is an efficient method for the degradation of recalcitrant organic matter present in the wastewater. The COD, color and CP reduction for PC effluent was 65.1%, 92.6% and 68.7% respectively and for SC effluent was 83.8% COD, 96.8% color and 83.8% CP. The color reduction was good by this method which may be a better option for paper industry.
- EC enhances the biodegradability of pulp and paper mill wastewater. BOD_5/COD ratio of the effluent was increased from 0.22 to 0.50. This technique can be used as a pre-treatment step before the conventional biological wastewater treatment.
- The electrical energy consumption for the present effluent under optimized conditions with stainless steel electrodes was found to be 0.9 KWh/m^3 of wastewater. The consumption was lower in comparison to other workers.
- 1.05 gL^{-1} of sludge was produced on the dry weight basis. The characteristics of the sludge indicate that it can find application in cement production.

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Chapter 4

ELECTROCHEMICAL DEGRADATION OF CHLOROPHENOLS

4.1. INTRODUCTION

The use of chlorine and chlorine based chemicals for pulp bleaching generates a variety of chlorinated phenolic compounds, originating from chlorination of residual lignin, in the bleach plant effluent. The chlorophenolics are formed during the chlorination stage (Cstage) of pulp bleaching and these get solubilized in the first extraction stage (E stage) [1]. Chlorinated phenolic compounds such as chlorophenols (CP), chloroguaiacols (CG), and chlorocatechols (CC) are readily found and these are refractory and are often toxic to biological treatment systems. Chlorophenols (CP), chloro-resins and fatty acids (cRFA), and polychlorinated dioxins and furans etc., collectively estimated as adsorbable organic halides (AOX), these are found in bleach plant effluent [2-4]. The values and concentration of chlorophenolics formed will depend upon the nature of the lignin in the raw material and bleaching conditions [2]. US EPA listed Chlorophenols (CP's) as the priority toxic pollutants under Clean Water Act [5-8] because 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 [9]. All the chlorophenols have ability to bioaccumulate in organisms and possess phytotoxicity and bactericidal activities. The *ortho*-substituted compounds are generally have lower toxicity than *para*- and *meta*- positions, because *ortho*- substituted chlorine group shields OH group in the phenol ring, which apparently react with the active sites in the aquatic organism [10]

There are several treatment techniques available to remove such refractory organic compounds. Both destructive and non-destructive methods of treatment are available. The methods which are non-destructive include adsorption (activated carbon, granular activated carbon) and extraction method (e.g. liquid-liquid extraction), but these methods cannot change the chemical nature of the toxicants; instead they concentrate the contaminants into more hazardous form. The chemical treatment methods are generally destructive and convert the contaminants to simpler form by oxidation; these methods include the Advanced Oxidation Processes (AOP's). Various AOP's are attempted to degrade these organic toxicants like ozonation, fenton oxidation, photocatalytic oxidation etc. [11, 12]. These include the generation of $^{\cdot}$OH radicals and are very effective at initiating the oxidation of the target compounds by attacking the C-H bonds or addition at unsaturated and aromatic centers.

Among the various advanced treatment methods, electrochemical (EC) technology is one of the emerging processes that attracted attention of many researchers in past few years [13, 14, 15, 16, 17, 18, 19, 20]. Toxic phenolic compounds can be effectively oxidized by electrochemical process using electric current with various features like simplicity, compact structure and operation [21, 22, 23]. 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 heavy metal containing waste for metal recovery [24, 25], dye containing wastewater from textile industry [26, 27], waste water from restaurant [28] and oil containing waste [29] has also been treated successfully with good removal efficiencies. 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. With the increased popularity and advancement in the EC process, many electrodes called dimensionally stable anodes (DSA) were prepared and used, but their degree of success for phenolic compounds were not very satisfying as they are highly expensive [15].

In this study, a less expensive anode material, stainless steel is used for the treatment of paper industry wastewater. Yuksel et al. 2013, has done a comparative study on EC treatment of a reactive orange 84 dye and on textile wastewater using by SS and iron (Fe) as sacrificial electrodes. He reported that the EC process with SS electrodes consumes less electrode material (longer service life) and also produced less amount of sludge as compared to Fe electrodes under similar experimental conditions. The operating cost with SS electrodes was about 0.7 times less as compared to the cost with Fe electrode. Thus SS has advantage of less overall operating cost and longer life than the Fe electrode [30].

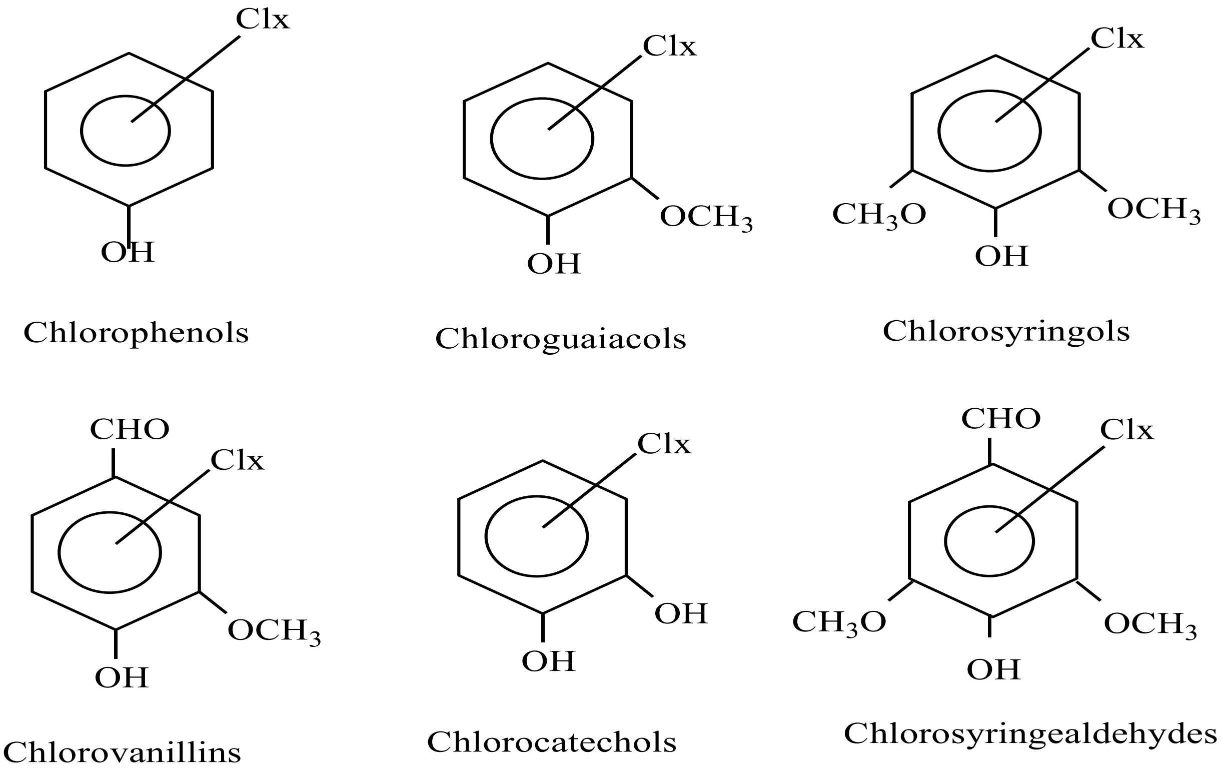
This chapter deals with the identification of the intermediates appeared during the chlorophenolics from pulp and paper mill primary and secondary clarifier effluent. High performance Liquid Chromatography (HPLC) and Gas Chromatography Mass Spectroscopy (GCMS) was used for the identification of these intermediates. The results on qualitative and quantitative determination of various chlorophenols in the combined pulp and paper mill effluent are also presented.

4.2. RESULTS AND DISCUSSION

4.2.1. Chlorophenols detection

GC-MS analysis facilitates the identification of various types of chlorophenolic compounds in pulp and paper mill effluent. The GCMS analysis of effluents has identified 20 low molecular weight chlorophenolic compounds in primary effluent (PC) and 18 compounds in secondary clarifier (SC) effluent. In terms of their chemical family i.e., Chlorophenols (CP), Chloroguaiacols (CG), Chlorocatechols (CC), Chlorovanillins (CV), Chlorosyringols (CS) and Chlorosyringaldehyde (CSA) were found. The structures of various chlorophenolic compounds by their family are depicted in Figure 4.1**.** The gas chromatogram of laboratory prepared mixtures of 26 reference chlorophenolic compounds (Acetyl derivatives) is shown in Figure 4.2. The corresponding retention time (RT), base peak mass/charge ratio, and extraction efficiencies (EE) values are given in Table 4.1**.** These results are in accordance with earlier findings [31, 32].

The total chlorophenolics concentration in primary effluent was quantitatively analyzed as 44.06±7.04 µgL^{-1} and secondary clarifier effluent concentration was 22.65±4.26 µgL^{-1}. The results are presented as the mean standard deviations of the triplet values performed (Table 4.2). 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 (i.e. 24.96 µgL^{-1} in primary effluent and 8.99±5.34 in secondary effluent) and 4,5-DCG (4.19 µgL^{-1} in primary effluent and 1.18 µgL^{-1} in secondary effluent) 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.



Chlorophenols Chloroguaiacols Chlorosyringols

Chlorovanillins Chlorocatechols Chlorosyringealdehydes

Figure 4.1: Structure of various chlorophenolic compounds by their chemical family

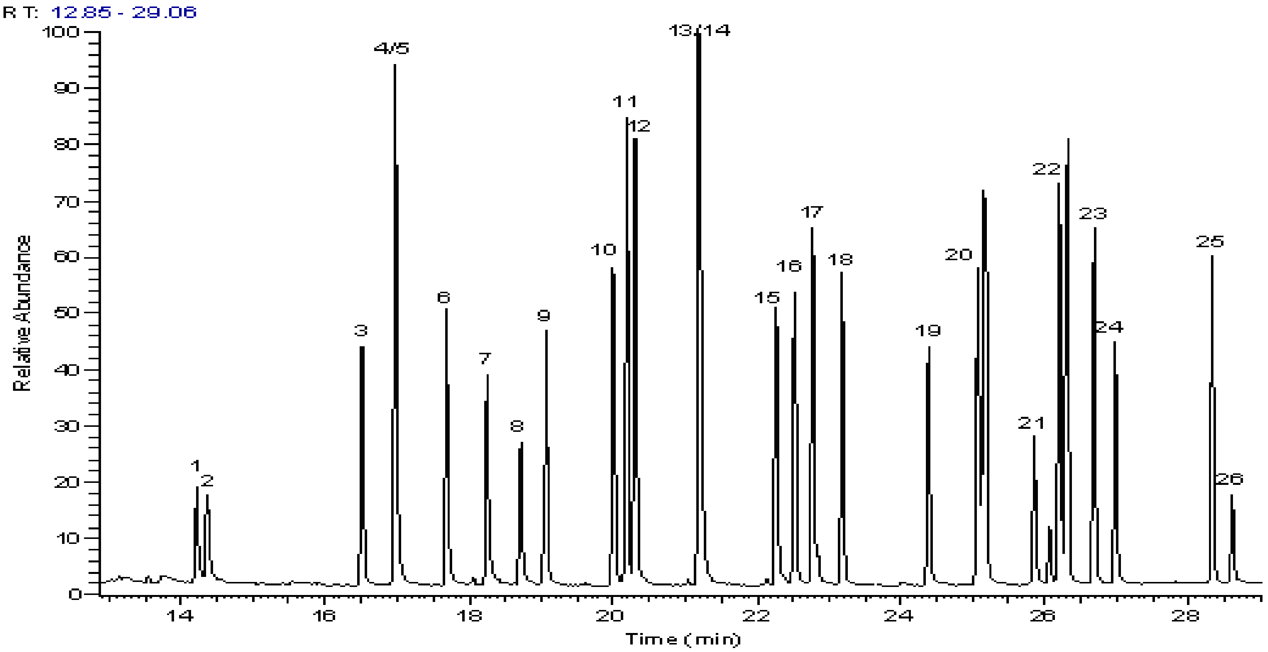


Figure 4.2: Chromatogram showing separation of a mixture of pure chlorophenolic compounds on TR-5 capillary column

Table 4.1: RT (min), m/z ratio, and EE (%) of various chlorophenolic reference compounds (acetyl derivatives) separated on TR-5 capillary column

S. No.	Compound	RT (min)	m/z	EE (%)
1.	3-Chlorophenol (3-CP)	14.20	127.9	49
2.	4-Chlorophenol (4-CP)	14.36	127.9	98
3.	2,6-Dichlorophenol (2,6-DCP)	16.52	161.9	64
4.	2,5-Dichlorophenol (2,5-DCP)	16.96	161.9	106
5.	2,4-Dichlorophenol (2,4-DCP)	16.98	161.8	87
6.	2,3-Dichlorophenol (2,3-DCP)	17.69	161.8	108
7.	3,4-Dichlorophenol (3,4-DCP)	18.27	161.9	81
8.	4-Chloroguaiacol (4-CG)	18.70	157.9	104
9.	2,4,5-Trichlorophenol (2,4,5-TCP)	19.07	195.8	77
10.	2,3,6-Trichlorophenol (2,3,6-TCP)	20.01	195.8	93
11.	2,3,5-Trichlorophenol (2,3,5-TCP)	20.17	195.9	88
12.	2,4,6-Trichlorophenol (2,4,6-TCP)	20.31	195.8	83
13.	4,5-Dichloroguaiacol (4,5-DCG)	21.19	191.9	79
14.	2,3,4-Trichlorophenol (2,3,4-TCP)	21.23	195.8	63
15.	4,6-Dichloroguaiacol (4,6-DCG)	22.27	191.9	102
16.	3,6-Dichlorocatechol (3,6-DCC)	22.50	177.9	3
17.	3,5-Dichlorocatechol (3,5-DCC)	22.77	177.9	5
18.	3,4,6-Trichloroguaiacol (3,4,6-TCG)	23.16	225.9	70
19.	3,4,5-Trichloroguaiacol (3,4,5-TCG)	24.40	225.8	99
20.	4,5,6-Trichloroguaiacol (4,5,6-TCG)	25.07	225.9	100
21.	5,6-Dichlorovanillin (5,6-DCV)	25.85	219.9	73
22.	Pentachlorophenol (PCP)	26.22	265.7	51
23.	2,3,5,6-Tetrachloroguaiacol (Tet-CG)	26.66	261.8	51
24.	Trichlorosyringol (TCS)	26.96	255.8	110
25.	Tetrachlorocatechol (Tet-CC)	28.31	247.8	33
26.	2,6-Dichlorosyringaldehyde (2,6-DCSA)	28.59	249.9	75

Table 4.2: Concentration of chlorophenolics in primary (PC) and secondary clarifier (SC) effluent

