STUDIES ON THE GENERATION OF CHLOROPHENOLICS FORMED DURING BLEACHING OF CHEMICAL PULPS

A THESIS

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by
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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **STUDIES ON THE GENERATION OF CHLOROPHENOLICS FORMED DURING BLEACHING OF CHEMICAL PULPS** in partial fulfilment of the requirements and for the award of the Degree of Doctor of Philosophy and submitted in the Department of Paper Technology of the Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during a period from January, 2003 to April, 2007, under the supervision of Dr. Satish Kumar, Professor, Indian Institute of Technology Roorkee, Roorkee and Dr. N.J. Rao, Formerly Professor, Indian Institute of Technology Roorkee, Roorkee.

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

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ABSTRACT

During the production of bleached chemical pulp, chlorine and chlorine containing bleaching agents are used, that form the chlorinated organic compounds. The bleach plants effluents are known to be the main contributor to the effluent toxicity, color and BOD. The chlorinated organic compounds formed during bleaching of pulp have proved to be highly toxic to aquatic organism that affects unfavorably human health as well. These compounds are quite continual in the environment and readily accumulate in organisms. These compounds are also responsible for the deterioration of flavour of sea food. So these compounds are of great environmental concern. The end of the pipe treatment methods employed by Indian paper mills consist of primary treatment (clarification) and secondary treatment plants (mostly aerobic).These methods while being effective in reducing suspended solids and BOD significantly, with small reduction in COD, AOX and color loads. Thus the treated wastewater discharged from Indian paper mills is expected to contain chlorinated organic compounds. The bleach plant effluents contribute about 65% of total BOD and 90% of total color load discharged from a paper mill. Chlorination (C) and extraction (E) stages often account for the largest toxicity.

The aim of present investigation is to identify a set of pulp chlorination conditions in which the production of chlorinated phenolic compounds would be minimal without any adverse impact on pulp quality. Such studies have mostly carried out on soft wood and some hard wood pulps. A very little information is available on non-wood and agro-residue pulps, which are important in Indian context, as wood resources are continuously decreasing.

In view of above the following objectives were formulated for this study:

I. To identify and quantify various chlorophenolic formed during different stages of pulp bleaching.

II. To study the impact of change in chlorination condition on the production of toxic chlorinated phenolics in C, E and H stages.

III. To study the integration of oxygen delignification stage with conventional CEH and DED bleaching sequences and its impact on the generation of chlorophenolics.

IV. To study the impact of partial or complete replacement of chlorine by chlorine dioxide in C stage and full replacement by chlorine dioxide in H stage on generation of chlorophenolic compounds.

V. To study the impact of addition of peroxide in E stage (E_P) on the generation of chlorophenolic compounds.

VI. To study the impact of modified sequences (to obtain 80% target brightness pulps) on the generation of chlorophenolic compounds.

VII. To study the effect of above changes on :

- Pulp characteristics
- Pollution load generation

The study was carried out on bamboo and jute cady pulps.

Estimation of various chlorophenolics has been carried by gas chromatography. The impact of changes in C stage bleaching conditions and modification in CEH bleaching sequences have been investigated for the generation of chlorophenolics formed in effluents during CEH bleaching. Efforts have also been made to make bleached pulp of 80% brightness through different bleaching routes with in a view to reduce the generation of chlorophenolic compounds. The results indicate that in various bleaching effluents six categories of chlorophenolic compounds are present. These are chlorophenols, chlorocatechols, chloroguaiacols, chlorosyringaldehydes, chlorosyringols and chlorovanillins. These chlorinated compounds have been categorized into mono, di, tri, tetra, and penta chlorophenolic compounds and also as catechols, phenols, guaiacols and other chlorophenolic compounds. The results show that the impact of all modifications are similar in both bamboo and jute cady pulps with few exceptions such as 2,3 dichlorophenol is observed in effluent from jute cady and the concentration of tetrachlorocatechol, pentachlorophenol, 5,6 dichlorovanillin and trichlorosyringol is much higher in jute cady effluents in comparison to bamboo effluents. These results of various modifications in bleaching conditions for the two pulps are summarized under these broad heads:

Changes in C stage bleaching conditions

- An increase in C stage pH from 1.5 to 4, resulted in the reduction of total chlorophenolic compounds formed in C, E and H stage effluents, with the reduction in effluent color, and pulp viscosity.
- By decreasing C stage temperature from 35 to 15°C, the formation of total chlorophenolic compounds is decreased, as well as COD and color values also reduced. The pulp CED viscosity is also improved.
- The formation of total chlorophenolic compounds increase sharply as C stage consistency increased from 2 to 4%. COD and color values are also increased. The pulp viscosity drops.
- By changing the distribution of bleach chemical between C and H stages, it is observed that chlorophenolic compounds in C and E effluent increases sharply but the quantity of chlorophenolic compounds decreases in H stage effluent. The results show that the quantity of total chlorinated phenolic compounds increase by 135% in C stage effluent, 96% in E stage effluent and decrease by 39% in H stage effluent as distribution of bleach chemical between C and H stages is varied from 45:55 to 65:35.
- The formation of total chlorophenolic compounds decreases appreciably as chlorine is substituted by chlorine dioxide from zero to 100% in C stage, a substantial reduction in total chlorophenolic compounds is observed at 100% substitution. The effluent COD and color values are also reduced; a brightness and pulp viscosity is improved substantially.
- The result indicates that splitting of chlorine dose reduced the formation of chlorinated phenolic compounds when washing or no washing has been done after completion of C_1 stage. The effluent COD and color values are reduced; the brightness and pulp viscosity is improved.

Modifications in CEH bleaching sequences

- The complete replacement of hypochlorite by chlorine dioxide will change the bleaching sequence to CED. The bleaching result and environmental load from C and E stage effluent remain unchanged. The contribution of H stage effluent to the bleaching sequence in terms of chlorinated phenolic compounds, effluent COD and color is small, but the biggest gain is in terms of pulp viscosity and brightness.

- The addition of peroxide in E stage i.e. E_P reduce the total chlorophenolic compounds. The pulp viscosity and brightness is also improved. Peroxide is an oxidizing and decolouring agent. The chlorophenolic compounds are oxidized and thus reducing the quantity of chlorophenolics in E_p stage effluent. The oxidation reaction results in increased dissolution of lignin fragments giving an effluent of lower COD and a small reduction in CE kappa number of pulp. The bleaching action of peroxide also improves the brightness of the pulp.
- Due to the introduction of oxygen pre bleaching stage followed by CEH the formation of total chlorophenolic compounds decrease in C, E and H effluents. The effluent COD and color value is also reduced. It was observed that there is a drop in viscosity. The process of oxygen delignification is another way to reduce the amount of chlorophenolic compounds. This procedure is used to reduce the pulp kappa number by 40 – 50% which in turn reduces the bleach chemical demand in the following C, E, and H stages to nearly the same extent which reduces the environmental loads – chlorophenolic compounds, COD and color very significantly. Oxygen pre bleaching stage reduces the pulp kappa number and bleach chemical demand, thus reduces the formation of chlorophenolic compounds.
- Oxygen pre bleaching stage followed by DED further reduces the formation of total chlorophenolic compounds very significantly. The pulp brightness is improved but pulp viscosity drops slightly.

80% ***brightness pulp by different routes***

- 50% replacement of chlorine by chlorine dioxide i.e. $D_{50}C_{50}$ in C stage gives reduction in the formation of total chlorophenolic compounds, effluent COD and color. And the pulp viscosity improves.
- Splitting of chlorine dose gives lower formation of chlorinated phenolic compounds in C, E and H stage effluents. Pulp viscosity is also improved.

- Oxygen delignification followed by DED reduces the formation of total chlorophenolic compounds. The effluent COD and color values are also reduced and the pulp viscosity is also reduced slightly.
- By changing all the C stage bleaching conditions the new bleaching conditions are applied. In this stage the formation of chlorophenolic compounds decreased. Effluent COD and color value also decreased but the pulp viscosity drops down sharply.

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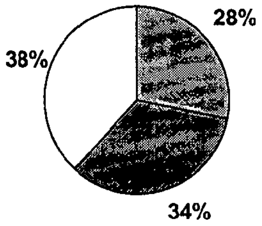
INTRODUCTION

1.1 PRESENT SCENARIO OF PAPER INDUSTRY IN INDIA

The paper industry plays a very prominent role in the world economy. This sector's global annual revenue today, from its over 300 million tones of product, exceeds 500 billions US Dollars. Indian paper industry also plays an important role in the Indian economy. The overall paper consumption in India has reached 5.8 million tones in 2004-05 [25]. The demand for paper, paper board and newsprint is expected to rise steadily in the future. Future paper demand will be determined by certain factors including- the level of national income, the level of industrial production, the level of literacy and education, the size of population, the price of paper etc. It can be said that the demand for paper will increase and the industry will have to gear itself for modernization, process up gradation, cogeneration schemes, quality and environmental improvement etc [25].

Based on the raw material usage, the Indian pulp and paper industry can be classified into three categories- wood based, agro based and waste paper based. The utilization of waste paper plays a pivotal role in meeting the raw material demand of the paper industry. In the year 2005 waste paper contributed 38% of the total paper produced in the country. And by 2010 the contribution of waste paper is likely to go up to 40% [25].