S. No.	Compounds	PC effluent (μgL^{-1})	SC effluent (μgL^{-1})
1.	3-CP	1.04±0.50	0.39±0.23
2.	4-CP	0.56±0.01	0.14±0.07
3.	2,6-DCP	0.94±0.29	0.72±0.16
4.	2,5-DCP	3.99±0.16	0.27±0.029
5.	2,4-DCP	1.49±0.15	0.06±0.10
6.	2,3-DCP	ND	0.03±0.004
7.	3,4-DCP	0.10±0.02	ND
8.	4-CG	3.06±0.08	0.18±0.15
9.	2,4,5-TCP	24.96±4.59	8.99±1.34
10.	2,3,6-TCP	0.06±0.01	ND
11.	2,3,5-TCP	0.15±0.01	0.17±0.10
12.	2,4,6-TCP	ND	0.05±0.03
13.	4,5-DCG	4.19±0.70	1.18±0.71
14.	2,3,4-TCP	0.16±0.05	0.07±0.02
15.	4,6-DCG	0.42±0.01	0.51±0.22
16.	3,6-DCC	2.04±0.15	5.90±0.37
17.	3,5-DCC	ND	2.66±0.47
18.	3,4,6-TCG	0.12±0.03	ND
19.	3,4,5-TCG	0.05±0.01	0.05±0.01
20.	4,5,6-TCG	0.11±0.01	ND
21.	5,6-DCV	0.12±0.02	0.08±0.015
22.	PCP	0.18±0.12	ND
23.	Tet-CG	0.19±0.09	ND
24.	TCS	ND	ND
25.	Tet-CC	ND	0.20±0.14
26.	2,6-DCSA	0.13±0.03	ND
	Total	**44.06±7.04**	**21.65±4.16**

ND-Not detected

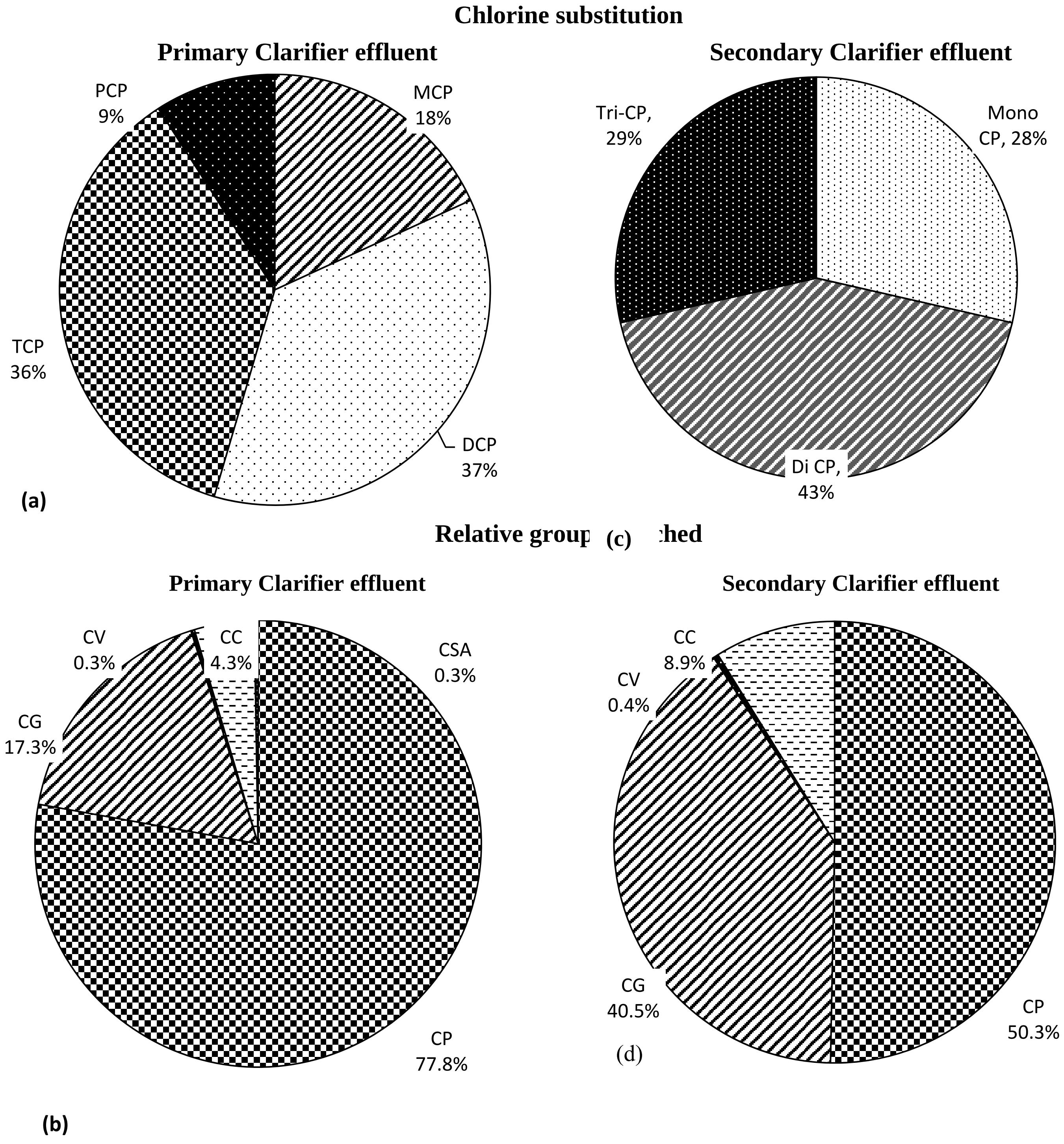


Figure 4.3: Proportion (%) of chlorophenolic compounds identified in (a) - (b) primary clarifier (PC) and (c) - (d) secondary clarifier (SC) effluent

4.2.2. Chlorophenolics removal

4.2.2.1. Chlorophenolics removal in secondary clarifier (SC) effluent

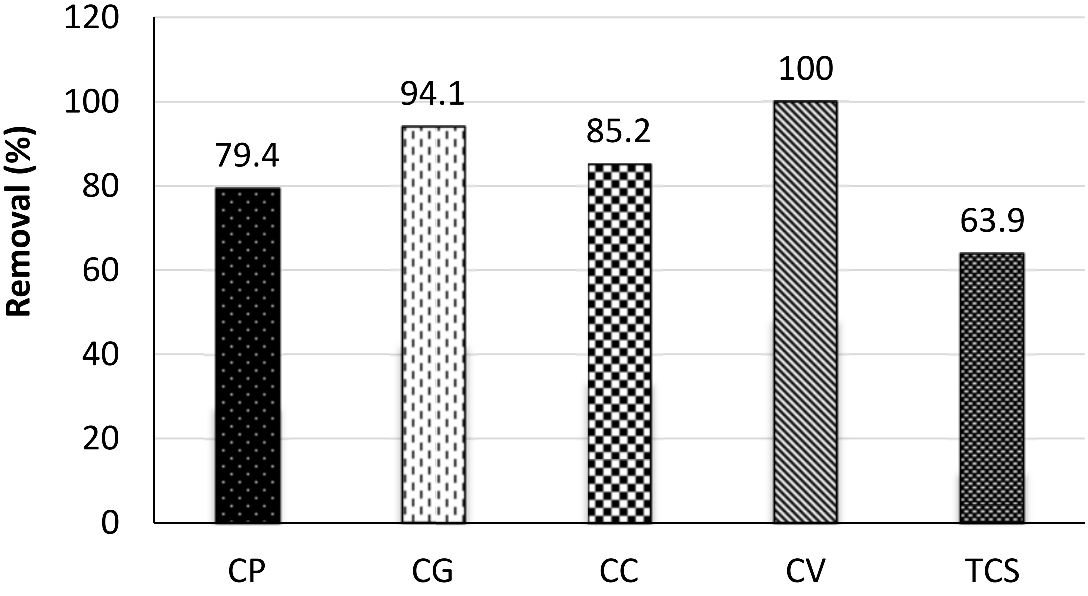
The concentrations of individual compounds were analyzed in SC effluent by EC treatment process and the results are presented, as the percent removal (%), in Table 4.3. For secondary clarifier effluent, the chlorophenols were removed by 83.6 % from their initial concentration of 23.83 μgL^{-1} to 3.92 μgL^{-1} under optimum conditions. Most of the compounds were removed from 30-100% in the sample. 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 (100%) or concentration falls below the detection limit of the instrument and are not detected. 2,4,5-TCP was removed almost completely upto 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 addition of these low molecular weight compound from the degradation of high molecular weight compounds in the system because mostly *ortho*- and *para*-chlorinated phenols were encountered during the electrochemical conversions [35]. TCS was removed 63.9% followed by Tet-CG which was removed 45.9% (Table 4.3). The group wise removal chlorophenolics is TCS (63.9%) followed by CP (79.4%), CC (85.2%), CG (94.1%) and CV (100%) (Figure 4.4a).

The removal of TCP was highest (91.6%) followed by MCP (88.1%) and DCP (38.9%) (Figure 4.4b). The removal of high chlorinated chlorophenolics (TCP) was higher as compared to lower chlorinated chlorophenolics (MCP and MCP) (Figure 4.4b). 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 due to the degradation of higher molecular weight compounds to lower molecular weight compounds [36]. Removal of higher chlorinated chlorophenolics (TCP and Tet CC) by EC also favors to reduce the toxicity of paper mill wastewater as these compounds are more toxic in comparison to lower chlorinated chlorophenolics (MCP and DCP).

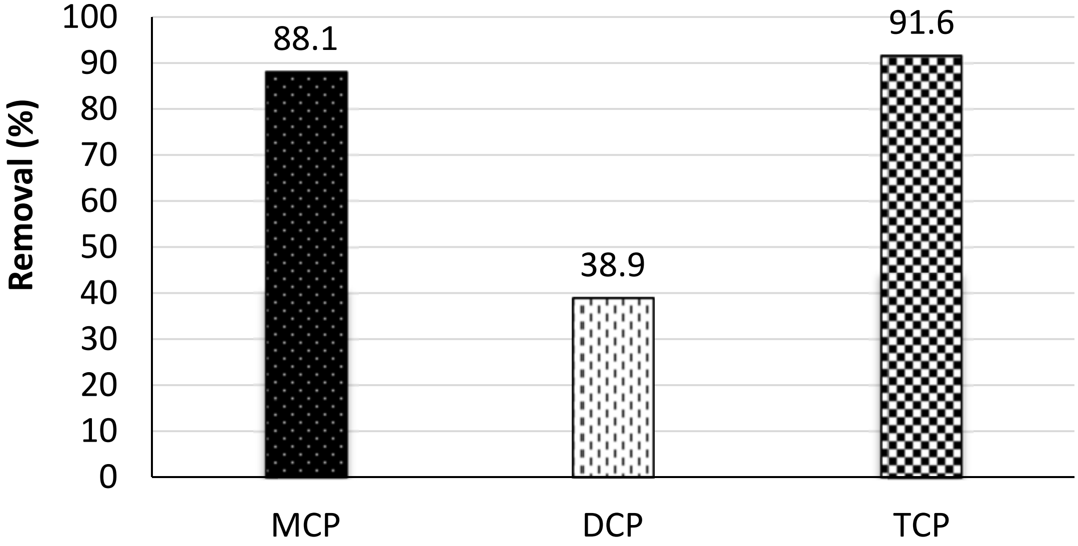
Table 4.3: Removal of chlorophenols (%) from secondary clarifier (SC) effluent using EC treatment

S. No.	Compounds	Initial Conc. (μgL^{-1})	Final Conc. (μgL^{-1})	Percent reduction (%)
1.	3-CP	1.56	0.21	86.5
2.	4-CP	0.20	ND	100.0
3.	2,6-DCP	1.61	1.10	31.6
4.	2,5-DCP	0.93	0.51	45.1
5.	2,4-DCP	0.26	0.10	60.9
6.	2,3-DCP	ND	ND	ND
7.	3,4-DCP	ND	ND	ND
8.	4-CG	0.12	ND	100.0
9.	2,4,5-TCP	7.75	0.68	91.2
10.	2,3,6-TCP	ND	ND	ND
11.	2,3,5-TCP	0.15	ND	100.0
12.	2,4,6-TCP	0.05	ND	100.0
13.	4,5-DCG	5.32	ND	100.0
14.	2,3,4-TCP	0.10	ND	100.0
15.	4,6-DCG	0.09	ND	100.0
16.	3,6-DCC	0.14	0.01	62.0
17.	3,5-DCC	2.50	0.53	78.8
18.	3,4,6-TCG	1.18	0.15	87.2
19.	3,4,5-TCG	0.04	ND	100.0
20.	4,5,6-TCG	ND	ND	ND
21.	5,6-DCV	0.09	ND	100.0
22.	PCP	ND	ND	ND
23.	Tet-CG	0.51	0.28	45.9
24.	TCS	0.97	0.35	63.9
25.	Tet-CC	0.26	ND	100.0
26.	2,6-DCSA	ND	ND	ND
Total		**23.83**	**3.92**	**83.55**

ND- Not detected



(a)



(b)

Figure 4.4: Percentage removal of chlorophenolics by (a) chemical family and (b) number of attached chlorine atoms in SC effluent

4.2.2.2. Chlorophenolics removal in primary clarifier (PC) effluent

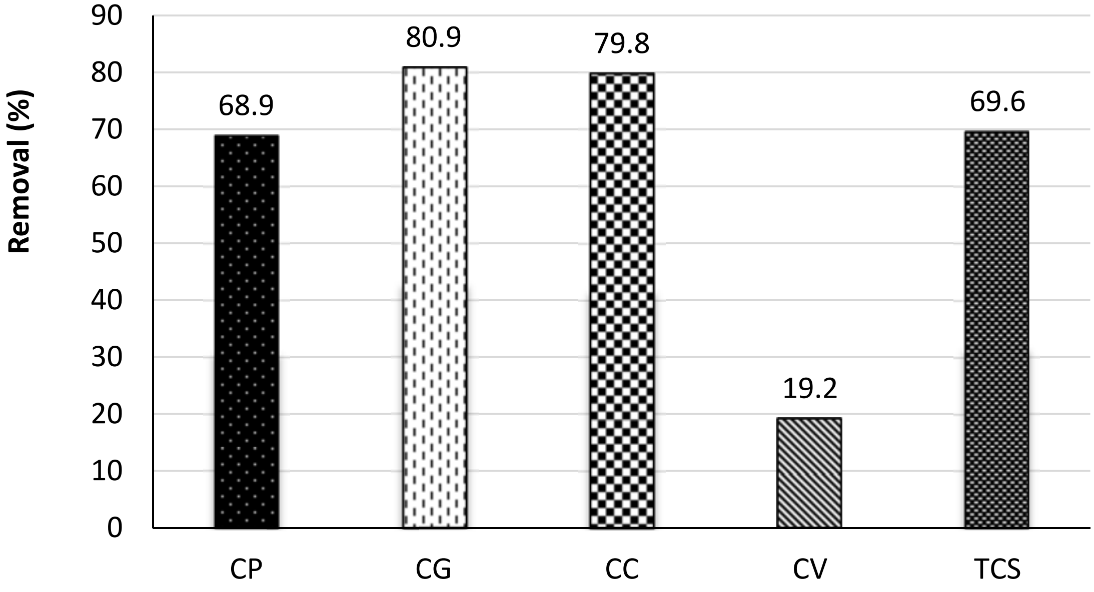
There is a considerable reduction of chlorophenols using stainless steel anode, within 2 h of treatment, 68.7 % of chlorophenols were removed from initial concentration of 49.82 μgL^{-1} with 44.5% of TOC removal. The results are presented in Table 4.4**.** It can be noted that after 2 h of the treatment, the concentration of most of the chlorophenolics reduced by 50-100%. Compounds like 3-CP, 2, 3, 6-TCP, 2, 3, 5-TCP, 3, 6-DCC, 3, 4, 6-TCG and PCP are completely removed (100%) or concentration falls below the detection limit of the instrument. Although some lower chlorinated phenol derivatives are formed during the process of treatment as intermediates which are converted into polymeric compounds and are oxidized eventually and thus were not detected after the completion of the treatment after 2 h (Section 4.2.2.2.1.) [33].

4-CP (99.4%) is almost completely removed from the reaction mixture. 4, 5-DCG, 3, 6-DCC are reduced upto 80% from their initial concentration. The results indicate that 2,5-DCP and 2,4-DCP, 2,6-DCP are removed to 65.6, 69.8and 40.7% respectively, which may be due to the degradation of high molecular weight compounds into the smaller ones like *mono-, di- and tri-* chlorophenol and this leads to their higher concentration in the solution. 4,6-DCG reduced to 52.3%. If we see the reduction of 3, 4, 5-TCG and Tet CG, they are reduced to 54.5 and 28.5% respectively. Whereas 5, 6-DCV was reduced only upto 19.2 %, it may be due to its conversion into respective smaller group compounds. The group wise removal of chlorophenols has highest removal percent of CG (80.9%) followed by CC (79.8%), TSC (69.5%) and CP (68.9%) and CV (19.2%) (Figure 4.5a). For CP, mono chlorophenols removed almost completely (99.7%), then TCP (66.6%) and DCP (58.5%) (Figue 4.5b)

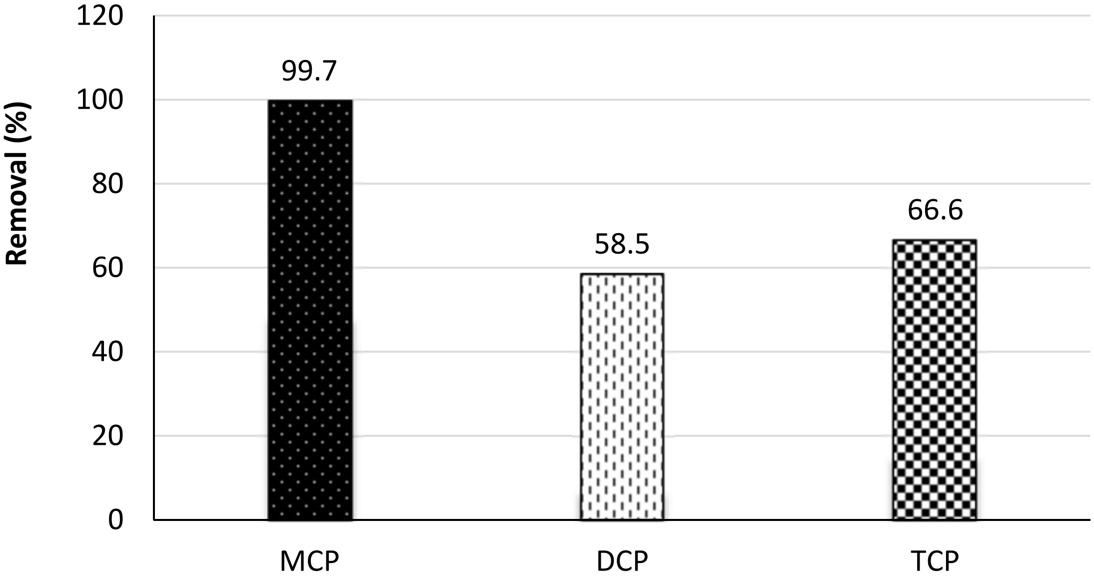
Table 4.4: Removal of chlorophenols (%) from primary (PC) effluent using EC treatment

No.	Compounds	Initial Conc (μgL^{-1})	Final Conc (μgL^{-1})	Percent reduction (%)
1	3-CP	3.07	ND	100
2	4-CP	1.57	0.01	99.4
3	2,6-DCP	3.15	1.87	40.7
4	2,5-DCP	4.87	1.68	65.6
5	2,4-DCP	1.59	0.48	69.8
6	2,3-DCP	ND	ND	ND
7	3,4-DCP	0.11	ND	100
8	4-CG	3	0.62	79.3
9	2,4,5-TCP	19.41	6.56	66.2
10	2,3,6-TCP	0.06	ND	100
11	2,3,5-TCP	0.15	ND	100
12	2,4,6-TCP	ND	ND	ND
13	4,5-DCG	4.68	0.89	80.9
14	2,3,4-TCP	0.19	0.05	73.7
15	4,6-DCG	0.42	0.2	52.3
16	3,6-DCC	3.96	0.8	79.8
17	3,5-DCC	ND	ND	ND
18	3,4,6-TCG	0.14	ND	100
19	3,4,5-TCG	0.11	0.05	54.5
20	4,5,6-TCG	ND	ND	ND
21	5,6-DCV	2.76	2.23	19.2
22	PCP	0.14	ND	100
23	Tet-CG	0.07	0.05	28.5
24	TCS	0.33	0.1	69.6
25	Tet-CC	ND	ND	ND
26	2,6-DCSA	ND	ND	ND
	Total	**49.78**	**15.59**	**68.68**

ND- Not detected



(a)



(b)

Figure 4.5: Percentage removal of chlorophenolics by (a) chemical family and (b) number of attached chlorine atoms in PC effluent

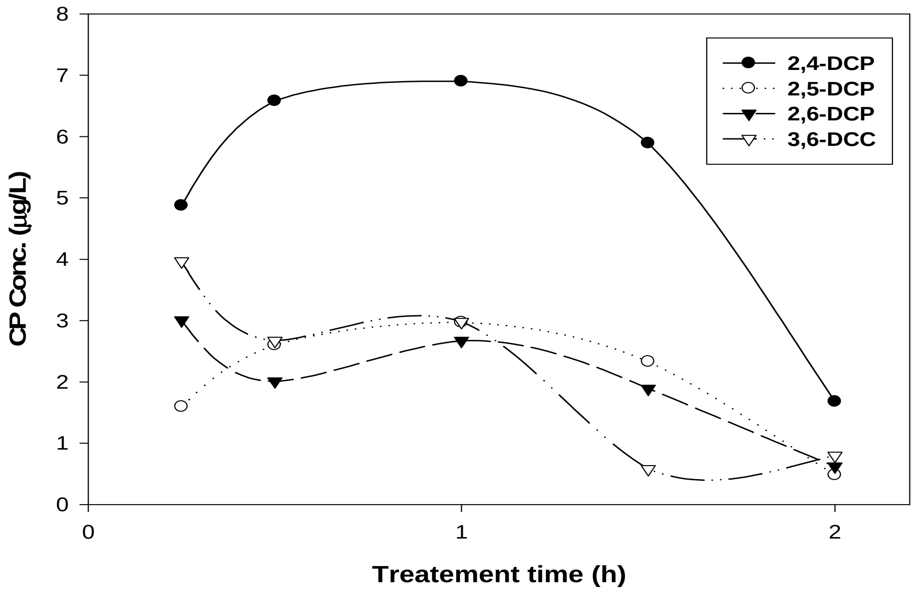
4.2.2.2a. Chlorophenolics degradation regime and its intermediate products

The variation in the concentration of various chlorophenolic compounds, by electrochemical degradation, was studied with treatment time, using both GCMS and HPLC. The results with GC-MS during the whole electrolysis duration have been presented in Figures 4.6a-f. It was found that there is an increase in the concentration of few chlorophenolic compounds in the initial hours of treatment (1h), few compounds appeared in the middle of the reaction, but not detected initially (Table 4.5) and few others decreased with time. Same findings are reported by other workers also and they indicated that there is the formation of intermediate compounds by electrochemical treatment method [34, 23].

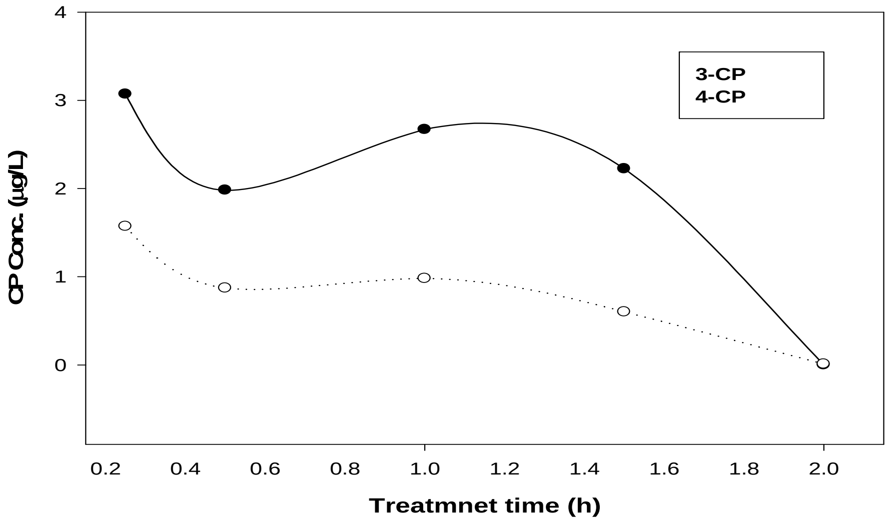
The results show that concentration of large number of chlorophenolics decreased after 0.5 h, then increases and become maximum after 1h and the concentration decreased significantly after 1.5 h and further decreased after 2 h of treatment. These intermediates have short life span in the system and contribute to the formation of polymeric structure to a certain extent, while part of them may be oxidized [34]. It may be due to the complex reactions occurring during the electrochemical conversion of chlorophenols. In the phenol ring, the hydroxylic group with non-bonded electrons on the ring attached oxygen atom, is a strong electron pair donor and is a strong *ortho,* and *para* director, just like the chlorine atom [35]. Since *ortho, para* directors lowers the energy of activation, leading to the resonance-stabilized intermediates, that is why mostly *ortho*- and *para*-chlorinated phenols were encountered during the electrochemical conversions. Korbahti and Tanyolac, 2003 have suggested a reaction pathway and a kinetic model for the degradation intermediates. According to them, the slowest reaction (with the smallest rate constant) result in the oxidation of chlorophenol and intermediates to CO_2 and H_2O [34].

Figure 4.6a shows the degradation regime of 2,4-DCP and 2,5-DCP and it can be seen that 2,5-DCP (1.59 to 2.97 μgL^{-1}) and 2,5- DCP (4.87 to 6.90 μgL^{-1}) concentration increased after 1 h of treatment, but decreased further and these compounds get removed upto 65% from their initial concentration at the end of the treatment. Same is the case with 3-CP (Figure 4.6b), the concentration decreased from 1.57 to 0.87 μgL^{-1} in 0.5 h and again increased to 1.98 μgL^{-1} after 1h of treatment, but degraded completely (100% removal) after 2h of treatment. The concentration of 4 CG, 2, 4, 5-TCP and 4, 5 DCG (Figure 4.6c) decreased at 0.5 h and then increases slightly at 1 h and get removed after 1.5 h. If we further see 2, 3, 4-TCP, 2, 3, 6-TCP and 2, 3, 5-TCP the same trend was observed (Figure 4.6d) [34]. The concentration of 2, 3, 5- TCP increases slightly after 0.5 h and a very large increase was observed after 1 h and it get removed nearly 100% after 1.5 h (Figure 4.6d). But, it was observed that concentrations of 3, 4, 5-TCG (Figure 4.6e) decreased with time and removed to 100% after the completion of the treatment. The behavior with PCP is similar to 2, 3, 5-TCP except that, it decreases after 0.5 h (Figure 4.6f).

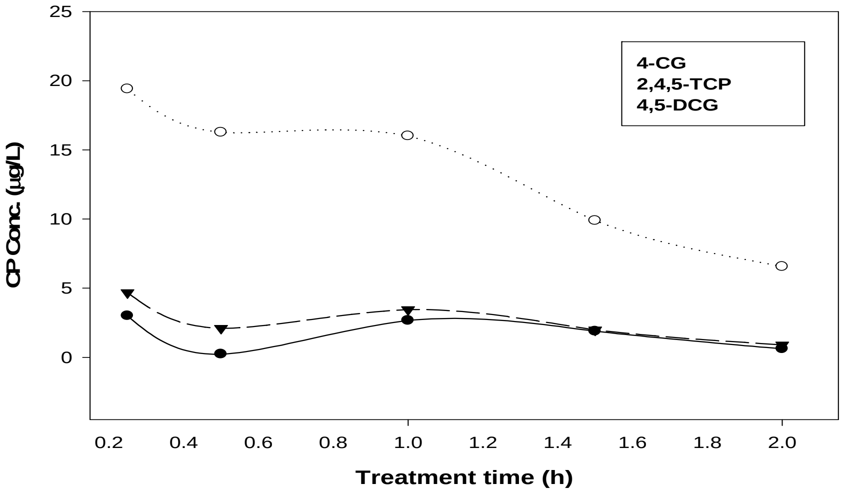
(4.6a)



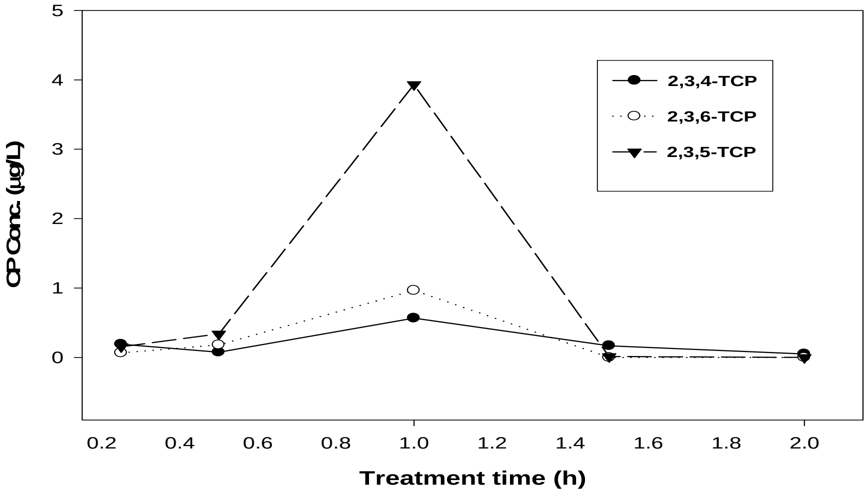
(4.6b)



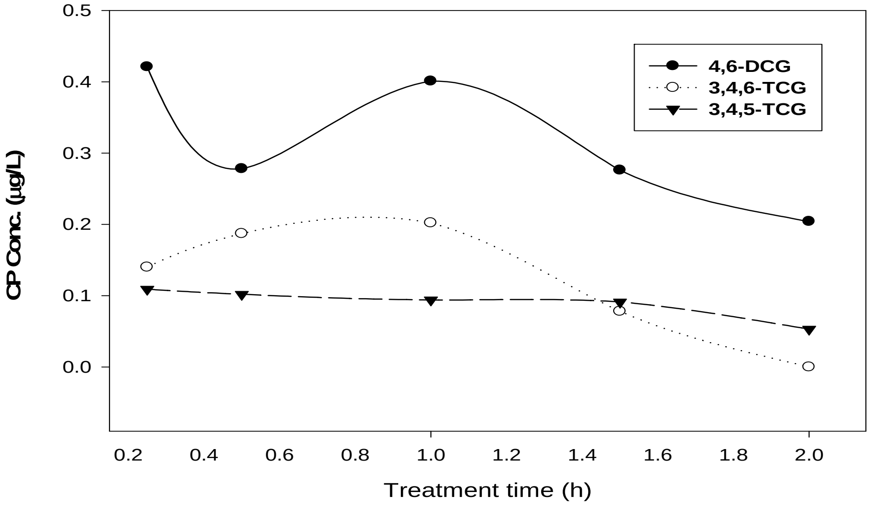
(4.6c)