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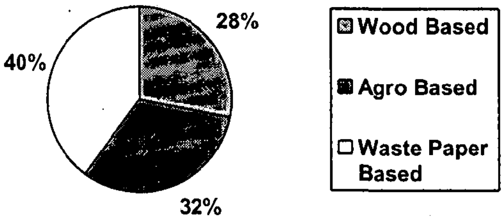

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The dependence on agricultural residues and secondary fibres has increased significantly in the last 15 years primarily due to shortage of forest based raw materials [42]. Indian paper industry is domestic market oriented which is largely due to Government industry policy initiated in the 1970's. There are around 666 paper manufacturing units. Large units (above 100tpd) are 57, medium units (50 – 100tpd) are 88 and small units (less than 50tpd) are 525; Nearly 1.25 million tones of capacity is closed mainly due to technological obsolescence and environmental reasons [25]. The Indian paper industry has an installed capacity of 6.2 million tones per annum [25, 42], the industry produced about 5.79 million tones in year 2005-06 as compared to 5 million tones in 2002. India's paper manufacturing capacity is expected to grow attaining 8.75 million tones by the end of 2008-09 and 10 millions tones by 2010 [25, 42].

Environmental pollution control polices have been introduced in India at different times, such as the water Act 1974 and Air Pollution Control Act 1981. In recent years CREP has become more environment conscious because of public perception about environment and has begun to force industry to perform or close down. In the year 2003, Ministry of Environment and Forestry, Govt. of India has come out with a responsibility for environment protection for paper industry which is required to be complied by entire industry between 2005 to 2008 [25]. Pulp and paper industry is amongst the top 20 highly polluting industries in India. The paper industry is confronted with environmental issues which differ from one segment to another. The problem is most acute with regard to liquid effluent as the requirement of water is very high. A rough estimate shows that a large kraft paper mill where chemical recovery forms an integral part, the water requirement varies from 120 – 200 m^3/ t of paper, where as in a small paper mill based on agricultural residue with no chemical recovery, water requirement is 100 – 200 m^3/ ton of paper [42]. As such, these small paper mills are discharging liquid effluent to the receiving streams causing a high pollution load. Some of the key problems that the Indian paper mills confront with are - AOX and color in discharge effluents, disposal of lime sludge and also toxic gases and odour during pulping stage. Due to these reasons pulp and paper industry in its present form is considered to be a major polluting industry. However, to control water pollution, presently the Indian pulp and paper mills have set up effluent treatment plants.

1.2 BLEACH PLANT EFFLUENT CHARACTERISTICS

The fibrous raw materials essentially consist of cellulose, lignin and other extraneous substances. During pulping process mostly 80% of the lignin and other extraneous substances are dissolved in the cooking liquor (as black liquor). The aim of pulping process is to remove maximum lignin selectively without affecting the cellulose. The residual lignin imparts brownish color to the pulp, due to the presence of chromophoric compounds which are the functional groups of degraded and altered lignin bound to the fibres. This must be removed or converted in the bleaching process to be followed to obtain a pulp of high brightness which can be further used in the manufacture of high grade white paper [30]. This is done by multistage bleaching process using oxidizing chemicals such as chlorine, chlorine dioxide, hypochloride, hydrogen peroxide, ozone and oxygen. The suitability of chlorine for pulp bleaching was documented in 1868 and still it is the most widely used bleaching chemical in Indian pulp and paper mills. In India due to the economical reasons, the conventional CEH or CEHH bleaching sequences are commonly used to bleach the pulp to the desired brightness level.

The bleaching of pulp with chlorine or chlorine based chemicals generate various chlororganics which include chlorinated resin and fatty acids, chlorinated phenolics, dioxins and furans which are found to have high toxic effects on the receiving environment [34,35,91,110,123,131]. Hence bleach plants are a major source of environmental pollution and the effluent released from the bleach plant have high BOD, COD, AOX and color loads [39]. The AOX, EOX and POX are used normally to indicate the level of the organochlorine compounds formed in the bleaching process in the environmental samples. Regulation to limit the discharge of AOX has been established in many countries [107], while some countries are still debating on it [28]. In India the maximum discharge limit for TOCl in mill effluent has been specified to be 2 kg / ton [92].

The nature and extent of formation of chloro phenolic compounds is determined primarily by the residual lignin content in the pulp and type of bleaching chemical employed. There have been attempts to minimize the generation of organochlorine compounds during pulp bleaching by substituting chlorine gas by chlorine dioxide or eliminating the use of chlorine containing compounds [57,95]. In response to environmental concerns, governmental regulations on emission of chlorinated organic matter, pulp and paper mills are forced to develop and introduce a number of new processes and process modification in order to minimize the discharge of chlorinated phenolic organics.

1.3 TOXICITY OF BLEACH PLANT EFFLUENT

The toxicity of bleach plant effluents have been studied extensively [1,6,59,62,63,66,74,78,101,127,128]. The studies have indicated that during chloro bleaching of pulp the lignin macro molecules are degraded to non volatile smaller species which have harmful effects on the environment and the human health. The researches have been going on to identify and study the toxicity of various chemicals coming from different sections of pulp and paper mills. Toxicity is a vague and variable parameter. The toxicity of the whole mill effluent of a given mill directly depend upon the total organically bound chlorine, the extractive content of the raw material being used and to what extent these extractives are remove during pulping and other processes [48]. A small increase in the concentration of chlorinated phenolic compounds will change the toxicity effect from zero to 100%. Chlorinated phenolic compounds are the most toxic substance in the bleach plant effluent. The toxicity of the effluent will depend on the residual lignin content of the pulp which invariably is the result of the increase in the kappa number of unbleached pulp [29]. Quantification of toxicity in effluent is difficult as the results are strongly influenced by the intricacies in the test methods. Lethal Concentration (LC) is usually expressed as $^{96}LC_{50}$ which indicates the level of effluent toxicity. The sub lethal effect of bleach plant effluent are probably of more importance for the environment than the lethal effects, because they show the long term effects from the accumulation of toxic substances in the organisms [36,69].

Free chlorine among the chlorinating agents used for the bleaching process is most reactive to fish. Hypochlorite, chlorine dioxide and chlorate are also toxic compounds but normally the concentration of these compounds will be low in bleach plant effluents. Chlorates can be transformed to chlorites in some organisms such as algae or bacteria, and can be poison to them. It undergoes a complex and series of reactions involving chlorination, oxidation and de-methylation which result in the formation of a wide range of structurally diverse organic compounds. Some of them are considered to be harmful to the environment due to the following reasons:

1. Highly resistant to biotic and abiotic degradation.
2. Toxic to biota.
3. Bio-accumulation at higher level [124,128].

The main contributors to the toxicity of the plant effluent are the effluent of chlorination and first alkaline extraction stages [19,71]. In the C stage effluent the toxicity are mainly due to chlorophenols, which contributes 80% of the toxicity at a charge equivalent to 50% of chlorine demand. In E stage effluent 90% of toxicity is due to 3,4,5- trichloroguaiacol, tetrachloroguaiacol and several fatty acids (mono and dichlorohydroabietic acid and epoxystearic acid) [26]. The chlorinated phenols are generally biologically degradable. The biodegradation rate decreases as the level of chlorine substitution (i.e. the number of chlorine atoms which have been added to the basic phenolic structure) increases [26].

One of the key impacts of the discharge of bleached plant effluent to the surrounding ecosystem is that the toxic compounds such as polychlorinated dibenzodioxin (PCDD) and dibenzofuran (PCDF) persistently bioaccumulate in higher level organisms such as crabs, clams, mussels and fish. Among the congeners, 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) is the most toxic. Chlorinated dioxins and furans are two particular forms of chlorinated compounds which warrant special mention, based on the focus of public discussions. Research has indicated that the major part of dioxin/furan formation occurs in the first chlorination stage (C) and is then carried through successive bleaching stages [26].

The chlorinated organic compounds are found to be carcinogenic, mutagenic and causing acute and chronic toxicity to aquatic life [3,21,38,52,60,112]. They also persist in the environment and pose the threat of bioaccumulation [6,33,73]. 2,4 dichlorophenol, 2,4,5 trichlorophenol, pentachlorophenol, chlorinated dioxin, dibenzofurans and chloroforms are carcinogenic, whereas chlorocatechols are strongly mutagenic [104]. A large number of organic compounds present in pulp and paper mill waste water are acutely toxic to fish [3,21,38,52,70,77,82,86,102,113,119]. Low molecular weight chlorinated compounds such as resin acids, fatty acids, neutral diterpenes, phenols and their chlorinated analogues are major contributors to the poisoning of fish. The toxicity of compounds in pulp and paper mill effluents is related to the bioaccumulation. Chlorinated phenolics and other chlorinated compounds in bleaching waste water accumulate in fish tissues particularly in lever. Recent studies have even shown that reproduction of fish is affected at concentration of the pulp mill effluents. The analysis of samples of fish species showed that they contained small amounts of chlorinated phenols and guaiacols in their extractable fats. Similarly mill effluents were found to have an inhibitory effect on growth of plants and animals. Inhibition of photosynthesis may be caused due to toxic properties of the effluent. It has been found that physical parameters such as pH, temperature etc. in the aquatic environment may strongly influence the toxicity of pollutants [36].

Hence it is pertinent to identify these organically bound chlorine compounds to minimize their effects on the environment.

1.4 ORIGIN AND IDENTIFICATION OF CHLOROORGANICS

Chlorinated phenolic compounds such as chlorophenols, guaiacols and catechols are produced as degradation products of lignin during pulp bleaching using chlorination procedures. The lignin molecule in soft wood and hard wood is composed of p-coumaryl, coniferyl and sinapyl alcohols. Softwood lignin is guaiacyl lignin derived mainly from coniferyl alcohol while hard wood lignin is guaiacyl-syringyl lignin formed by co-polymerization of coniferyl and sinapyl alcohols. 1 to 5% of p-coumaryl alcohol also participates in the formation of both softwood and hardwood lignins. Grass lignins appear to be like hardwood lignins but some grass lignins are thought to contain p-coumaryl units as well [132].