4-CG
2,4,5-TCP
4,5-DCG
CP Conc. (µg/L)
25
20
15
10
5
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Treatment time (h)

(4.6d)


2,3,4-TCP
2,3,6-TCP
2,3,5-TCP
CP Conc. (µg/L)
5
4
3
2
1
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Treatment time (h)

(4.6e)


4,6-DCG
3,4,6-TCG
3,4,5-TCG
CP Conc. (µg/L)
0.5
0.4
0.3
0.2
0.1
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Treatment time (h)

(4.6f)

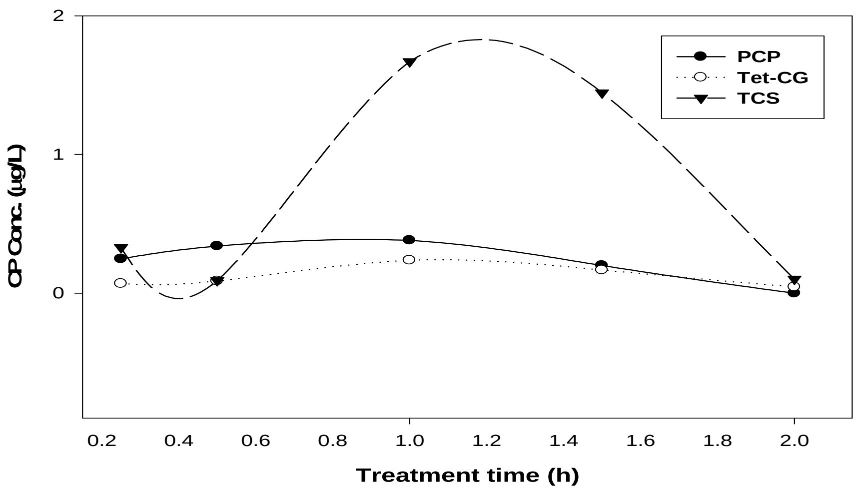


Figure 4.6: Variation in the concentration of chlorophenolics as a function of treatment time during EC degradation of PC effluent

It was found that mostly MCP, DCP and TCP are increased after 1 h during treatment, it may be because the higher molecular weight compounds like PCP, DCG, TCG etc., get degraded with the course of time and get converted into smaller molecular weight compounds, MCP, DCP and DCG. Besides these compounds, presented in Figure 4.6, few compounds were also detected in the middle of the reaction but were not present initially, these may be the intermediates formed during the electrochemical treatment (Table 4.5). 2,3-DCP was detected at 1.5 h in 0.020 µgL^{-1} concentration and disappear afterwards. Similarly, 3, 5-DCC and 4, 5, 6-TCG were detected at 1 h and degraded after further treatment. Tet-CC was detected at 0.5 h (0.167 µgL^{-1}), and disappears after 1.5 h.

Table 4.5: Chlorophenolic compounds detected in the reaction medium during EC treatment

Compounds	**Concentration of chlorophenolics (µgL^{-1}) at different treatment time**				
	0.25h	**0.5h**	**1.0h**	**1.5h**	**2h**
2,3-DCP	ND	ND	ND	0.020	ND
3,5-DCC	ND	ND	0.670	ND	ND
4,5,6-TCG	ND	0.065	0.014	ND	ND
Tet-CC	ND	0.167	0.986	0.056	ND

ND-Not detected

The literature showed that many aliphatic acids are also formed as intermediates during the oxidation of phenols and chlorophenols [15, 23, 37, 38], efforts were made to identify the aliphatic intermediates formed at various treatment times during the electrochemical degradation of chlorophenols by using HPLC. The peak areas obtained are given in Table 4.6. There are many intermediates formed during the course of treatment, due to the short life span of intermediates, it is difficult to identify all the intermediates. At least the important ones can be identified and their retention times (RT) were found, further analysis of samples was done on GC-MS. The quantification of some of these intermediates (chlorophenolics) was conducted with GC-MS (Section 3.2). The peak at retention time (RT=2.63 stands for hydroquinone, the peak at RT=6.35 is identified as benzoquinone. The retention times of some important standards run under the given condition (Section 2.4) are presented in Table 4.6**.**

The study on the degradation of chlorophenolic compounds as a function of treatment time reveals that mainly lower substituted chlorophenolics like mono, di and tri substituted chlorinated phenol products are formed as intermediate along with the polymeric compounds and that were consumed thereafter to CO_2 and H_2O. The other non chloro intermediates included aromatic compounds of benzoquinone, hydroquinone, guaiacol and catechol [39].

Besides aromatic intermediates a number of aliphatic acids were formed during the chlorophenolics degradation on SS electrode (Table 4.6). The intermediate acids detected were formic acid, oxalic acid, succinic acid and maleic acid which get completely oxidized during the course of electrolysis. These results are in agreement with the earlier findings [33]. The results in Table 4.6 show that, the peak areas of almost all the detected compounds and intermediates reduce with time, the overall peak area reduced by 44.9% (from 784931 to 432496.98) after the 2 h of treatment. Few peaks also disappear in the course of treatment. It simply implies that there is complete degradation and removal of compounds is taking place.

Table 4.6: Retention time and peak areas of various intermediates on HPLC (column C-18) formed during electrolysis of chlorophenols in PC effluent

S.No.	**Compounds**	**Retention Time (min)**	**Peak area at different treatment time**				
			0.25h	**0.5h**	**1h**	**1.5h**	**2h**
1.	Formic acid	3.62	ND	ND	105680	ND	ND
2.	Acetic Acid	4.08	ND	75680	40765	ND	ND
3.	Oxalic acid	4.50	ND	ND	63458	35789	989
4.	Maleic Acid	6.09	ND	ND	ND	4572	960
5.	Succinic acid	6.35	ND	ND	10780	2789	567
6.	Hydroquinone	2.63	1986	1045	ND	ND	ND
7.	Benzoquinone	3.21	46234	3906	1190	ND	ND

ND- Not detected

4.2.2.2b. Mechanism by EC degradation

Electrochemical mechanisms in aqueous systems are complex and there are three possible mechanisms that have been proposed: electro-coagulation, electro-flotation and electro-oxidation [40]. Pletcher and Walsh, 1990 proposed an oxidation and reduction mechanisms at an iron anode and cathode as represented below [41];

$$Anode: 4\,Fe \leftrightarrow 4\,Fe^{2+} + 8e^- \quad (4.1)$$

$$4\,Fe^{2+} + 10\,H_2O + O_2 \leftrightarrow 4\,Fe(OH)_3 + 8H^+ \quad (4.2)$$

$$Cathode: 8H^+ + 8e^- \rightarrow 4H_2 \quad (4.3)$$

The anodic oxidation reactions also include the effect of chlorine and oxygen. However, this additional reaction causes the electrochemical degradation mechanism to become more complicated. The degradation of chlorophenols at a stainless-steel electrode may be attributed to electrochemical formation of hydroxyl radicals at anode through a sequence of reactions. Dissolved oxygen may also undergo two-electron reduction at the cathode to produce H_2O_2 as follows [42, 43]:

$$O_2\,(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{4.4}$$

The H_2O_2 formed in above (equation 4.4), then undergoes a classical electro-Fenton's reaction to produce hydroxyl radicals ($OH^•$) [44, 45]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^• + H_2O \tag{4.5}$$

$OH^•$ is a powerful oxidizing agent which reacts with organic compounds producing dehydrogenated or hydroxylated derivatives. Eventually, the final degradation byproducts will be CO_2 and other inorganic ions. Production of protons from water oxidation reduces the pH of the reaction mixture [43].

4.2.2.2c. Probable mechanism of EC degradation of chlorophenols at SS electrode

The pathway of phenol and chlorophenol degradation by electrochemical oxidation has been studied by several investigators for different anode materials [15, 23]. In order to confirm the formation of intermediates as reported by various investigators, efforts were made to identify some of these intermediates (Figure 4.7), by using HPLC and GC-MS (Section 4.2.2.2.2). The organic compounds (chlorophenolics) in aqueous solutions are oxidized by two possible mechanisms; direct and indirect electron transfer [15, 46]. A MCP degradation pathway (Figure 4.7) in chlorophenol degradation has been proposed by Xie, 2006 [33]. This involves three basic processes;

(i) Degradation of chlorophenolic compounds to corresponding smaller molecular weight chlorophenols, benzoquinone, guaiacols and some catechols by generated $OH^•$ radical (Equation 4.5)

(ii) Aromatic ring cleavage which leads to the formation of aliphatic acids

(iii) Complete degradation of organic acids into CO_2 and H_2O

In the direct electron transfer mechanism, the chlorophenolics (represented as CP) are adsorbed on the anode surface and give up electrons to the anode i.e.

$$\mathrm{CP} - \mathrm{ne}^- \rightarrow \mathrm{Product} \qquad (4.6)$$

In the case of indirect process, of electron transfer, it is believed that, the oxygen radicals (hydroxyl radical) are generated from the electrolysis of water. The formation of hydroxyl radical on the anode surface as shown in Equation 4.4 [44, 45]. These generated hydroxyl radicals ($\cdot$OH) are powerful oxidizing agents which readily react with the organic molecules and get adsorbed on the surface of anode to initiate the oxidation of the organic compounds (Chlorophenolics) in this case as below;

$$\mathrm{CPh} + \mathrm{A}[{}^{\cdot}\mathrm{OH}^-] \rightarrow \mathrm{Products} \qquad (4.7)$$

Simultaneously, the hydroxyl radicals in the reaction medium will also react with each other to form the molecular oxygen to complete the electrolysis of water molecules as follow

$$2\ \mathrm{A}[{}^{\cdot}\mathrm{OH}^-] \rightarrow 2\mathrm{A} + \mathrm{O}_2 + \mathrm{H}^+ + 2\mathrm{e}^- \qquad (4.8)$$

Without the generation of strong oxidizing agent benzoquinone and hydroquinone would accumulate in the system and leads to the polymeric compounds formation that are more difficult to remove than the organic pollutants. So, the generation of hydroxyl radical leads to the non-selective oxidation of aromatic ring and leads to its opening and succinic acid formation will be expected [14, 22]. However with the formation of further radicals the formation of maleic acid and formic acid will takes place, which subsequently are oxidized to CO_2. Therefore the last step is the predominant and important step in the degradation process.

The identification of the lower chlorinated phenolics as reaction intermediates and detection of aromatic acids and quinones in the reaction mixture at varying treatment time (Section 4.2.2.2), supports the above proposed reaction mechanism for SS electrode also, which proposes the formation of these compounds.

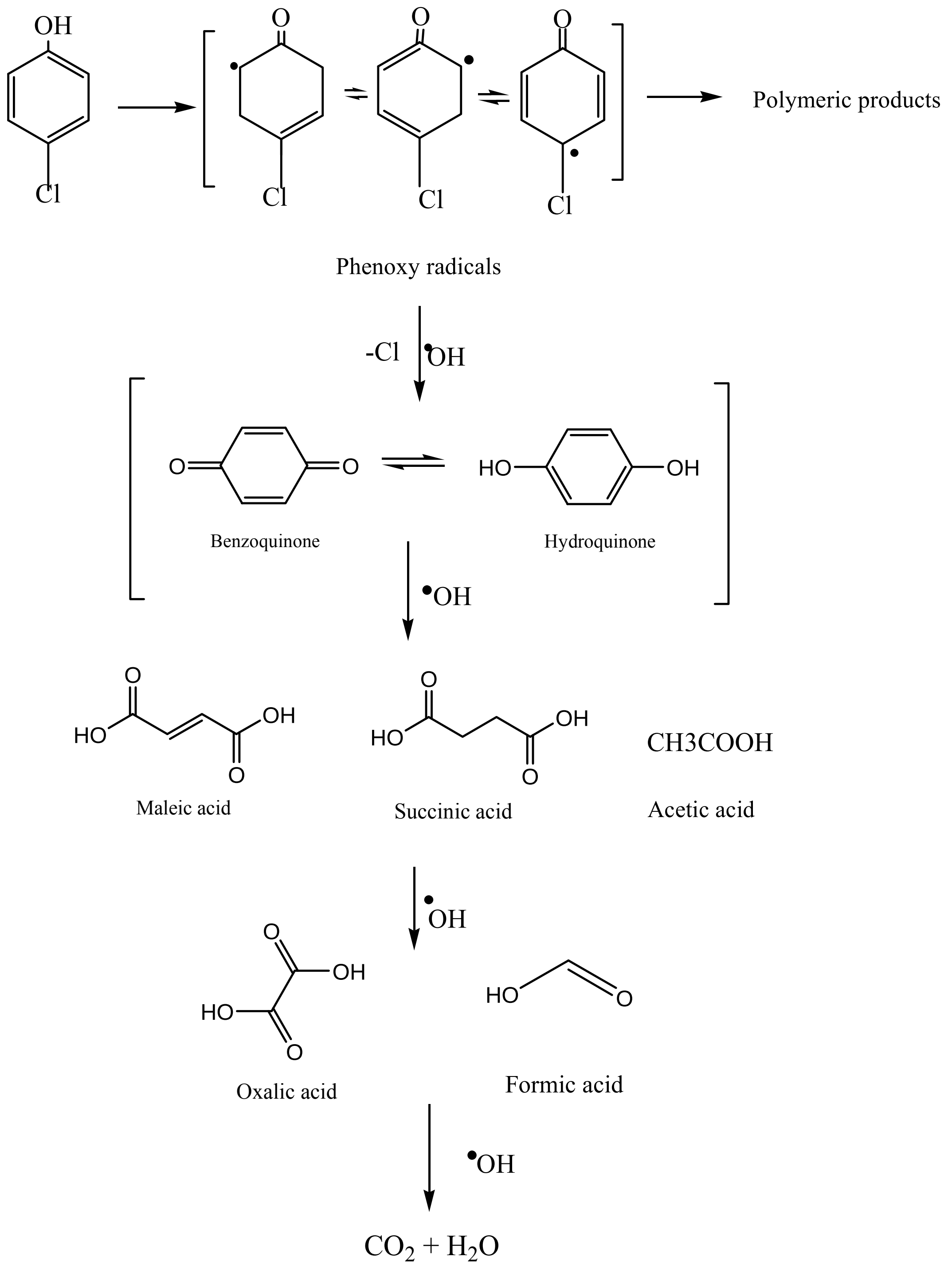


Figure 4.7: Degradation pathway for electrochemical oxidation of chlorophenols (MCP) [33]

4.2.2.2d. The pH of solution and TOC removal during electrolysis

The TOC removal (44.5%) in the system is lower than the chlorophenols (68.7%) reduction and there is some residual TOC in the system. The residual TOC in the system indicates the formation and accumulation of remaining organic intermediates. The removal of the TOC suggests that, the substrate get degraded to carbon dioxide and water (mineralization) [40]. The pH of the solution was also observed during the treatment and it changes according to the formation and degradation of the intermediates in the system [33]. During the treatment process the pH dropped from 6.8 to 4.4 in 1 h (60 min) due to the chlorophenols degradation and again increased to 6.6 as the degradation reached completion at 2 h (120 min) (Figure 4.8). The pH drop was apparently caused by the formation of aliphatic acids from chlorophenol destruction and subsequent oxidation to CO_2 increase the pH. The similar findings were observed by many workers [13, 23, 37, and 49].

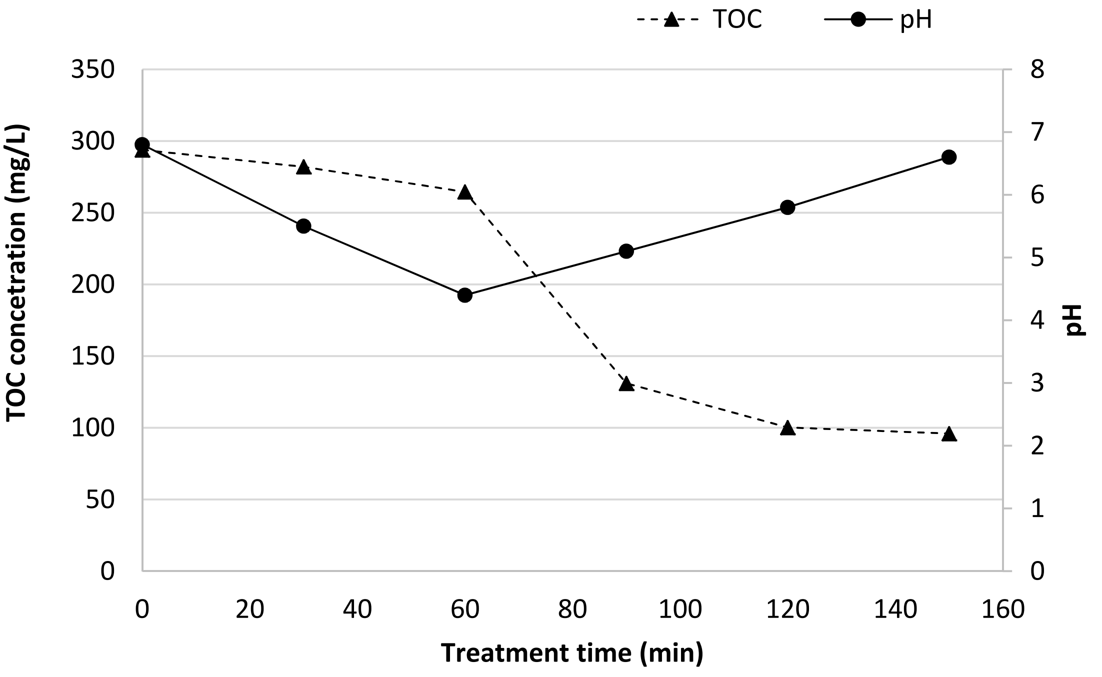


Figure 4.8: Variation in pH with respect to change in TOC concentration

4.2.2.2e. Effect of chloride concentration

The presence of chloride ions in the paper mill effluent can significantly affect the electrolysis process of chlorophenolics, and dechlorination was supposed to be one of the important steps in chlorophenol oxidation [50, 47]. Keeping this fact in mind, the chloride concentration was measured, parallel to the degradation process and found that there is an increase in the chloride concentration with time and that reached maximum at 1 h when the degradation was the highest and decreased subsequently with time (Figure 4.9**).** The results are in accordance with Kim et al., 2003, who employed a chlorine based coagulant (PAC) for the EC process of textile wastewater and reported that the rate of oxidation increases with increase in the chloride concentration of coagulated effluent [44]. Similar observations were also reported by some other workers [40, 48].

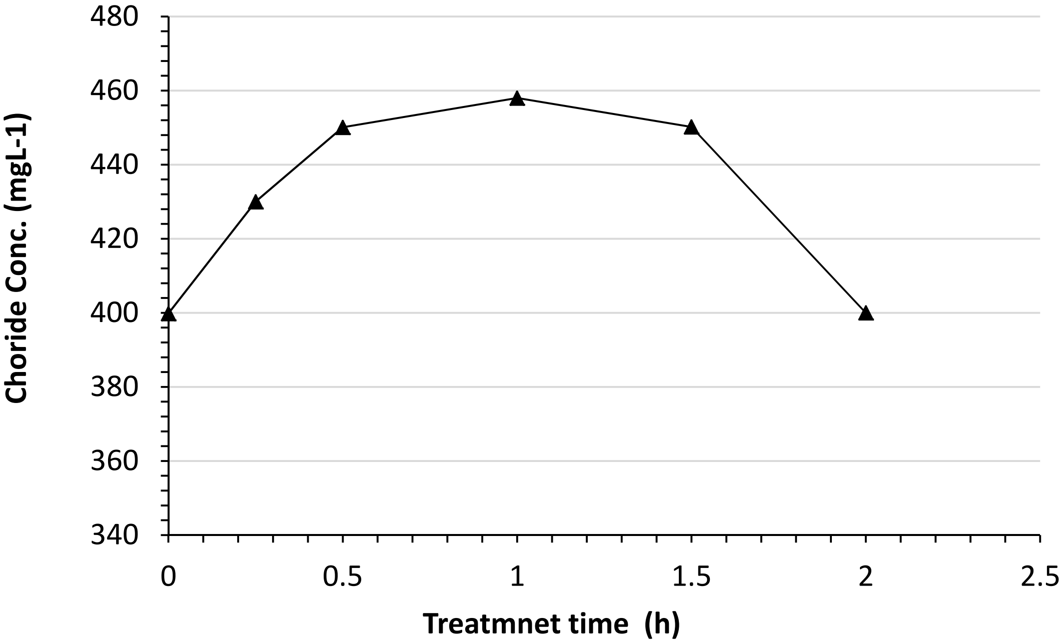


Figure 4.9: Variation in chloride ion concentration with treatment time

The presence of chloride ion serves two functions, by participating in the electrochemical redox reactions and also acting as a supporting electrolyte. Increase in the electrolyte conductivity leads to the significant decrease in the electricity consumption due to decrease in cell voltage. Chloride ions also participate in indirect electrolysis of the organic compounds. During electrolysis, the chloride ions are converted into chlorine and then to hypochlorite ions at neutral pH. These conversions occur by the following reactions [40].

$$Cl^- \leftrightarrow Cl_{ads} + e^- \qquad (4.9)$$

$$Cl^- + Cl_{ads} \leftrightarrow Cl_2 + e^- \qquad (4.10)$$

$$Cl_2 + H_2O \leftrightarrow HClO + H^+ + Cl^- \qquad (4.11)$$

$$HClO \rightarrow H^+ + ClO^- \qquad (4.12)$$

Then ClO^- participates in the oxidation of organic compounds by following reaction;

$$ClO^- + H_2O + 2e^- \leftrightarrow Cl^- + 2OH^- \qquad (4.13)$$

The chloride ions in turn lead to the chloride electrolysis and as the overpotential of chlorine is slightly lower than oxygen evolution, it leads to the chlorine evolution (Equation 4.10). Since chlorine is an effective oxidant, it would works on the oxidation of chlorophenols and its intermediates [33].

4. 3. MAJOR FINDINGS

- The GCMS analysis has identified 20 low molecular weight chlorophenolic compounds in primary clarifier effluent and 18 compounds in the secondary clarifier wastewater. Higher contribution to the chlorophenols comes from di-substituted compounds in the paper mill effluent.
- Chlorophenols could be readily mineralized by electrolysis at the stainless steel anode. Chlorophenolics degradation of PC effluent (68.7%) was lower than SC effluent (83.5%), under the similar operating conditions.

- Lower TOC removal than the chlorophenols reduction may due to the formation and accumulation of organic intermediate products.
- A number of intermediate degradation products like quinones, aliphatic acids and lower chlorinated phenols were identified suggesting that, dechlorination was a critical step in chlorophenol degradation.
- Detection of reaction intermediates provides experimental support to the proposed degradation reaction mechanism.

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Chapter 5

RECYCLING OF TREATED WASTEWATER

5.1 INTRODUCTION

The pulp and paper sector is one of the energy intensive and polluting industrial sectors in India. The manufacture of paper generates a significant quantity of wastewater; India's current average fresh water consumption is 100-220 m^3 of fresh water per tonne of paper [1]. The corresponding wastewater generation is also high, reaching the value of 75-225 m^3 per tonne of paper [2]. This figure is far above the global best specific water consumption of 28.66 m^3/t of paper (for large scale wood based pulp and paper mill). This large gap is because of the use of conventional manufacturing and treatment technologies and less water management practices by the industry [3]. Around 905.8 million m^3 of water is consumed and around 695.7 million m^3 of wastewater is discharged annually by this sector. Looking into the serious nature of pollution, the pulp and paper industry in India has been brought under one of the 17 categories of highly polluting industries [4].

The fresh water consumption and respective pollutant discharge depends upon the process and type of paper manufacture. Figure 5.1 illustrates the basic wastewater sources from various processes in a pulp and paper mill [5]. The quantity and quality of the fresh water used differs from one process to another, among the various sections, the most significant source of pollution are pulping and bleaching operations. Although, the pulping liquor is recovered, so the problem by this section becomes less. These stages are responsible for most of the color, organic matter and toxicity of the wastewater discharges of this industry [6].

In India no standards have been set for water consumption by any agency so far. However, CPCB has prescribed standards in terms of wastewater discharge for different categories of pulp and paper industry. The wastewater discharge with additional 21% (for evaporation losses) is used to give an estimate of water consumption. The wastewater discharge standard of 150 and 50 m^3/tonne of product for small agro and wastepaper based mills respectively and 200 m^3/tonne for large scale mills prescribed by CPCB. Further, this standard in the current scenario is outdated as the current average water consumption 150 m^3/tonne of product. The CSE finding gives an idea that most of the industries are already achieving the water consumption norms as agreed upon by them under CREP program 2002. The National Productivity council (NPC), suggested in one of its report that, the quality of treated wastewater after the tertiary treated is fit for recycling back completely to the system especially in wastepaper based mills and partially for other mills. However, there is a limitation to continuous recycle of wastewater within the plant for a long period as it leads to slime generation. This is prevented by optimized addition of biocide and chemicals in the water at regular intervals [7].

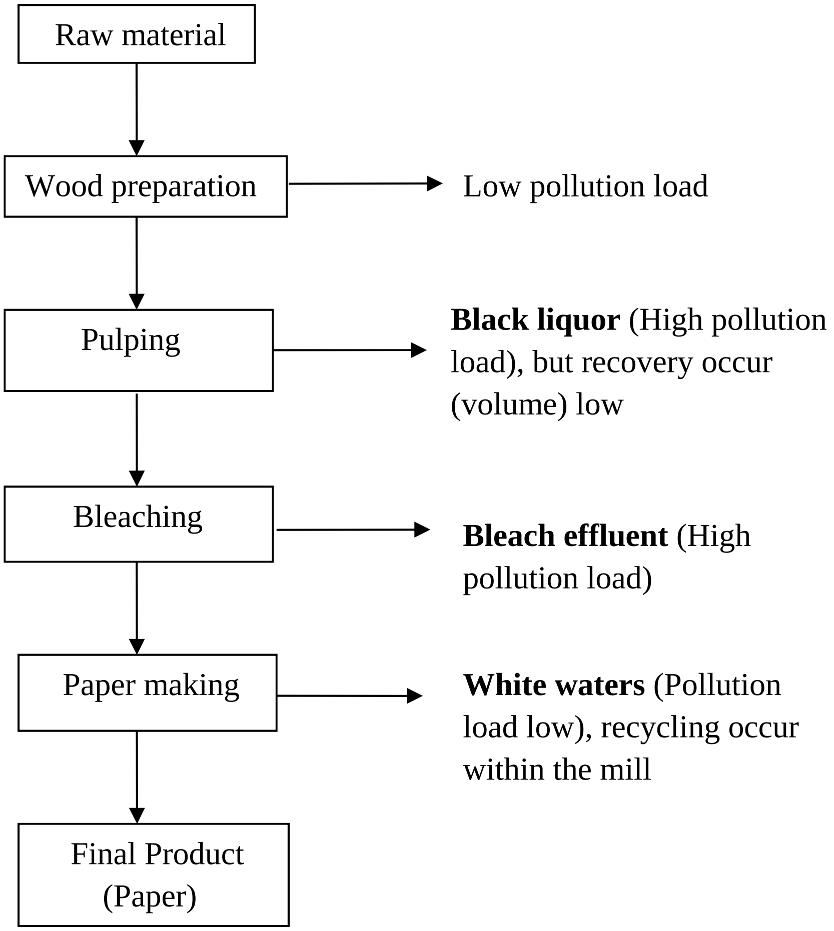

Figure 5.1: Schematic of wastewater sources in pulp and paper industries [5]

Paper manufacturing requires water for various unit operations in particular for cellulose dissolution, pulp washing and preparation of steam and chemicals [8]. Various treatment technologies have been used for making industrial wastewater into reusable form [9]. Paper mills in India adopt physico-chemical coagulation treatment followed by biological oxidation [10]. Biological oxidation process is widely used for reduction of dissolved organic matter from the effluents for its relative cost and ease of operation. The final treated wastewater after the biological processes is reasonable for discharge into inland surface waters [11]. However, further treatment (tertiary) is required to make it usable. Chemical treatment is fairly inexpensive, but addition of chemicals further complicates waste controlling. Specific purification technologies such as flotation, evaporation, and membrane filtration are used to concentrate and fraction spent liquor, remove color and treat bleach effluent [12], [13], [14] and [15]. Increased water use efficiency by modern process techniques is one of the major challenges faced by the paper industries using obsolete technologies in India [16].

5.1.1. Wastewater reuse options

(a) Direct use

In this scenario the generated wastewater is used directly in other operation without intermediate treatment provided that the level of contamination in the wastewater does not interfere the operations. This type of reuse is called water allocation planning [17]. In any wastewater reuse approach, direct reuse should always be preferred, because of its simplicity [18].

(b) Regeneration reuse

In this scenario a fraction of the total wastewater with lower contaminant concentration by the system is regenerated for reuse with remaining wastewater with higher concentration treated for discharge. [18].

(c) Treatment reuse

In this approach the total wastewater generated by the system is treated in a single on-site treatment facility to meet the water quality requirement as discharge limit, as shown in Figure 5.2**.** The wastewater treatment system treats the wastewater produced to two different levels, one at a relatively high level for reuse in the water utilization system and the other at a level that meets the discharge limit for disposal [18].

The objective of this chapter is to study the possibility of using EC treated secondary wastewater as wash water and to study the recycling of this treated wastewater in pulping and bleaching sections of paper mill, for better water management. This study particularly focused on organic matter removal.

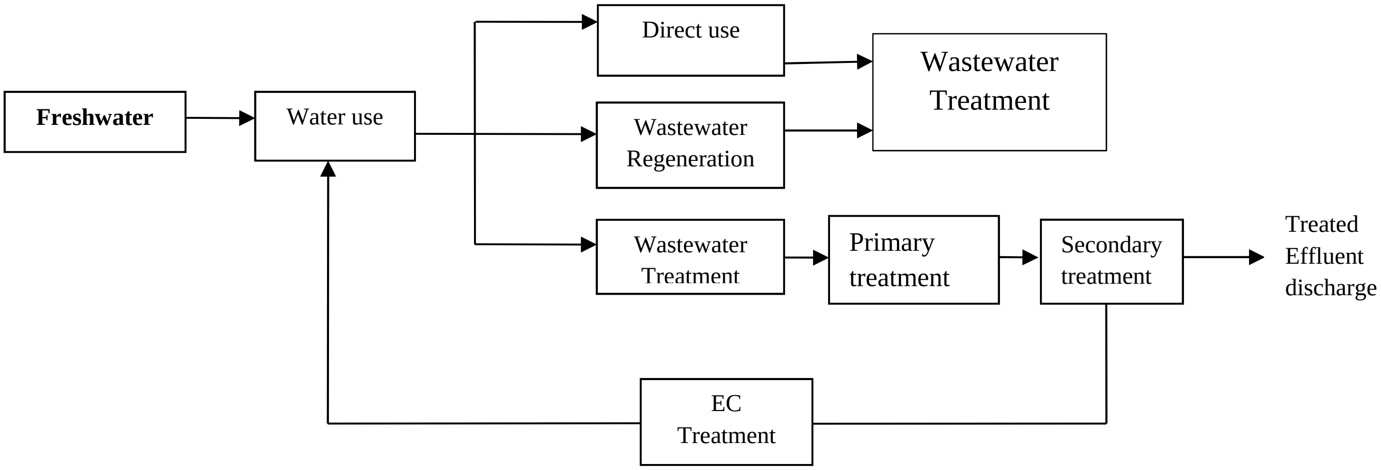

Figure 5.2: Water recycling probability in pulp and paper mill

5.2 RESULTS AND DISCUSSION

5.2.1. Recycling of treated effluent

The secondary clarifier effluent was treated by electrochemical treatment method under optimum treatment parameters (chapter 3) for washing purpose. The EC treated wastewater was used as wash water to study the recycling. To perform the recycling of EC treated water in the paper mill, two points were selected; the unbleached pulp washing (just after blow tank) and washing in bleaching stages.