The chlorination and first alkaline extraction stages together are generally considered as a continuation of the delignification process whereas the later bleaching stages mainly serve to bleach the pulp. Reactions of chlorine with lignin involve oxidation, substitution and addition. The last two reaction types that is substitution and addition leads to formation of chlorinated organics. These reactions are important from the chloro bleaching point of view, since they are responsible for the break down of lignin macro molecules to small fragments to be soluble in acidic C stage filtrate or serve to modify the lignin that it becomes soluble in the alkaline extraction stage [48]. Although the contents of chlorophenolics in spent bleaching liquors mainly depend on kappa number of unbleached pulps, yet the characteristics of morphology and texture and the characteristics of the lignin structure also strongly influence the formation of chlorinated phenolics during pulp bleaching. In addition to this, the chlorination condition such as pH, temperature, chlorine dose, use of chlorine dioxide and splitting of chlorine dose have significant effect on the structures and quantity of chlorinated phenolics compounds generated in spent bleach liquor [33,122,124,132].

About 80% of organically bound chlorine that is formed during the bleaching of pulp is associated with high molecular weight lignin material (MW > 1000 D) [17,67,90]. The main environmental concern is the generation of low molecular weight chloro lignins which have the capacity to penetrate the cell membranes and are potentially toxic [16,92]. New development in the field of analytical chemistry, applying computer assisted Gas Chromatography – Mass Spectrometry (GC – MS) [53] and capillary columns of Gas Chromatography have led to successful identification and estimation of the presence of chlororganics in the bleach effluent [19,96]. Lindstrom and Nordin categorized chlororganics present in spent bleach liquor [75]. The maximum studies conducted after Lindstrom and Nordin further confirmed and extended their findings [123].

1.5 ABATEMENT OF BLEACH PLANT POLLUTION

The aim of the all pollution control efforts is to leave the natural environmental unaltered. The presence of the high amount of toxic chlorinated organic compounds in the bleach plant effluent has become a great environmental concern [10,37,67,94]. All the pollution reduction strategies of the bleach plant effluent are based on developing and introducing a number of new processes and process modification in order to minimize the discharge of chlorinated organic compounds [4,18,46,98,126]. An effective abatement of bleach plant effluent can be achieved in two ways as explained below:

1. Internal measures
2. External measures

(1) Internal measures

The main strategy behind the development of internal process changes has been to remove as much lignin as possible before the pulp enters the bleach plant and also to replace elemental chlorine in bleaching process by other bleaching agents. To achieve this, the following measures should be considered to be taken:

a) Control of contaminations, spills and leakages

Pentachlorophenol which is used as wood preservative should be prohibited as chlorinated dioxins which are known to be highly toxic are formed as byproducts in the production of pentachlorophenols [28,47,125]. In few countries the sale and use of wood chips from PCP treated woods is prohibited. The quality of chips should be improved to prevent dirt and shives from entering the bleach plant. Care should be taken to avoid spillage and leakage of fibre and liquor to minimize loading on the external effluent treatment facilities. Oil based defoamers, improved deknotting and screening result in reduced environmental load in bleach plant effluent [16,111].

b) Extended delignification prior to bleaching

Extended delignification can be obtained by introducing modified cooking like Modified Continuous Cooking (MCC) [58,109], Extended Modified Continuous Cooking (EMCC) [11,58], Cold Blow Cooking [36], Rapid Displacement Heating Systems (RDH) [11,36] and Oxygen Delignification [54,55,58,84] to reduce kappa number of pulp before bleaching. The combination of oxygen and extended delignification result in reduction in Total Organo Chlorine (TOCl) formation [36]. Anthraquinone (AQ) or Poly sulphide (PS) or both are used as additives in pulping processes to give low kappa pulps [80]

c) Improved pulp washing

Better washing of the pulp after cooking minimizes the carryover of organic matter with the pulp to bleach plant, thus decreasing the amount of chlorine and chlorine based bleaching chemicals due to which the concentration of chlorinated organics generated in the bleach plant effluents is reduced [47,50].

d) Improved chemical mixing

Proper mixing of chemicals in bleach plant helps a rapid and uniform distribution of chemicals through the pulp, thus giving a uniform bleaching with decreased formation of tetrachlorinated phenolic compounds [15,34] and dioxins [51].

e) Modification of lignin before bleaching

The acid pretreatment [14] and enzymatic pretreatment [12,13,108] of pulp modify the lignin structure, thus reducing the chemical consumption in the bleach plant, consequently generating less amount of chlororganics without affecting the pulp properties.

f) Modification of bleaching process and use of newer bleaching chemicals

(i) Effect of chlorination conditions

The total chlororganics generation can be reduced by lowering the chlorination temperature, by raising end pH of C stage [33,122] and by splitting the chlorine dosage into two or three portions [49]. By splitting the chlorine doses in C stage, the rate of the chlorination reaction slows down due to lower chlorine concentration, hence the reduction in the formation of chlororganics. By carrying out the bleaching processes at medium or high consistency, the effluent load generated can be reduced [34].

(ii) High or total substitution of first chlorination stage with chlorine dioxide

High substitution of chlorine dioxide in chlorination stage lowers the formation of chlorinated organics. The presence of chlorine dioxide in chlorination stage improves strength and brightness stability of the pulp and also reduces the chlororganics formation and the color of the effluent. Concentration of chlorinated phenolic compounds and dioxins in the filtrate of first two bleaching stages (CE) decreases in the proportion to the increase in the level of substitution of chlorine by chlorine dioxide to the extent of 100% [7,9,43,85,89,97,114,121,129,133]. It was reported that about 50% reduction in chlororganics including AOX and monomeric chlorinated phenols was achieved by drop wise addition of a mixture of chlorine and chlorine dioxide in the ratio of 50:50 as compared to the conventional addition of a single charge [83]. In order to minimize the formation of chlorinated organic material, 100% substitution by chlorine dioxide was done on the oxygen delignified pulp [10]. The formation of organically bound chlorine during the bleaching of chemical pulp with chlorine dioxide can be reduced by equimolar replacement of a part of the chlorine dioxide by chloride [68,88].

(iii) Oxidative extraction

Oxidants such as oxygen, hydrogen peroxide etc. are added to the first caustic extraction hydrogen peroxide for additional fortification. Modified extraction stages are designated as (E_O), (E_P) and (E_{OP}) [20,23]. Oxidative extraction enhances delignification, thus minimizing use of chlorine and chlorine dioxide consumption in the next bleaching stage and ultimately reduces the color and toxicity of the effluent [23,31,56,64,120].

(iv) Chlorine free bleaching

Oxygen, peroxide and ozone are few of the chlorine free bleaching agents [84]. As ozone is a powerful oxidant, the bleaching conditions must be carefully controlled to prevent pulp degradation [105,130]. Oxygen bleaching seems to very efficient for the reduction of chlorinated phenolics. Inclusion of an Oxygen stage in a bleaching sequence reduces concentration of chlorides in the total bleachery effluent [27]. The BOD, COD and color of the effluent in which oxygen is used as a bleaching agent are found to be considerably lower than those effluents generated from conventional bleaching [22,54]. Therefore oxygen bleaching is well accepted commercially.

(2) External measures

The waste water contains relatively large amounts of suspended solids and substances which raise the level of oxygen required for biological or chemical oxidation. The mills usually employ a combination of the following methods to control water pollution:

a) Pre-treatment

Pre-treatment wherein coarse solids are removed by screening. Excessive acids or alkaline content can also be neutralized at this stage.

b) Primary treatment

Primary treatment comprises of removal of suspended solids by sedimentation using settling ponds or clarifiers.

c) Secondary treatment

It is the purification process in which the dissolved organic matter in the waste water is reduced by biological treatment carried out under contained and controlled conditions usually at accelerated rates [72,79,81]. To achieve this treatment which are applied in the mills are given below:

- **(i)** Oxidation lagoon
- **(ii)** Aerated stabilization basin (ASB)
- **(iii)** Activated sludge process (ASP)

(iv) Biological filter process, such as trickling filter, rotatory disc etc.

(v) Anaerobic process

Aerated lagoons have a mechanical aeration device to increase the supply of oxygen. Anaerobic lagoons have methane bacteria to carry out the reduction. Anaerobic biological treatment has shown promise as one option for the declorination of organochlorine compounds found in bleached kraft mill effluent [44,45]. The activated sludge process utilize microorganism for treatment of organic matter. It has been reported that in the activated sludge process, maximum AOX reduction was occurred due to microbial metabolism [24,76]. Microbial waste treatment system helps in detoxification of mill discharges [127]. The reductions in AOX and in chlorinated phenolic compounds were found to be lower in the aerated lagoon treatment than in the activated sludge treatment [40]. The secondary treatment methods are not capable to reduce the color and toxicity.

d) Tertiary treatment

This technique (physiochemical treatments) has been developed to control the discharge of deleterious substances from chemical pulp bleach plants which are slow to biodegradation and are usually little affected by conventional secondary treatment methods. The major tertiary treatments are given below:

(i) Adsorption and ion exchange methods

(ii) Flocculation and chemical precipitation methods

(iii) Membrane methods

The above treatments are mainly used for the removal of effluent color, COD and toxicity.

e) Other techniques

A few microorganisms are capable of degrading lignin in aqueous medium. Pure and mixed algal culture of algal species like Microcystis aeroginosa and Anabaena flos-aqua reduced color of dilute bleach kraft mill effluent. Tranetes versicolor and Phanerochaete chrysosporiun are some of the fungi used for the treatment of effluent from pulp mills. These have been reported to degrade a variety of chlorinated toxics [116]. Actinomycetes such as Streptomyces, Nocardia and Actinomyces are known to exhibit chlororganics degradation [65]. Treatments with SO_2 or Na_2SO_3 reduces or eliminates the acute toxicity and mutagenic activity of bleaching effluents [32]. Ozone treatment in combination with ultra filtration reduces color as well as biological active chlorinated compounds such as chlorinated phenols and guaiacols.