5.2.1.1. Washing of pulp

Replacement of fresh water by treated water is envisaged at two points; in washing of unbleached pulp and at bleaching stages. Figure 5.3 illustrates the recycling points in bleaching stages, i.e., at Ep stage only and in all the stages. The effluent recycling is studied considering four parameters i.e., Cl^- and SO_4^{2-} ions which are responsible for corrosion, and COD and color which can result in reactants overconsumption, loss of pulp brightness and odor release [19, 20]. A study gives the concentration of COD, SO_4^{2-} and color for recycled effluent in the kraft process; their values are respectively 75 mgL^{-1}, 200 mg L^{-1} and 40 mg Pt-Co [21]. The characteristics of treated water used for washing in our study are given in Table 5.1**.** According to the Table 5.1, the water sample satisfies most of the parameters considered for recycling by Dorica, 1999 [21].

Table 5.1: Characteristics of EC treated water (wash water) used for washing

Parameters	**Value**
pH	7.2±0.3
Color (Pt-Co units)	35±5.2
COD (mgL^{-1})	35.6±15
BOD (mgL^{-1})	7.0±03
Cl^- (mgL^{-1})	180±08
SO_4^{2-} (mgL^{-1})	84.0±06
Ca^+ (mgL^{-1})	75.0±04
Na^+ (mgL^{-1})	21.0±02

5.2.1.2. Bleaching to target brightness

The pulp was bleached to 84% ISO target brightness using DEpD bleach sequence in the laboratory. The two DEpD sequences were done in parallel using fresh water (DEpD) for washing and EC treated water (RC_DEpD) for washing to achieve the target brightness.

(a) Chemical consumption for target brightness

The pulp was bleached to 84% target brightness using DEpD, DEp(RC)D and RC_DEpD sequences. DEp(RC)D sequence is the bleach sequence in which only Ep stage was washed with the treated water and rest stages were washed using freshwater. Whereas in DEpD all the stages were washed with freshwater and RC_DEpD sequence all the stages were washed with recycled water. The pulp bleaching conditions for different stages of bleaching sequences are mentioned in Table 2.4 (Chapter 2). The kappa factor (KF) was varied form 0.25-0.37 for attaining the 84% ISO target brightness during different bleaching sequence. Figure 5.4 illustrates the effect of KF on pulp brightness during bleaching sequence for achieving 84% ISO target brightness. For DEpD sequence KF of 0.28 was found to be optimum for attaining the target brightness of 84% ISO. Chemical charge for various bleaching sequences is given in Table 5.2**.**

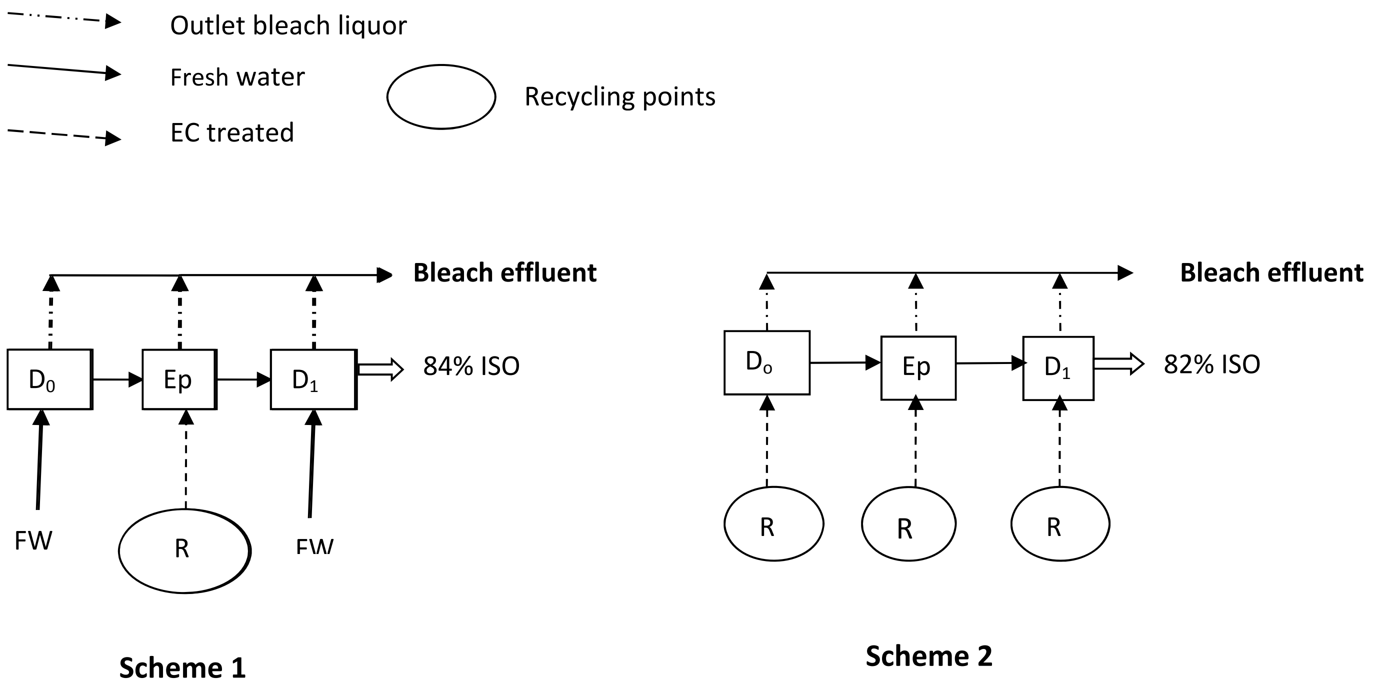

Figure 5.3: Recycling points in the bleaching section of paper making process (Target brightness 84 % ISO)

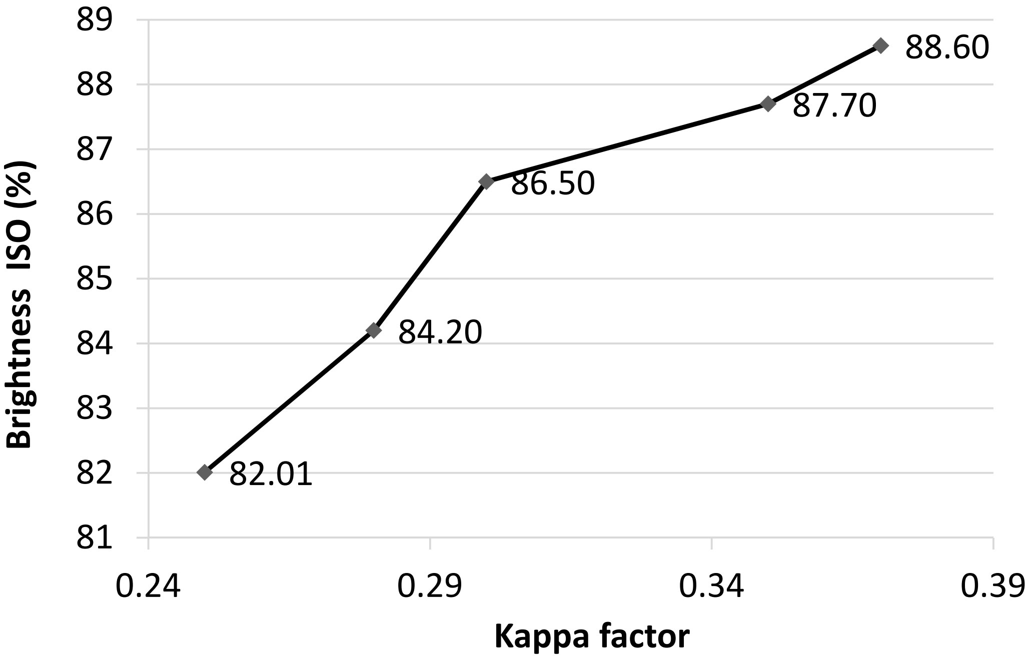

Figure 5.4: Effect of kappa factor on pulp brightness during DEpD sequence for 84 % ISO target brightness

Table 5.2: Chemical charge (kg/t O.D. pulp) required for different bleaching sequences for achieving 84 % ISO target brightness

Stages	**Chemical**	**Chemical charge (kg/t O.D. pulp)**		
		DEpD	**DEp(RC)D**	**RC_DEpD**
D_1	ClO_2	31.4	31.4	32.5
E_p	NaOH	10	10	10
	H_2O_2	3.0	3.0	3.0
D_2	ClO_2	13.4	13.4	13.9
Final brightness (% ISO)		83.9±0.24	83.6±0.16	82.5±0.50

(b) Pulp strength properties

The bleached pulp was beaten to the same CSF (300 mL ± 20) in a PFI mill for making the paper hand sheets for testing mechanical strength properties. The pulp beating was done to improve the runability-strength properties of the paper and to improve the bonding ability of the fibers [22]. After making the paper hand sheets, the tear, tensile and burst indexes were determined for both DEpD and RC_DEpD sequences. Figure 5.5 shows the effect of recycling on pulp tear index; tensile index burst index and viscosity. The pulp tear, tensile, burst and viscosity shows insignificant change in these parameters in RC_DEpD as compared to DEpD and DEp(RC)D. The tear, tensile, burst and viscosity values for DEp(RC)D are 6.9 mNm^2/g, 76 N.m/g, 4.4 $kPa.m^2/g$ and 12.5 cP respectively, which are not much deviate from the values of DEpD sequence (Figure 5.5**).** There is not very significant difference in Tear index of RC_DEpD (6.82 mNm^2/g) and DEp(RC)D (6.9 mNm^2/g) as compared to DEpD which is 6.8 mNm^2/g (Figure 5.5a**).** There is no change in the burst of the RC_DEpD sequence as compared to DEpD (Figure 5.5b**)**. Similarly, there is a small decrease in tensile index from 76.0 N.m/g to 75.8 N.m/g in RC_DEpD sequence (Figure 5.5c). The viscosity loss was also insignificant (0.2 units) and it comes under the error (Figure 5.5d). So, we can say that there is not any significant change in the pulp properties after the recycling of treated water and these properties remain same in RC_DEpD and DEp (RC)D sequences.

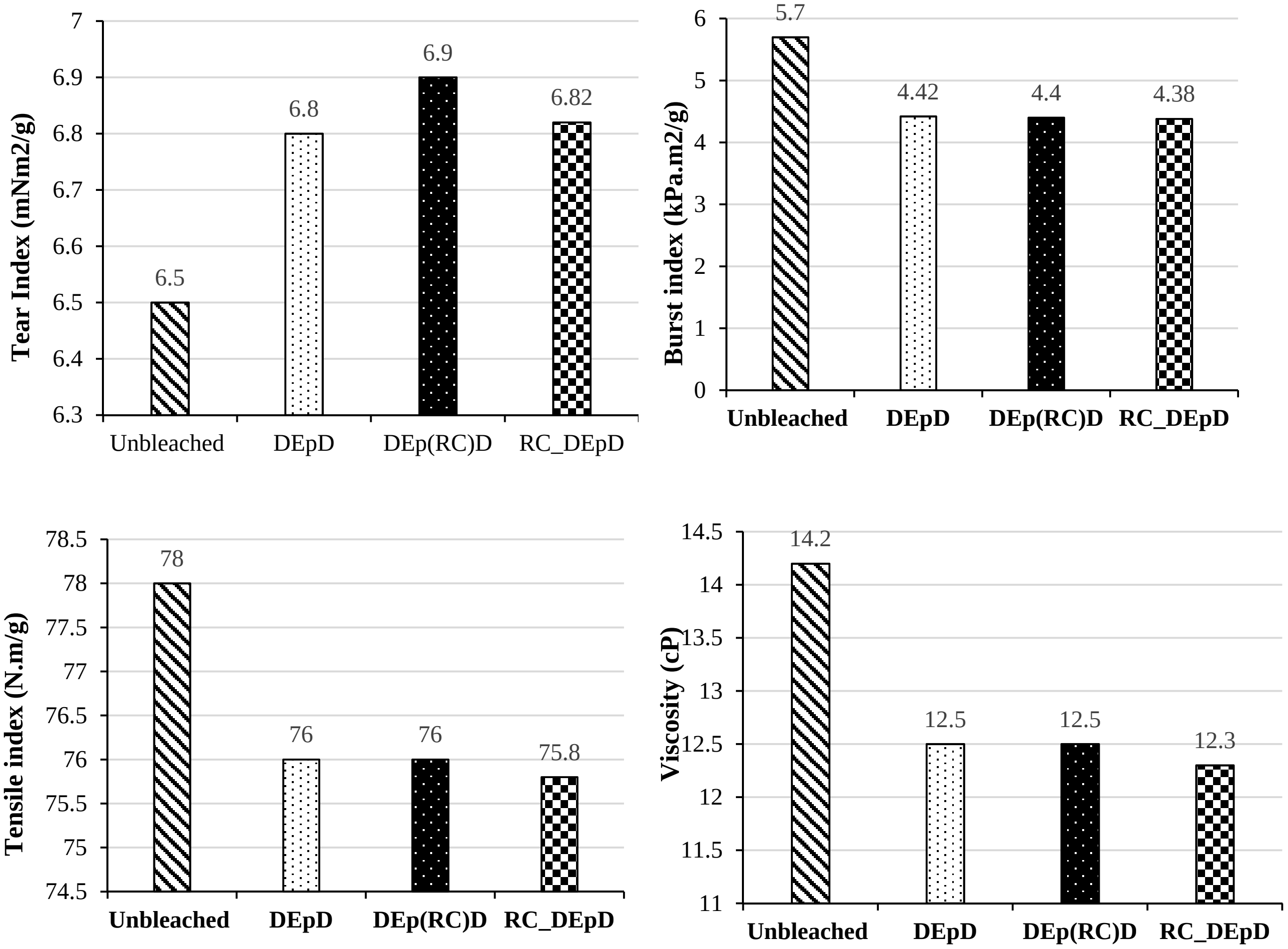

Figure 5.5: Effect of different bleaching sequences on pulp properties; (a) Tear index, (b) Burst index, (c) Tensile index, (d) Viscosity

5.2.1.3. Environmental load generation in bleach effluent

Bleach effluent of the individual stage (D_1, Ep & D_2) was characterized for various environmental parameters like COD, BOD, Color, AOX and chlorophenols in order to study the increased environmental load after washing of pulp with recycled water.