Traditionally Indian paper mills use the End of Pipe Treatment Plant (ETP) to reduce the pollution. Generally it is a combination of primary and secondary treatment plants and aims at reducing or eliminating the entire pollution from a plant. This kind of ETP reduces the release of suspended solids and BOD significantly, with a small reduction of COD, AOX and color loads. Though the tertiary treatment techniques are quite efficient for removal of AOX and color loads, yet being expensive it is not viable for Indian paper mills under the present operating conditions. In view of all the above aspects, it can be safely concluded that to minimize the formation and discharge of toxic substances, the best way is to adopt in plant controls and process modifications. Though in plant technologies are generally more efficient than external methods, the latter may still be necessary as a supplement to in plant methods to further reduce and minimize the pollution load to meet the environmental regulations.

1.6 BACKGROUND OF PROBLEM

It has been observed that bleach plant effluents are highly polluted. It consists of both easily and slowly biodegradable compounds. Around 65% of the total BOD and 90% of the total color discharged from the pulp and paper mills are from the bleaching section. The chlorination and first extraction stage often account for the largest amount of chlorinated organic matter [19,58,71]. These chlorinated organic compounds exhibit mild acute toxicity, some are persistent, some bioaccumulate and some cause sub lethal effect [1,123,127]. The colored compounds in bleach plant reduce light penetration into water and therefore; affect photosynthetic activity of the aquatic ecosystem. The large integrated pulp and paper mills in India are using forest based materials for paper making whereas small and medium size mills are dependent on non wood or agro residue raw materials for their pulp manufacturing. But in all these sectors, still conventional pulping and bleaching technologies are employed, as modern technologies developed in the west are prohibitively expensive for Indian mills, particularly because the production technologies applied in these mills are many times old and poorly maintained. Moreover, these modern technologies may not be suitable for the raw materials or incompatible with existing production setup [118].

The bleaching processes used by Indian paper mills are chlorination, followed by alkali extraction and calcium hypochlorite. The bleaching sequences include CEH, CEHH, CE_PHH and CE_OHH. The oxygen delignification as a pre bleaching stage is being attempted by some mills. Use of chlorine dioxide, hydrogen peroxide and oxygen reinforced alkali extraction is limited to very few large mills which are producing rayon grade pulp and high brightness quality pulp. An estimate indicates approximately 2.5 million tones of chemical pulp is produced in India. 60% of this is high brightness bleach pulp, mostly bleached by chlorine and chlorine based chemicals [92]. Many of the Indian paper mills are now producing paper of brightness above 80% ISO to compete with international brands, as result of globalization. This high level brightness is achieved at the cost of increased chlorine consumption resulting in the high level of AOX generation.

During the research for identification of pollutant in bleach plant effluents, it has been observed that chlorinated phenolics are toxic to aquatic organisms and hence the chemical and biological characterization of these effluents has been extensively studied. It has been found that the toxicity of most of the first chlorination effluents are due to tri and tetra chlorocatechols, 2,6 dichlorohydroquinone and a group of polychlorodihydroxybenzenes and the caustic extraction effluents have a toxicity which may be described to tri and tetrachloroguaiacols, mono and dichlorodehydroabietic acid [128]. Traditionally the bleaching is performed using elemental chlorine which is most effective delignifying agent and least expensive of all the bleaching chemicals. Moreover due to the existing infrastructure of mills and very high cost in altering the infrastructure for other bleaching stages [5,8], chlorination as the first bleaching step will continue for some years to come. Despite this, due to environmental factors, chlorine is gradually being replaced by several other chemicals such as chlorine dioxide, hydrogen peroxide, oxygen and ozone. Now a days, hydrogen peroxide or oxygen is used at alkali extraction stage and is being practiced by many of the large mills in the country.

The studies have mostly carried out on softwood and some hardwood pulps [29,61]. A very little data is available on agriculture residue pulps which are important in Indian context due to decreasing wood resources [87,99,106,117]. Therefore there is need to study the generation of various pollutants formed during bleaching of non wood pulps in Indian mills [12,93,115]. Generally in India paper industries are using clarification methods for reducing suspended solids and biodegradation methods which effectively remove BOD. The need for AOX and color reduction is almost overlooked in most cases. The various biological treatment methods currently in operation are stabilization ponds, aerated lagoons, activated sludge process etc. [2,103]. So the effluent discharged is highly colored and expected to contain large amounts of pollutants contributing to high COD and AOX. Therefore it is imperative to develop suitable methods to reduce color, COD and toxic chlororganics from bleach plant effluents which may be simpler, cost effective and readily adaptable for pulp and paper mills in India [100].

1.7 STATEMENT OF THE PROBLEM

The experimental investigation have primarily been undertaken in current study to identify and estimate different chlororganics compounds generated during C, E and H stages. The main objective of the work is to aim for environmental friendly bleaching to reduce generation of chlororganics from bleach plants. To achieve the above two agro residue pulps – Bamboo and Jute Cady are taken. The work planned is as under:

(i) To identify and quantify various chlorophenols formed during different stages of pulp bleaching.

(ii) To study the impact of change in chlorination condition i.e. pH, temperature, consistency, distribution of bleach liquor between C and H stages on the production of toxic chlorinated phenolics in C, E and H stages.

(iii) To study the impact of partial or complete replacement of chlorine by chlorine dioxide in C stage and full replacement of hypochlorite by chlorine dioxide in H stage on generation of chlorophenolic compounds.

(iv) To study the impact of addition of peroxide in E stage (E_P) on the generation of chlorophenolic compounds.

(v) To study the integration of oxygen delignification stage with conventional CEH and DED bleaching sequences and its impact on the generation of chlorophenolics.

(vi) To study the impact of modified sequences (when 80% target brightness is achieved) on the generation of chlorophenolic compounds.

(vii) To study the effect of above changes on :

- Pulp characteristics
- Pollution load generation

The experimental results of this research study are expected to form a basis for establishing suitable process sequences, optimizing operational parameters and integrating them with existing mill configurations. All these are expected to provide significant benefits in terms of improved product quality and better environmental management.

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Chapter - 2

EXPERIMENTAL PROCEDURES

EXPERIMENTAL PROCEDURES

The experimental procedures essentially consist of the following:

(a) Generation of effluents in the laboratory by bleaching of the pulps.

(b) Gas chromatographic studies to establish conditions for the separation of mixture of the pure standards.

(c) Extraction of chlorophenolic compounds from effluents.

(d) Identification and quantitative analysis of chlorophenolic compounds by GC.

2.1 MATERIALS

a) Chemicals

Various isomers of chlorophenols (Aldrich, USA) Chloroguaiacols, chlorocatechols, chlorovanillins, chlorosyringaldehydes, and chlorosyringols (all from Helix, Canada) were used as authentic reference compounds. n-hexane and acetone used were of HPLC grade and diethyl ether of LR grade. Analytical grade acetic anhydride was used after redistillation. Other reagents used for identification studies were of analytical reagent grade. Standard solutions of chlorophenols were prepared in 10% acetone water.

b) Pulps

Unbleached Bamboo (Bambusa Vulgaris) and Jute Cady (Cassia Acetifolia) pulps were procured from "Cachchar Paper Mill, HNL, Assam" and "Shreyans Paper Mill, Ahmedgarh, Punjab" respectively. The pulps were washed and screened in the laboratory and air-dried. Oxygen pretreatment conditions were optimized for both the pulps.

2.2 TEST METHODS

- TAPPI (T – 236) was used to determine the kappa number of pulp [9].
- SCAN – C 15:62 was used to determine the viscosity (CED) of pulp [9].
- Brightness of pulp (ISO Standard 2469) was measured on TECHNIBRITE ERIC 950 from Technibrite Corpn. USA [10].
- COD of bleach effluent was estimated by standard method. (508 B) closed reflex titrametric method [11,12].

2.3 TEST PROCEDURES

2.3 1. Analysis of hypochlorite / chlorine dioxide / bleach liquor

In 5 ml of bleach liquor, 10 ml of 10% potassium iodide & 10 ml of acetic acid were added. This solution was titrated with standard 0.1 N sodium thiosulphate solution with 0.5% starch as an indicator till the color of the solution changes from blue to colorless [5].

Active chlorine concentration (gpl) = Normality of bleach liquor x 35.5

2.3.2. Analysis of residual bleach liquor

Same procedure as described above was used except volume of spent bleach liquor taken was 100 ml and titrated with standard 0.1N sodium thiosulphate solution [5].

2.3 3. Analysis of hydrogen peroxide solution

In 5 ml of diluted H_2O_2 solution (25 times) 10 ml of 10% KI, 10 ml of 4N H_2SO_4 and 1 ml of ammonium hepta molybdate were added. This solution was titrated with standard 0.1N $Na_2S_2O_3$ solution with 0.5% starch as an indicator.

Concentration of H_2O_2 (gpl) = Normality of H_2O_2 solution x 34

2.3 4. Disintegration of pulps

Before bleaching and oxygen delignification the air-dried pulp was disintegrated to break the fiber bundles & lumps. Air-dried pulp was soaked in water overnight and then disintegrated in a laboratory disintegrator (Maximum 40 g OD pulp). The water was drained on a screen and the pulp was kept in refrigerator in plastic bags for not more than 7 days. This wet pulp was used for further bleaching experiments.

2.3.5. Determination of viscosity of pulp solution in cupriethylenediamine (CED) solution.

The viscosity of the pulp suspension was calculated by capillary viscometer method using 1 M CED as a solvent. TAPPI T 230 test method was followed. The copper rod stirring technique was used. The viscometer constant was found by using glycerol solution of known viscosity & specific gravity & this constant was used further for viscosity calculations. The procedure followed was briefly described as follows :

Pulp sample equivalent to the 0.25 g OD was put it in a 50 ml capacity plastic bottle. 25 ml of distilled water was pipetted into the bottle. Also put 2-3 copper beads in the bottle. The bottle was tightly closed and shaken gently for 30 seconds and 25 ml of 1M CED solution was pipetted in to the pulp suspension and shaken the suspension for 1 minute on a shaker. Fill the viscometer by immersing it into the solution by suction. Place the viscometer in the constant temperature bath at 25± 0.1° C to attain constant temperature. Draw the solution up into the measuring leg of the viscometer. Determine the efflux time by drawing the liquid above the upper mark and measuring the time required for the meniscus to pass between the two marks. Repeat the measurement of efflux time. Calculate the viscosity of the pulp solution from the formula

$$\mathbf{V = c \times t \times d}$$

where V = Viscosity of pulp solution
c = Viscometer constant
t = Average reflux time, seconds
d = Density of the pulp solution, g/cm^3

2.3.6. Preparation of hand sheets (for brightness, viscosity, kappa number & CE kappa number determination)

The consistency of the disintegrated pulp was adjusted to 1%. The pulp suspension was then transferred to a buchner funnel. Water was drained through a screen of 22 mesh, so as to give a sheet of about 5 g OD weight. This wet sheet was pressed between two blotting papers and air-dried, which was then cut into test pieces. It was ensured that these sheets were guarded from contamination. The brightness was measured with in 12 hr after drying. These sheets were used for kappa number and pulp viscosity.

2.3.7. Bleaching of pulps

The purpose of the bleaching is to impart the desired final chemical & physical properties to the pulp, the most obvious being the brightness. This is done by removal of some constituents of the unbleached pulp & by modification of the remaining ones.

In principle, it consists of chlorination for the degradation of the lignin followed by an alkali stage for the neutralization & dissolution of the degraded product & finished by an oxidative stage with intermediate alkaline extraction. After the oxidation, the final discoloration is removed & full high brightness is obtained.

a) Chlorination (C stage)

The wet disintegrated pulp equivalent to 40 g OD was dispersed & the pH of the suspension was reduced to 2 with dilute $H_2 SO_4$ before adding bleach liquor to it. The pulp suspension was transferred into a plastic bottle. Calculated fixed amount of H_2SO_4 was also added, so that the pH of the suspension will remain 2 and in this pulp suspension desired calculated amount of distilled water was added to the pulp to maintain 3% consistency. The pH of the bleach liquor was reduced to 4 by dilute H_2SO_4 and transferred to the bottle containing the pulp suspension at pH 2. The contents of the bottle were well shaken. The chlorination was carried out at 30°C. The pulp was shaken from time to time and kept for a period of 45 minutes. The pulp was then washed on a buchner funnel using 100 ml fractions of water. The effluent was collected for identification & estimation of chlororganics by GC & for evaluation of effluent quality. The brightness observed was low due to low response of pulp that's why a lot of efforts have been done to achieve the target brightness for bamboo pulp, but due to low kappa number and differences in morphological structure resisting the easy diffusion of chemicals and the presence of condensed lignin in the inaccessible regions of the fibres, the bleach liquor demand is increased. The bleaching conditions are summarized and are given in Table 2.2.

b) Splitting of chlorine dose in C stage

The process of chlorination (C) stage bleaching was modified by splitting the chlorine dose (with or without in between washing). Half of the required amount of bleach liquor was added to the pulp suspension. The bleaching under C stage conditions was continued for 20 minutes, where after the remaining quantity of bleach liquor was added to the pulp suspension. Further bleaching was continued for the rest of the time. In one case after first chlorination stage the pulp was washed on a buchner funnel. Remaining bleach liquor was added to washed pulp and after completion of C_2 stage the pulp was again washed. Both effluents were collected, mixed and used for effluent quality and estimation of chlororganics.

In other case, the washing after C_1 stage was not performed. The washing was done after C_2 stage. The effluent after C_2 stage was collected and used for effluent quality and chlororganics estimation.

c) Chlorine dioxide substitution in C stage

Chlorine dioxide is an unusual compound, since ClO_2 has 19 valence electrons. Thus it has an unpaired electron and it is really a free radical. This probably accounts for its relative instability.

The chlorination (C) stage bleaching was performed by partially substituting chlorine by chlorine dioxide as active chlorine. Partial substitution was varied from 25 – 100%. The addition of chlorine in advance of chlorine dioxide in a sequential chlorination decreases the chlorinated phenolic compounds and the toxicity. Adding the chlorine before the chlorine dioxide in the C stage is less effective in delignifying the pulp than the reverse mode of adding the ClO_2 first. D/C mode of addition in C stage was followed.

To the disintegrated pulp calculated amount of water and acid was added so that after addition of bleach liquor, the end pH remained between 2 and 4 and the reaction consistency as given in the Tables 2.4 and 2.5. The pulp was taken in a plastic bag and chemicals were hand mixed with pulp. The plastic bag was then suspended in water bath maintained at temperatures between 40 – 70°C for a time period between 50 – 90 minutes. After the completion of time, the bag was removed, the pulp was washed and the effluent was collected to carry out the estimation of residual bleach liquor, environmental parameters & chlororganics by GC.

d) Alkali extraction (E & E_p) bleaching

The required amount of NaOH of known strength was mixed with pulp suspension and required water was also added to get 10% consistency. The pH of this suspension was between 10 – 11.50. The pulp was repeatedly kneaded to uniformly distribute alkali into pulp suspension. The polythene bag was then vertically suspended in a water bath maintained at 70°C for 60 minutes. After every10 – 15 minutes polythene bag was removed, the pulp was kneaded and again placed in the water bath.

For E_p stage, calculated amount of H_2O_2 solution was also added along with the alkali. In both case the pulp was washed with water in fractions of 100 ml each and the effluent was collected for further analysis. The bleaching conditions are given in Tables 2.2 and 2.6.

e) Hypochlorite stage bleaching

The washed pulp after alkali extraction was then mixed with requisite amount of hypochlorite bleach liquor and water to adjust the pulp consistency to 10%. The initial pH was between 10 – 11.50. The contents were transferred to a plastic bag and it was placed in a water bath for 3.50 hr pre-heated to 40°C. After each 30 minutes, the pH of the pulp was checked and adjusted to pH 10, so as to give a final end pH of around 10.00. The bag was removed, the pulp was washed with water in fraction of 100 ml each and the effluent was collected for further analysis. The bleaching parameters are given in Table 2.2.

f) Chlorine dioxide (D) stage bleaching

The disintegrated pulp was mixed in a plastic bag with requisite amount of sodium hypochloride ($NaClO_2$), so that the starting pH remained around 4.5 and the pulp consistency was around 10%. The bleaching was performed for 180 minutes in plastic a bag which was kept in water bath at 70°C. The pulp was kneaded from time to time for proper shaking. The plastic bag was removed and the pulp was washed. Effluent was collected for further analysis. The bleaching parameters are given in Table 2.6.

g) Oxygen delignification

The pulp was bleached with oxygen in the electrically heated, rotary digester of capacity 15 liter. The disintegrated wet pulp was mixed with 20-gpl-sodium hydroxide at various doses and magnesium sulphate (0.2 g per 100 g OD pulp). The pulp consistency was brought to 10%. The pulp was transferred to autoclaves fitted on stands, which had the capacity to hold about 100 g of wet pulp. After expelling air, autoclaves were filled with oxygen to a pressure of 6 kg/cm^2.

These leak proof autoclaves were then immersed into a pre-heated (to the level of required temperature) glycol bath for a period of 75 minutes (5). Thereafter, the autoclaves were taken out from the oil bath, cooled by immersing in water and pulp washed on a screen. The pulp was then squeezed to drain extra water and stored in a polythene bag for further bleaching experiments.

The oxygen and non-oxygen treated pulps were then characterized for kappa number, viscosity and brightness. The oxygen prebleaching conditions and pulp characteristics of oxygen delignified pulp are shown in Tables 2.7 and 2.8. The oxygen bleaching was targeted at a kappa number drop of 50 – 55% without much sacrificing on viscosity.

2.3.7. Characterization of effluents

The bleach effluents generated during each stage of bleaching were collected, diluted to 2 liter and 100 ml of this collected effluent is used for COD and color.

a) **COD determination** – Closed reflux titrametric method (508 - B) [11,12].

b) **Color measurement**

Color measurement was performed spectrophotometrically on Shimadzu Spectrometer model UV 2100/s at the wavelength of 465 nm. The method is outlined below – To prepare a standard solution of 2500 Pt – Co color units, 250 mg of platinum wire (purity 99.99%) was dissolved in hot aquaregia. The resulting solution was heated to dryness to extricate nitric acid (as oxides of nitrogen) by repeated evaporation and addition of fresh quantity of concentrated HCl. The residue was dissolved in distilled water and thereafter, 500 mg of $CoCl_2 .6 H_2O$ (equivalent to 125 mg Co) was added along with 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 Pt – Co color units [10,11,12].

Standard solution of 50, 250, 350, 500, 1000, 1500, 2000 Pt – Co units were prepared by diluting 0.5, 2.5, 3.5, 5, 10, 15 and 20 ml of standard stock solution to 25 ml in a volumetric flask. A calibration curve at 465 nm was plotted as shown in Fig (2.1). This curve was used to determine the color of the effluent. The pH of effluent was adjusted to 7.6 and then the suspended particles were removed by centrifuging the effluent for 5 minutes at 1500 RPM. The absorbance of the solution was then determined at 465 nm and color of the effluent was calculated from the calibration curve (Fig. 2.1).