5.2.1.3a. General parameters

The bleach effluent from different sequences was characterized for various environmental parameters. Table 5.3 and Figure 5.6 (a-d), show the BOD, COD, Color and AOX generation during various bleaching stages and total quantities respectively for DEpD, DEp(RC)D and RC_DEpD sequences. DEpD and DEp(RC)D sequence effluent was found to be having lower pollution load as compared to RC_DEpD sequence (84% ISO). This was due to the use of recycled water for washing of all the stages of RC_DEpD bleach sequence and increase in bleach chemical dose to achieve the desired brightness. The major pollution load came from the first two bleaching stages (D_1 and Ep) for all the bleaching sequences. During kraft pulp bleaching, a significant amount of organic matter is dissolved in the first two bleaching stages i.e., chlorination and alkaline extraction [23]

As seen in Figure 5.6a and b RC_DEpD sequence effluent has a higher COD and BOD load as compared to DEpD and DEp(RC)D sequences. This is due to higher chemical dose (0.29) requirement in RC_DEpD sequence to achieve the target brightness (84% ISO) because an increase in the kappa factor leads to the increased COD generation [23]. The color was also highest in RC_DEpD sequence as compared to other bleach sequences (Figure 5.6c). It is also due to presence of higher bleach chemical demand to meet the required brightness level. The COD and Color in a bleach effluent is also a function of the kappa number of the unbleached pulp and KF, the kappa number being the variable has the highest impact. The decrease in the kappa number also decreases the environmental load in terms of COD, BOD, Color and AOX [23, 24]. Same is the case of AOX, as the KF is increased in RC_DEpD sequence the AOX level generation was also at a higher end. The AOX level increases with increase in KF [24].

Table 5.3: Generation of (kg/t O.D. pulp) COD, Color, BOD and AOX during different stages of DEpD, DEp(RC)D and RC_DEpD sequences

Bleaching sequence	**Stages**	**Quantity (Kg/t O.D. pulp)**			
		COD	**Color**	**AOX**	**BOD**
DEpD	D_1	12.9	10.9	0.23	2.4
	E_p	7.3	14.2	0.19	1.7
	D_2	4.5	2.1	0.06	0.6
DEp (RC) D	D_1	12.4	11.8	0.22	2.4
	RC_E_p	8.0	13.6	0.19	1.8
	D_2	4.2	2.4	0.06	0.7
RC_DEpD	RC_D_1	14.6	12.0	0.26	2.7
	RC_E_p	9.3	15.8	0.20	1.8
	RC_D_2	4.4	3.6	0.06	0.7

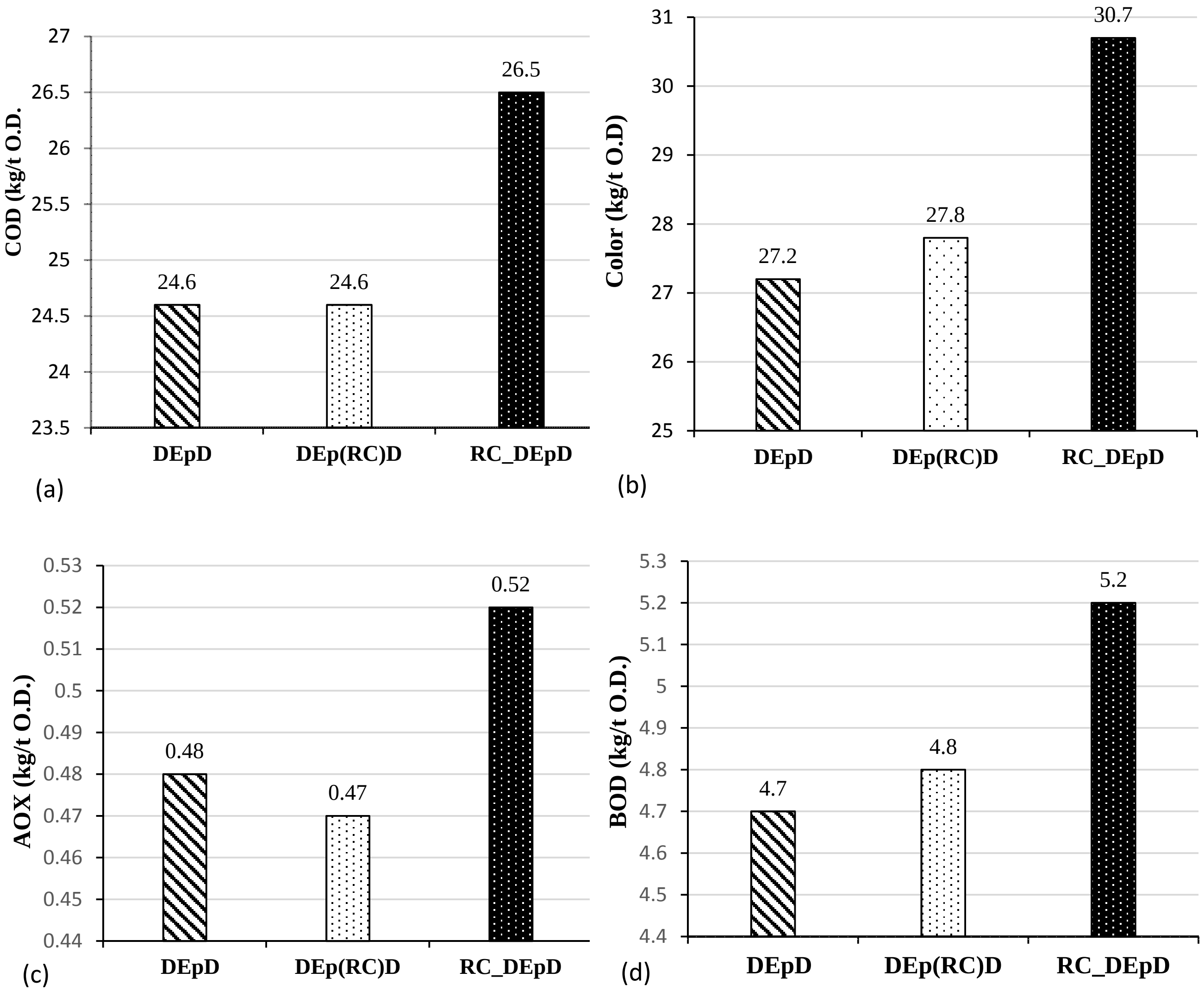

Figure 5.6: Generation of (kg/t O.D. pulp) (a) COD, (b) BOD, (c) Color and (d) AOX during different bleaching sequences

Among total identified compounds in D_1 stage effluent the major share comes from CG (62%) followed by CC (31%) and CP (7%) (Figure 5.7a). Among CP's the DCP are the dominant group followed by TCP and MCP. Among DCP's, 2, 3-DCP is not detected and PCP is also not detected in D_1 stage effluent (Figure 5.8a). Among all the groups the 4-CG (35.8 mg/t O.D. pulp) and 4, 5-DCG (118.2 mg/L of O.D. pulp) has the highest concentrations and 4, 6-DCG (1.2 mg/t O.D. pulp) and 3, 4, 5-TCG (0.5 mg/t O.D. pulp) are detected in small quantities. CV, CS and CSA are not detected in D_1 stage effluent (Table 5.4).

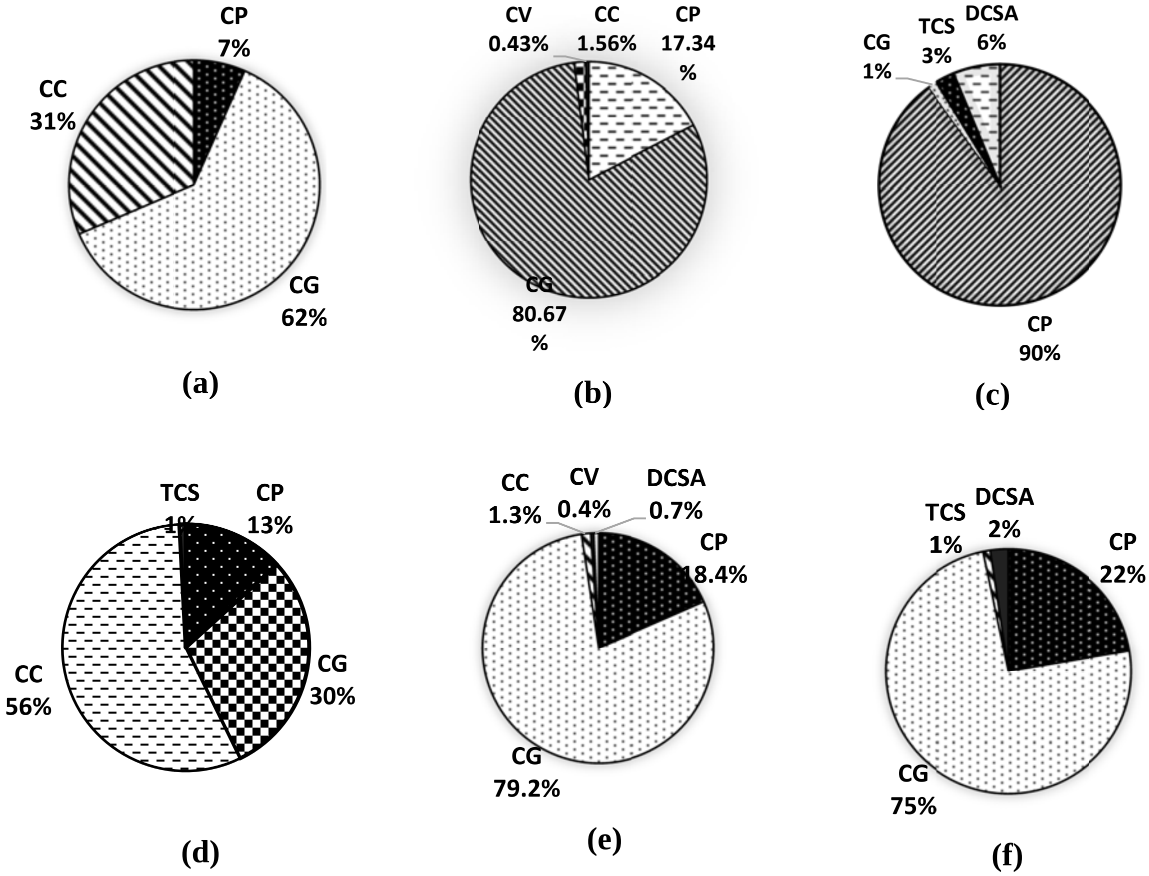

Figure 5.7: Chlorophenols detected in DEpD and RC_DEpD sequences based on chemical family; (a) D_1 stage, (b) Ep stage, (c) D_2 stage, (d) RC_D_1 stage, (e) RC_Ep stage, (f) RC_D_2 stage

5.2.1.3b. Chlorophenolics generation

The wastewater from the individual stages of bleaching sequences DEpD and RC_DEpD was analyzed for chlorophenolic compounds generation (Environmental load) by GC-MS.

(I). Chlorophenols generation during DEpD sequence

The chlorophenolic compounds identified in DEpD sequence effluent is presented in Table 5.4. In DEpD sequence the highest quantity of chlorophenolic compounds were found in extraction stage (Ep), followed by D_1 and D_2. It is due to the fact that during the pulp bleaching process the lignin in the pulp break down and get chlorinated to chlorophenolic compounds which have low solubility in acidic medium (D_1 stage). These compounds get solubilized in alkaline E stage of bleaching [24].

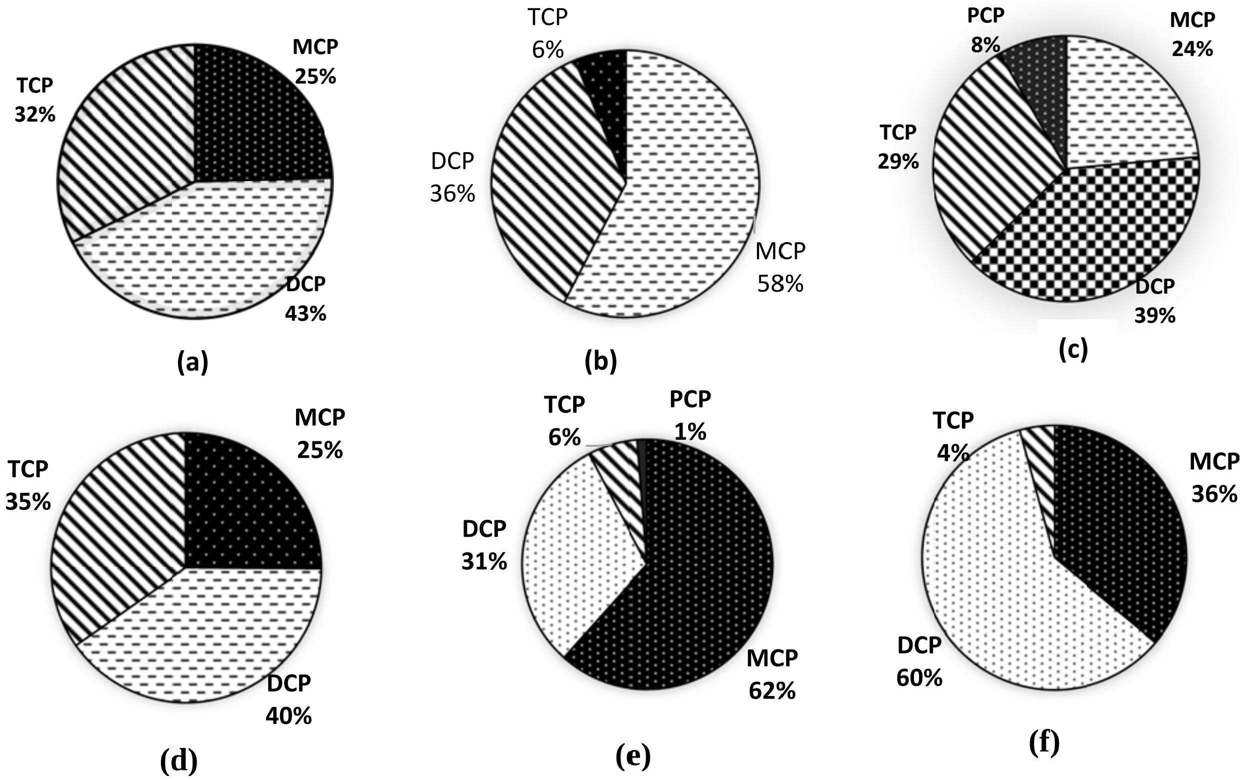

Figure 5.8: Chlorophenols detected in DEpD and RC_DEpD sequences based on number of Cl_2 group attached; (a) D_1 stage, (b) Ep stage, (c) D_2 stage, (d) RC_D_1 stage, (e) RC_Ep stage, (f) RC_D_2 stage

In case of Ep stage effluent, the highest concentration (372.1 mg/t O.D. pulp) of chlorophenolic compounds were detected in DEpD sequence. Among all the detected groups the highest contributor is CG (80.7%) followed by CP (17.3%), CC (1.6%) and CV (0.43%) which are detected in trace quantity. As it can be seen that CV are not detected in D_1 stage effluent but these are detected in Ep stage (Figure 5.7b). Among the CP, the highest concentration comes from 3-CP (35.6 mg/t O.D. pulp) followed by 2,5-DCP (19.8 mg/t O.D. pulp), 2,3,4-TCP (2.5 mg/t O.D. pulp) , 3,4-DCP (1.8 mg/t O.D. pulp), 4-CP (1.5 mg/t O.D. pulp) and 2,4,5-TCP (1.5 mg/t O.D. pulp) and 2,6-DCP (0.9 mg/t O.D. pulp) are detected in trace quantities (Table 5.4). 2,3-DCP, 2,3,6-TCP, 2,3,5-TCP and 2,4,6-TCP are not detected in the effluent. Among CG, the highest concentration comes from 4,5-DCG (169.2 mg/t O.D. pulp) followed 4-CG (126.7 mg/t O.D.

pulp), 4,6-DCG, 3,4,5-TCG and 4,5,6-TCG. Among other chlorophenolics, a significant contribution comes from Tet-CC (5.8 mg/t O.D. pulp), 5, 6-DCV (1.6 mg/t O.D. pulp and PCP (0.6 mg/t O.D. pulp) and others are not detected (Table 5.4).