2.3.8. GC analysis

Modern analytical methods such as high performance liquid chromatography, thin layer chromatography and gas chromatography alone or in combination with mass spectrometry have been used for determining chlorophenolic compounds in the pulp and paper mill effluents. Of these methods GC or GC-MS are the more commonly used techniques [6,7,8]. In GC, the selective detection of the chlorophenols has been done using Flame Ionization Detector (FID) and Electron Capture Detector (ECD).

In principle, solvent extraction should provide a simpler and faster method of isolation for wastewater sample. Mainly two extraction procedures are in use today for chlorophenolic analysis in pulp and paper mill effluent. One proposed by BCRC (British Columbia Research Canada) and another by Lindstrom et al. [6]. The fundamental difference between the two is the method of isolation. The BCRC procedure removes chlorophenolic compound from the effluent under alkaline conditions (pH 9 – 10) by adsorption onto a porous polymeric resin (XAD 2), whereas second method removes the chlorophenolic compound under acidic conditions (pH 2) by extracting with diethyl ether. For the present study extraction of various chlorophenolic compounds has been done by diethyl ether as discussed in Flowchart (1).

The chlorophenols are converted into derivatives to make them readily volatile prior to GC analysis. Different procedures for derivatizing phenols directly in the water samples have been suggested including extractive alkylation with penta fluorobenzyl bromide and acylation with pentafluorobenzyl bromide and acylation with trichloroacetic anhydride, heptaflurobutyl anhydride or acetic anhydride. Reagents containing halogen will yield electron affinity product, even with non-halogenated phenols, thus diminishing the selectivity of the method. For the present study, acetylation was done with acetic anhydride based on procedure suggested by Abrahamsson & Xie [2,6,7,8]. The acetylated sample is analyzed by Gas Chromatography.

a) GC conditions

Shimadzu Gas chromatograph model GC-9A was used to analyze various chlorophenolics like chlorophenols, chloroguaiacols, chlorocatechols, chlorovanillins, chlorosyringols and chlorosyringaldehydes as acetyl derivatives.

The GC parameter were determined for separating the pure chlorophenolics standards on Ulbon HR – 1 glass capillary column (30 m x 0.32 mm ID). The injection was split less for two minutes.

b) Derivatization procedure

To 4.5 ml of sample taken in a PTFE lined screw capped glass tube, 0.5 ml of buffer solution of 0.5 M Na_2HPO_4 was added. Derivatization and extraction was performed by adding 1ml of n–hexane and 0.1 ml of acetic anhydride. After shaking the mixture for at least 3 minutes, 1 µl of the acetyl derivative was taken from the hexane layer through a syringe and it was injected into the capillary column for GC analysis [2].

c) Retention time determination

Standard solution of various chlorophenolic compounds (20 – 30 mg/l) was prepared in 10% acetone water. 1 ml of this solution was diluted to 4.5 ml and derivatized and extracted as explain under 2.3 8-b derivatization procedure. 1 µl of the derivative was injected into the capillary column and retention time was recorded.

d) Separation of chlorophenols from the effluent

The procedure suggested by Lindstrom K et.al was used. A schematic presentation of the method followed is shown in flow sheet (2.1).

2 liters each of C stage, E stage and H stage effluents were separately analyzed. The pH of these effluents was adjusted to 2 with 2M H_2SO_4 solution. Then each of the effluent was extracted with 400 ml of 90% ethyl ether and 10% acetone mixture per litre of effluent for 48 hours. The emulsion formed in ether layer was broken by using a heat gun. Then the whole etheral extract of the effluent was transferred into another separating funnel and shaken with 5 ml of 0.5 M $NaHCO_3$ solution to remove acidic impurities. Thereafter, the ether layer in each was shaken with 5 ml of 0.5 M NaOH to extract the chlorophenolics.

Aqueous NaOH layer, which contained chlorophenolics from bleaching effluent, was separated & washed with 10 ml of fresh diethyl ether to remove the neutrals [6]. The etheral portion was rejected. The extracted chlorophenolics were derivatized as under:

4 ml of extracted sample was acetylated using 0.1 ml of acetic anhydride. The remaining derivatization process was the same as per 2.3 8-b derivatization procedure. 1 µl of the derivatized sample was injected in to the column for identification & quantitative analysis of chlorophenolics.

e) Quantitative analysis of various pollutants

The response factor and extraction efficiency percentage of various chlorophenolic compounds were determined for quantitative analysis of chlorophenolics.

I. Response Factor

1 ml each of standard solution of chlorophenols was derivatized as per procedure described under 2.3 8-b and 1 µl of the hexane layer was injected into the column. The area of the peak was recorded and the response Factor (RF) was calculated as under –

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

II. Extraction Efficiency

For extraction of various standard chlorophenolics, 1 ml of standard solution of each chlorophenol was diluted to 1 liter with distilled water. The pH of the solution was adjusted to 2. The solution was then extracted with 400 ml of 90% ethyl ether and 10% acetone mixture for 48 hours and derivatized as acetyl derivative under 2.3 8-d for chlorophenolics. 1 µl of the hexane layer was injected into column and the peak area was recorded. From the area of peak the quantity of chlorophenolics present in the extracted sample was determined. The percentage extraction efficiency was calculated as under -

$$\text{Extraction Efficiency (\%)} = \frac{\text{Qty in the extracted sample}}{\text{Qty in the sample before extraction}} \times 100$$

The values of retention time, response factor and percent extraction efficiency of various chlorophenolic compounds are given in Table 2.10. These values are the averages of minimum three values. The various chlorophenolic compounds have been identified by matching time (± 0.1 min) of a component with that of pure standard. The values of retention time (Table 2.11) indicate that most of the chlorophenols can be resolved on capillary column of HR-1. Some important chlorophenolic compounds, whose concentration are higher or whose toxicity values are high i.e. lower $^{96}LC_{50}$ values have also been chosen for analysis (Table 2.11).

Table 2.1 Standard test method followed

S. No.	Description	Test Number
1	Kappa Number of pulp	T – 236
2	Brightness of pulp	ISO Standard 2469
3	Preparation of cupriethylenediamine (CED Solution)	SCAN – C – 16:6
4	Viscosity of pulp (Capillary viscometer method)	T – 230
5	Chemical Oxygen demand (Closed reflux titrametric method)	COD
6	Consistency of pulp suspensions	T 240
7	Determination of equilibrium moisture content of pulp	T 550
8	Preparation of indicators and standard solutions	T 610

Table 2.2 Bleaching condition for Bamboo pulp / Jute Cady pulp

Parameter	Unit	Pulp					
		Bamboo			Jute Cady		
		C	E	H	C	E	H
Cl_2 Applied	%	3.78	---	3.09	8.1	---	5.4
Cl_2 Residual (of total)	%	1.43	---	3.10	1.22	---	3.09
NaOH Applied	%	---	2.19	---	---	4.35	---
Consistency	%	3	10	7	3	10	7
Initial pH	%	2	11.56	11.79	2	11.23	11.05
End pH	%	1.97	11.09	10.38	2.09	10.65	10.04
Temperature	°C	30	70	40	30	70	40
Time	Minute	45	60	230	45	60	230
CE kappa Number	---	---	5.41	---	---	6.08	---
Brightness	% ISO	---	45.61	80.5	---	48.1	79.84
Unbleached Kappa No.	---	12.50			27.00		
Unbleached Brightness	%ISO	23.18			12.50		
Unbleached Viscosity	cp	16.0			29.0		

Table 2.3 Bleaching conditions of splitting of chlorine dose in C stage (with or without in between washing)

Parameter	Units	Bamboo						Jute Cady					
		$C_{w.w.}$ EH			$C_{w.o.}$ EH			$C_{w.w.}$ EH			$C_{w.o.}$ EH		
		C	**E**	**H**	**C**	**E**	**H**	**C**	**E**	**H**	**C**	**E**	**H**
Charge as active Cl	%	3.78	---	3.09	3.78	---	3.09	8.1	---	5.4	8.1	---	5.4
Alkali charge as NaOH	%	---	2.19	---	---	2.19	---	---	4.35	---	---	4.35	---
Residual chlorine (of total)	%	0.93	---	1.88	1.13	---	1.92	.096	---	1.93	1.46	---	2.01
Temperature	°C	30	70	40	30	70	40	30	70	40	30	70	40
Consistency	%	3	10	7	3	10	7	3	10	7	3	10	7
Retention time	Minute	45	60	230	45	60	230	45	60	230	45	60	230
End pH	---	1.79	12.57	11.46	1.82	12.40	11.34	1.69	12.07	11.57	1.88	12.16	11.78

Table 2.4 Bleaching conditions for chlorine dioxide substituted CEH bleaching sequences with Bamboo pulp

Parameter	Units	$D_{25}C_{75}$	$D_{50}C_{50}$	$D_{75}E_{25}$	D	E	H
Charge as active Cl	%	3.78	3.78	3.78	3.78	---	3.09
Alkali charge as NaOH	%	---	---	---	---	2.19	---
Residual chlorine (of total)	%	1.12	0.82	1.21	1.42	---	0.36
Temperature	°C	40	50	60	70	70	40
Consistency	%	4	6	8	10	10	7
Retention Time	Minute	50	60	75	90	60	230
End pH	---	2.10	3.07	3.85	4.14	11.59	10.92

Table 2.5 Conditions of chlorine dioxide substituted CEH bleaching sequences with Jute Cady pulp