For D_2 stage, it has the lowest concentration (23.01 mg/t O.D. pulp**)** of chlorophenolics detected. Among the identified compounds, the highest contribution comes from CG (75 %), followed by CP (22 %), DCSA (2 %), TCS (1 %) and CS and CV are not detected (Figure 5.7c). Among detected CP's, the highest concentration comes from 3-CP (1.3 mg/t O.D. pulp), 3, 4-DCP (1.3 mg/t O.D. pulp), 2, 4, 5-TCP (1.0 mg/t O.D. pulp), 2, 4, 6-TCP (0.9 mg/t O.D. pulp) and 4-CP (0.4 mg/t O.D. pulp). 2, 6-DCP, 2, 5-DCP, 2, 4-DCP and 2, 3, 4-TCP found in trace quantities. 2, 3-DCP, 2, 3, 6-TCP, 2, 3, 5-TCP and PCP are not detected in D_2 stage effluent (Table 5.4**).** CG contribution is highest and among them the highest contribution comes from 4, 5-DCG (15.6 mg/t O.D. pulp) followed by 3, 4, 5-TCG (0.1 mg/t O.D. pulp) and other CG are not detected in the effluent. Among others only TCS and 2, 6-DCSA are detected in D_2 stage effluent and that also in trace quantities (< 1.0 mg/t O.D. pulp).

Table 5.4: Chlorophenols generation (mg/t O.D. pulp) during different stages of DEpD sequence

S.No.	**Compounds**	**Quantity mg/t O.D. pulp)**			
		D_1	**Ep**	**D_2**	**DEpD**
1	3-CP	3.1	35.6	1.3	40
2	4-CP	1.0	1.5	0.4	2.9
3	2,6-DCP	1.4	0.9	0.01	2.31
4	2,5-DCP	4.1	19.8	1.3	25.2
5	2,4-DCP	0.2	0.8	0.2	1.2
6	2,3-DCP	ND	ND	ND	ND
7	3,4-DCP	1.5	1.8	1.3	4.6
8	4-CG	35.8	126.7	ND	162.5
9	2,4,5-TCP	2.3	1.5	1.0	4.8
10	2,3,6-TCP	ND	ND	ND	ND
11	2,3,5-TCP	ND	ND	ND	ND
12	2,4,6-TCP	1.5	ND	0.9	2.4
13	4,5-DCG	118.2	169.2	15.6	303
14	2,3,4-TCP	1.6	2.5	0.2	3.3
15	4,6-DCG	1.2	0.8	ND	2.0
16	3,6-DCC	57.8	ND	ND	57.8
17	3,5-DCC	15.8	ND	ND	15.8
18	3,4,6-TCG	ND	ND	ND	ND
19	3,4,5-TCG	0.5	1.2	0.1	1.8
20	4,5,6-TCG	ND	1.8	ND	1.8
21	5,6-DCV	ND	1.6	ND	1.6
22	PCP	ND	0.6	ND	0.6
23	Tet-CG	ND	ND	ND	ND
24	TCS	ND	ND	0.2	0.2
25	Tet-CC	5.5	5.8	ND	11.3
26	2,6-DCSA	ND	ND	0.5	0.5
	Total	**251.5**	**372.1**	**23.0**	**646.6**

ND- Not detected

(II) Chlorophenols generation during RC_DEpD sequence

The chlorophenolic compounds identified in RC_DEpD sequence effluent is presented in Table 5.5. In RC_DEpD sequence the highest quantity of chlorophenolic compounds were found in extraction stage (Ep), followed by D_1 and D_2. Among total identified compounds in RC_D_1 stage effluent the major share comes from CG (56%) followed by CC (30%) and CP (13%) and TCS (1%) (Figure 5.7d). Among CP's the DCP (40%) are the dominant group followed by TCP (35%)

and MCP (25%). Among DCP's, 2, 3-DCP is not detected and PCP is also not detected in D_1 stage effluent (Figure 5.8d). Among all the groups the CG contribute the highest concentration i.e., 4, 5-DCG (125.8 mg/L of O.D. pulp) followed by 4-CG (42.9 mg/t O.D. pulp) and 4,6-DCG (2.8 mg/t O.D. pulp) and 3,4,5-TCG (0.3 mg/t O.D. pulp) are detected in small quantities. CV and CSA are not detected in RC_D_1 stage effluent (Table 5.5).

For RC_Ep stage effluent, the highest contributor is again CG (79.2%) followed by CP (18.4%), CC (1.2%), DCSA (0.7%) and CV (0.4%). It can be seen that, unlike DEpD sequence CV is detected in RC_DEpD sequence **(**Figure 5.7e). RC_Ep contributes to the highest concentration (395.7 mg/t O.D. pulp) to chlorophenolics in RC_DEpD sequence. Among the CP, the highest concentration comes from 3-CP (43.8 mg/t O.D. pulp) followed by 2,5-DCP (20.0 mg/t O.D. pulp), 2,4,5-TCP (3.4 mg/t O.D. pulp), 3,4-DCP (1.7 mg/t O.D. pulp), 2,3,4-TCP (1.3 mg/t O.D. pulp), 4-CP (0.8 mg/t O.D. pulp). 2,6-DCP, 2,3-DCP, 2,3,6-TCP, 2,3,5-TCP and 2,4,6-TCP are not detected in the effluent (Table 5.5). Among CG, the highest concentration comes from 4,5-DCG (179.1 mg/t O.D. pulp) followed 4-CG (130.3 mg/t O.D. pulp), 4,6-DCG, 3,4,5-TCG and 4,5,6-TCG. Among other chlorophenolics, a significant contribution comes from Tet-CC (5.0 mg/t O.D. pulp), 5, 6-DCV (1.6 mg/t O.D. pulp), 2, 6-DCSA (2.8 mg/t O.D. pulp), and PCP (0.9 mg/t O.D. pulp) and others are not detected (Table 5.5).

In case of RC_D_2 stage effluent, the highest contribution comes from CG (75%) followed by CP (22%), DCSA (2%) and TCS (1%) **(**Figure 5.7f). The total concentration (31.02 mg/t O.D. pulp) is lowest among all the stages of RC_DEpD sequence. Among detected CP's, the highest concentration comes from 3-CP (3.1 mg/t O.D. pulp), 3, 4-DCP (1.5 mg/t O.D. pulp), 2, 4, 5-TCP (0.9 mg/t O.D. pulp), 2, 4, 6-TCP (1.2 mg/t O.D. pulp) and 4-CP (0.3 mg/t O.D. pulp). 2, 6-DCP, 2, 5-DCP, 2, 4-DCP and 2, 3, 4-TCP found in trace quantities. 2, 3-DCP, 2, 3, 6-TCP, 2, 3, 5-TCP and PCP are not detected in D_2 stage effluent (Table 5.5**).** Among other chlorophenolics 4, 5-DCG (21.6 mg/t O.D. pulp) followed by 3, 4, 5-TCG (0.4 mg/t O.D. pulp) and other CG are not detected in the effluent. Among others only TCS (0.5 mg/t O.D. pulp) and 2,6-DCSA (0.8 mg/t O.D. pulp) are detected in D_2 stage effluent and that also in trace quantities.

It can be observed from Table 5.4 and 5.5 that, the detected compounds and contribution of detected groups are almost same in the DEpD and RC_DEpD sequence. The difference is only in the concentrations of the chlorophenolics in both the sequences, RC_DEpD sequence has higher concentration of chlorophenolics (709.7 mg/t O.D. pulp) than the DEpD sequence (646.6 mg/t O.D. pulp), which is because of the washing of the pulp with recycled water.

Table 5.5: Chlorophenols generation (mg/t O.D. pulp) during different stages of RC_DEpD sequence

S.No.	**Compounds**	**Quantity (mg/t O.D. pulp)**			
		RC_D1	**RC_Ep**	**RC_D_2**	**RC_DEpD**
1	3-CP	4.0	43.8	1.8	49.6
2	4-CP	1.2	0.8	0.2	2.2
3	2,6-DCP	1.0	ND	0.02	1.02
4	2,5-DCP	5.2	20.0	1	26.2
5	2,4-DCP	1.2	0.5	0.5	2.2
6	2,3-DCP	ND	ND	ND	ND
7	3,4-DCP	2.1	1.7	1.4	5.2
8	4-CG	42.9	130.3	0	173.2
9	2,4,5-TCP	2.8	3.4	0.9	7.1
10	2,3,6-TCP	ND	ND	ND	ND
11	2,3,5-TCP	ND	ND	ND	ND
12	2,4,6-TCP	2.1	ND	1.1	3.2
13	4,5-DCG	125.8	179.1	18.3	323.2
14	2,3,4-TCP	2.3	1.3	0.2	3.8
15	4,6-DCG	2.8	2.0	ND	4.8
16	3,6-DCC	63.7	ND	ND	63.7
17	3,5-DCC	20.1	ND	ND	20.1
18	3,4,6-TCG	ND	ND	ND	ND
19	3,4,5-TCG	0.3	ND	0.1	0.4
20	4,5,6-TCG	ND	2.5	ND	2.5
21	5,6-DCV	ND	1.6	ND	1.6
22	PCP	ND	0.9	ND	0.9
23	Tet-CG	ND	ND	ND	ND
24	TCS	1.3	ND	0.4	1.7
25	Tet-CC	4.2	5.0	ND	9.2
26	2,6-DCSA	ND	2.8	0.6	3.4
	Total	**283**	**395.7**	**26.52**	**705.22**

ND- Not detected

5.2.1.4. Effect of recycling

The unbleached pulp after pulping was washed followed by bleaching to target brightness of 84% ISO. The washing at this point does not involve any problem and can successfully replace the fresh water with treated recycled water. The effect of recycling in pulping section does not involve any problem. The effect of recycling in bleaching section was estimated by calculating the change in bleach chemical dose, environmental load and fresh water consumption by recycling. The comparison is presented in Table 5.6, in terms of percentage change in all the parameters. The effect of recycling is not significant in DEp(RC)D sequence i.e., on washing only Ep stage in bleaching section, there is no effect on the beach chemical dose. Hence washing by recycled water at Ep stage is feasible and it will contribute very insignificantly to the environmental load of the bleaching effluent. The effect of RC_DEpD sequence on bleach chemical dose and environmental load has been found significant and results are presented in Table 5.6 and Table 5.7 respectively**.**

On replacing the recycled water for washing in bleaching stages, there is a decrease in the brightness of 2±0.5 % ISO was found. This requires an additional 3.4% chemical dose (Table 5.6). The impact of additional dose on environmental parameters are given in Table 5.7. Similarly, the environmental load was also compared after the recycling of treated water and there is an increase in the environmental parameters was found. The data given in Table 5.7 show that the COD was increased to 7.2%, the increase in BOD was 9.6%, the color was increased by 9.4% and AOX increase was 7.6%. The increase in the bleach chemical dose is 3.4% that can be compensated with the fresh water consumption in the bleaching section of the paper mill which is highly water intensive [5].

As far as ions removal and build-up is concerned, the ions i.e., Na^+, Ca^+, Cl^- and SO_4^{2-} are considered. The characteristics of EC treated SC effluent as given in Table 5.1 show that 65 % of Cl^-, 38% of SO_4^{2-}, 35% of Ca^{2+} and 55% of Na^+, 16% of COD, 65 % of BOD and 3% of color do not get removed by EC treatment and get recycled and contributes for some build up of these ions. Up to 90% of BOD and 50% of COD, color and some amount of Cl^- and SO_4^{2-} may get removed during secondary treatment of wastewater, thus the buildup of these ions may not be significant. In mill with chemical recovery, the wash water from pulp washing of unbleached pulp goes to recovery and it takes care of sodium and sulphate ions and some portions of Ca^{2+} and Cl^- also get reduced. Thus build up of the dissolved solid in the recycled water will remain within reasonable limit. These aspects have to be studied further in detail.

Table 5.6: Comparison of chemical charge (kg/t O.D. pulp) required for different bleaching sequences for achieving 84% ISO target brightness

Sequence	Kappa Factor	Target Brightness (% ISO)	Chemical charge (Kg/t O.D. pulp)	Increase in chemical charge (%)
DEpD	0.28	84	44.8	3.4
RC_DEpD	0.29	84	46.4	

Table 5.7: Comparison of generation of (kg/t O.D. pulp) environmental load during different DEpD, DEp(RC)D and RC_DEpD sequences

Parameters	DEpD	RC_DEpD	Percentage increase
COD (g/t O.D. pulp)	24.6	26.5	7.2
BOD (g/t O.D. pulp)	4.7	5.2	9.6
Color (g/t O.D. pulp)	27.8	31.4	9.4
AOX (g/t O.D. pulp)	0.48	0.52	7.6
CP (mg/t O.D. pulp)	646.6	705.22	8.3

5.4 MAJAOR FINDING

- EC treated wastewater can be used as wash water for washing of unbleached and bleached pulp.
- There is no change in the mechanical properties of washed unbleached or bleached pulp.
- No additional bleach chemical required when used for washing of unbleached pulp.

- Additional 3.4% bleach chemical charge is needed when used for washing of bleached pulp and generates approximately 10% additional environmental load.
- Recycling of EC treated secondary clarifier effluent may be an attractive option to reduce freshwater consumption in pulping and bleaching sections.

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Chapter 6

CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

Based on the present study, the following conclusions can be drawn:

1. EC is an efficient method for the degradation of recalcitrant organic matter present in the wastewater.
2. EC improved the biodegradability of the effluents by removal of recalcitrant organic compounds. This indicates the easy removal of degradation products in the biotreatment.
3. This technique can be used as a post-treatment step after the conventional biological wastewater treatment as a tertiary treatment option.
4. Recycling of the treated wastewater using EC treatment may be an attractive option to reduce the fresh water requirement in pulping and bleaching sections of pulp and paper mill.

6.2 RECOMMENDATION AND FUTURE WORK

1. Various electrode material can be studied for the desired pollutants. Different electrode coating materials need to be developed to decrease side reaction and to promote desired reaction for attractive benefit and return of investment. One can study titanium as a better option.
2. Using solar panels for the electricity requirement to run the system appears to be a better option for larger industrial application.
3. Electrochemical reactor design is big challenges in electrochemical technology due to its response on mass transfer during operation. The lack of mass transfer and

current distribution in electrochemical reactor will collapse all advantages of electrochemical technology. So, it is need to be studied in detail.

4. More extensive study on recycling is required as electrochemical technology is a good option for color and recalcitrant organic removal. One can study the non-process elements removal that can be done by one more step of treatment after EC and ion exchange can be a better option for that.