Parameter	Units	$D_{25}C_{75}$	$D_{50}C_{50}$	$D_{75}E_{25}$	D	E	H
Charge as active Cl	%	8.1	8.1	8.1	8.1	---	5.4
Alkali charge as NaOH	%	---	---	---	---	4.35	---
Residual chlorine (of total)	%	1.09	0.93	---	0.64	---	0.49
Temperature	°C	40	50	60	70	70	40
Consistency	%	4	6	8	10	10	7
Retention Time	Minute	50	60	75	90	60	230
End pH	---	2.53	3.72	3.89	4.05	11.87	11.43

Table 2.6 Bleaching condition for the different sequences

Parameter	Units	Bamboo						Jute Cady					
		CE_P H			CED			CE_PH			CED		
		C	E_P	H	C	E	D	C	E_P	H	C	E	D
Charge as active Cl	%	2.63	---	1.13	3.78	---	3.09	7.56	---	3.24	8.10		5.40
Alkali charge as NaOH Hydrogen Peroxide	%	---	1.61 0.30	---	---	2.19	---	---	4.08 1.00	---	---	4.35	---
Residual chlorine (of total)	%	1.9	---	2.01	1.43	---	0.82	1.96	---	2.19	1.22	---	0.78
Temperature	°C	30	70	40	30	70	70	30	70	40	30	70	70
Consistency	%	3	10	7	3	10	10	3	10	7	3	10	10
Retention Time	Minute	45	60	230	45	60	180	45	60	230	45	60	180
End pH	---	1.42	11.40	10.08	1.96	11.09	4.01	1.66	10.79	10.01	2.01	10.71	4.04

Table 2.7 Oxygen prebleaching conditions and characteristics of oxygen delignified pulps

Parameter		Units	Bamboo	Jute Cady
O_2 charge		kg / cm^2	6	6
Consistency		%	10	10
Time		Minute	75	75
Temperature		°C	100	110
Alkali charge		kg / t	25	35
Magnesium sulphate		kg / t	2	2
Kappa No.	Non O_2	---	12.50	27.0
	O_2 delignified	---	6.38	15.93
Viscosity	Non O_2	cp	16.0	29.0
	O_2 delignified	cp	10.92	22.74
Brightness	Non O_2	%ISO	23.18	12.50
	O_2 delignified	%ISO	32.39	25.92

Table 2.8 Bleaching condition for the different sequences

Parameter	Units	Bamboo						Jute Cady					
		OCEH			ODED			OCEH			ODED		
		C	E	H	D	E	D	C	E	H	D	E	D
Charge as active Cl	%	1.93	---	1.58	1.93	---	1.58	4.78	---	3.19	4.78	---	3.19
Alkali charge as NaOH	%	---	1.26	---	---	1.26	---	---	2.69	---	---	2.69	---
Residual chlorine (of total)	%	1.04	---	1.78	0.54	---	0.82	1.03	---	1.82	0.61	---	0.94
Temperature	°C	30	70	40	70	70	70	30	70	40	70	70	70
Consistency	%	3	10	7	10	10	10	3	10	7	10	10	10
Retention time	Minute	45	60	180	90	60	180	45	60	180	90	60	180
End pH	---	1.56	10.67	10.08	4.11	10.76	4.10	1.84	10.62	10.13	4.12	11.34	4.10

Table 2.9 GC conditions for the separation of chlorophenolics

Parameters	
Detector	FID
Detector Range	10°
Carrier gas (N_2) flow rate	20 ml / min.
Injection & Detector temperature	275°C
Column Temperature	80°C for 3 min.
	80°C - 160°C at 2°C / min.
	160°C for 5 min.
	160°C - 260°C at 10°C / min.
	260°C for 15 min.
Injection (Splitless)	2 min
Sample Size	1 µl
Chart speed	2 cm / min.

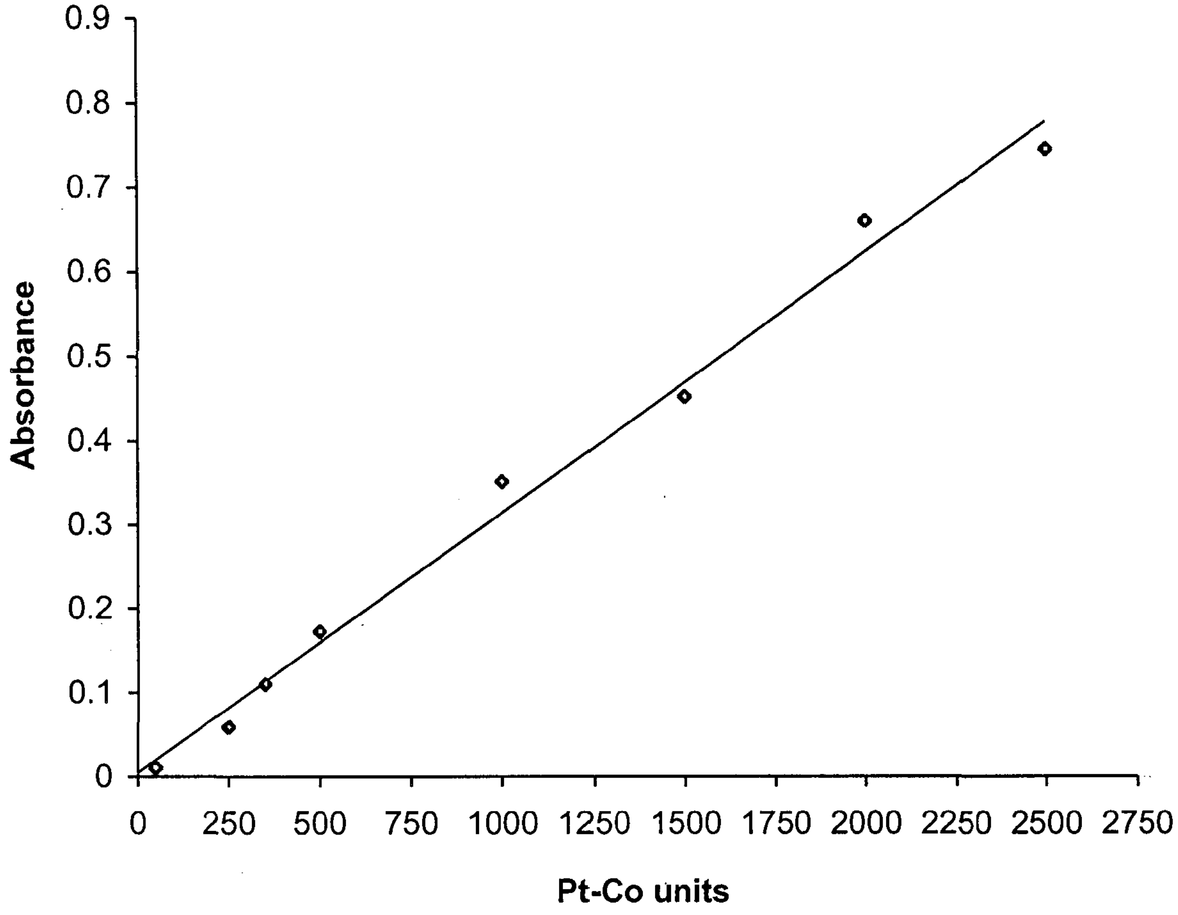
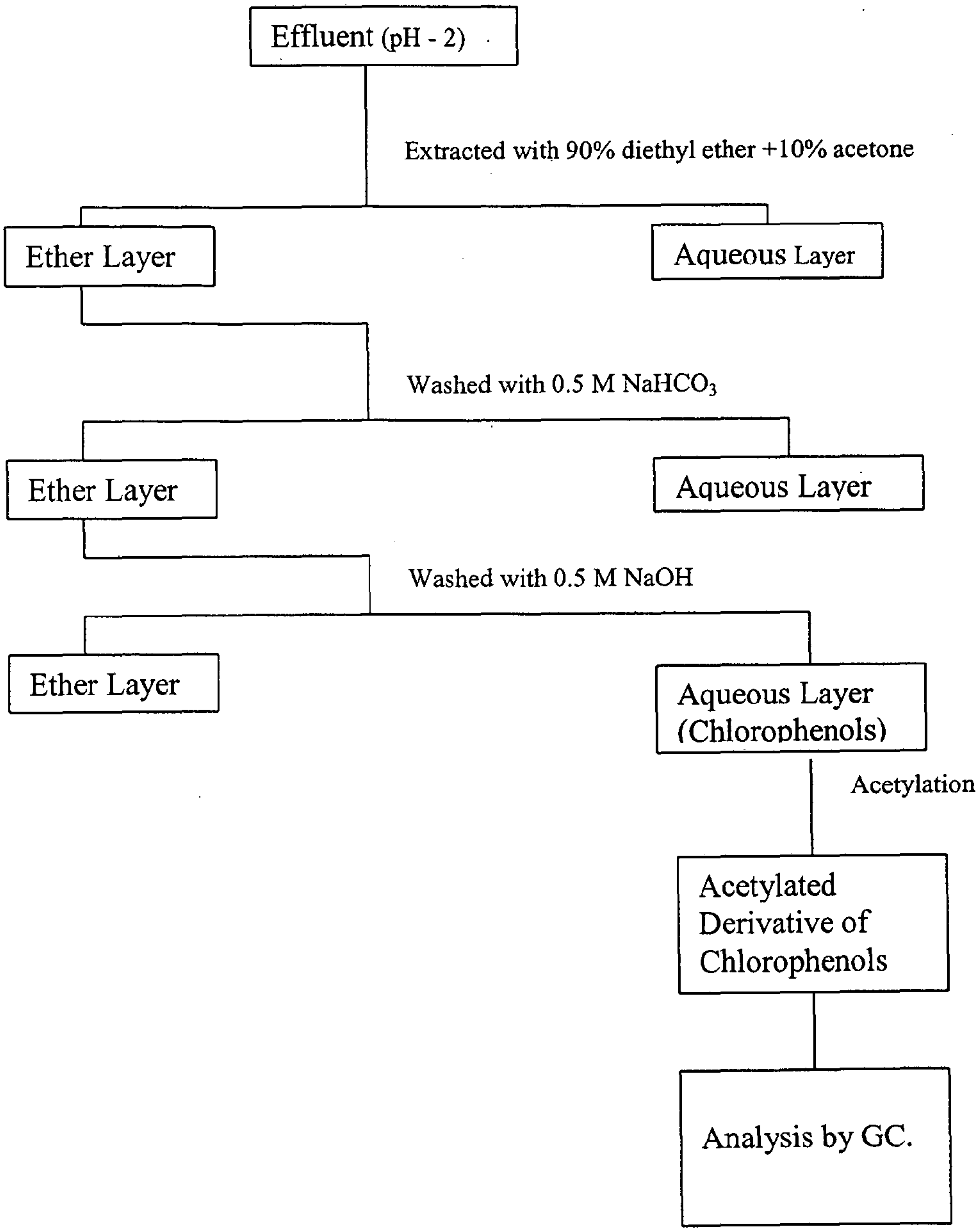


Fig. 2.1 Calibration curve for color measurement

Table 2.10 Concentration and absorbance of standard solutions

No	Concentrations (Pt – Co color units)	Absorbance
1	50	0.010
2	250	0.059
3	350	0.110
4	500	0.172
5	1000	0.351
6	1500	0.452
7	2000	0.660
8	2500	0.745



Flow Sheet 2.1 Separation of phenolic compounds from effluents

Table 2.11 Retention time, extraction efficiency & response factors of various chlorophenols

S. No	Chlorophenolic	Retention Time	Extraction Efficiency	Response Factor
		Min.	%	Pg
1	2,4-Dichlorophenol	7.26	34	1.67
2	2,5-Dichlorophenol	7.43	73	1.48
3	2,3-Dichlorophenol	7.64	98	2.33
4	3-Chloroguaiacol	8.12	59	1.96
5	2,6-Dichlorophenol	8.52	35	1.96
6	4-Chlorophenol	8.87	95	0.44
7	3-Chlorophenol	8.97	42	1.05
8	4-Chloroguaiacol	11.53	93	3.50
9	5-Chloroguaiacol	12.15	102	1.52
10	6-Chloroguaiacol	13.44	98	0.88
11	2-Chlorophenol	14.29	14	2.26
12	2,3,5-Trichlorophenol	14.58	89	3.28
13	2,4,6-Trichlorophenol	15.17	31	1.73
14	2,4,5-Trichlorophenol	15.68	63	1.28
15	3,5-Dichloroguaiacol	15.70	50	2.44
16	2,3,4-Trichlorophenol	16.02	85	1.68
17	2,3,6-Trichlorophenol	16.79	72	3.40
18	3,6-Dichloroguaiacol	17.17	105	2.57
19	3,4-Dichloroguaiacol	17.22	103	1.97
20	3,4-Dichlorocatechol	19.40	76	1.12
21	3,4-Dicholorophenol	20.12	106	1.35
22	4,5-Dichloroguaiacol	22.04	98	2.58
23	4,6-Dichloroguaiacol	22.27	52	2.10
24	5-Chlorovanillin	23.54	47	0.31
25	5,6-Dichloroguaiacol	24.34	57	1.69
26	4-Chlorocatechol	24.94	87	0.24
27	3,5-Dichlorocatechol	25.52	08	0.53
28	2,3,5,6-Tetrachlorophenol	25.65	53	2.91
29	2,3,4,5-Tetrachlorophenol	25.98	51	3.45
30	2,3,4,6-Tetrachlorophenol	26.08	76	1.48
31	3,5,6-Trichloroguaiacol	26.80	68	2.18
32	3,4,6-Trichloroguaiacol	27.15	81	1.71
33	3,5-Dichlorosyringol	27.45	57	2.63
34	3,4,5-Trichloroguaiacol	27.71	31	2.54
35	3-Chlorocatechol	28.20	103	0.30
36	6-Chlorovanillin	28.48	38	1.23
37	3,6-Dichlorocatechol	30.61	81	0.42
38	4,5,6-Trichloroguaiacol	34.16	99	1.12
39	2-Chlorosyringaldehyde	35.10	34	1.16
40	4,5-Dichlorocatechol	35.57	33	1.63
41	Pentachlorophenol	36.63	100	0.27
42	3,4,5-Trichlorocatechol	37.15	75	0.84
43	Tetrachloroguaiacol	38.21	49	0.87
44	Trichlorosyringol	39.29	17	1.14
45	3,4,6-Trichlorocatechol	40.62	76	0.48
46	2,6-Dichlorosyringaldehyde	40.74	100	0.38
47	5,6-Dichlorovanillin	41.80	109	0.44
48	Tetrachlorocatechol	43.11	31	0.54

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Chapter - 3

ESTIMATION OF CHLOROPHENOLS IN EFFLUENT OF BAMBOO

3.1 INTRODUCTION

3.2 RESULT AND DISCUSSION

Part – A : Changes in C stage bleaching conditions

- (1) pH
- (2) Temperature
- (3) Consistency
- (4) Distribution of bleaching chemical between C and H stages
- (5) Substitution of chlorine by chlorine dioxide in C stage
- (6) Splitting of chlorine dose in C stage
  - (a) With pulp washing
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Part – B : Modifications in CEH bleaching sequences

- (1) Replacement of hypochlorite by chlorine dioxide
- (2) Addition of peroxide in E stage (E_p)
- (3) Oxygen delignification stage followed by sequential CEH i.e. OCEH
- (4) Oxygen delignification stage followed by DED i.e. ODED

Part – C : 80% brightness pulp by different routes

- (1) D_{50} C_{50} EH
- (2) Splitting of chlorine dose in C stage
- (3) ODED
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SUMMARY OF RESULTS

TABLES AND FIGURES

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3.1 INTRODUCTION

Bamboo, often called green gold because of its economic value has found important usage in paper making also. 1250 species of 47 genera of bamboo are known to exist in the world. Bamboo's are widely distributed in the tropical and sub tropical regions of all continents except Europe and grows in plenty in countries with a rainfall of 1200 – 4000 mm. India accounts for 24% of world's total Bamboo production and out of the total Bamboo produced in India about 64% is contributed by North-East alone. In India out of 136 species identified, 30 – 40 species are extensively available for economic exploitation. Use of Bamboo as raw material for pulping was first started in Forest Research Institute (FRI), Dehradun (UA, India). In 1981, the world's largest bamboo pulp mill was established in Khon Kaen, Thailand by the Phoenix Pulp and Paper Company. The four major sub groups of Bamboo are *Arundinarieae, Eubambuseae, Dendrocalameae, and Melocanneae.* Bamboo is a very rapidly growing plant species that generally occurs in two types ***The Clump Type*** **-** endemic to countries with warm tropical conditions ***The Running Type:*** occurs in more temperate climates and conditions. On the basis of propagation bamboos are classified into three types *viz.*

(a) ***Monopodial type***: The rhizomes have one bud at each node, and it develops monopodially year after year. The clums are erect and with out branches.

(b) ***Sympodial type***: In this case the apex of the rhizomes which has nodes emerges out of the ground and grows into a culm.

(c) ***The intermediate type***: These have an intermediate development.

Bamboo has unusual habit of flowering at long intervals and the cycle may vary with species from 30-60 years. Flowered bamboo is not suitable for paper making. The wall of the bamboo stem is built up of the *Parenchyma tissue, Vessels, Fibres, Sieve tubes, Annular vessels.* The length of bamboo fibres vary from 1.5-4.4 mm. The average length is around the range 2.5 mm and fibre diameter 12 microns to 14 microns. Because of the round shape with thick membrane and small hollow it stands upright sturdily. Bamboo fibres are shorter than coniferous wood fibres in length. Chemically Bamboo is supposed to have basic Components, viz. *Pectin, lignin* and *celluloses*. The nodes of bamboo cause problem during pulping, as they are denser than rest of the stock and aren't all that easily penetrated by the liquor. The tropical bamboo "*Bambusa vulgaris*" is far superior paper making qualities because of its longer fibres.

It is a good raw material to produce quality writing and printing paper. Despite the high silica content, problems in chipping, difficulty in processing black liquor through the recovery section and difficulties in bleaching, bamboo is superior to bagasse, agricultural residues and tropical hard woods for making good quality paper. Today the Indian paper industry produces paper grades with up to 60% bamboo pulp in finish pulp [1].

Bamboo fibers morphologically differ from hard wood and soft wood fibers. Bamboo fibers are long, cylindrical with tapered ends and have got a high length to lumen ratio. These bamboo fibers do not have scalariform perforations found in hard wood or softwoods resulting in poor removal of lignin. In wood fibers the bleaching chemicals diffuse homogeneously and uniformly through the pitted perforations resulting in better removal of lignin. In the case of bamboo pulp the bleaching chemicals can diffuse only through the tapered ends of the lumen and this result in poorer removal of lignin. Another factor contributing physiologically towards relatively poor response to bleaching in bamboo pulp is the presence of condensed lignin, which amounts to nearly 25% of the total lignin present. Most of these condensed lignin remain in the inaccessible zone of the fibers. Further when delignification takes place, hemicelluloses swell and the flow of chemicals through the narrow lumen becomes less. This phenomenon is significant for bamboo pulp containing high proportion of both hemicellulose and lignin. For the above reasons bamboo pulp cannot be bleached beyond 78% brightness without impairing its strength properties [6,7,18,26,27,32,34, 39,40,47,52,55].

The conventional CEH or CEHH bleaching sequences are used in Indian Industries; where the element chlorine used in the bleaching of pulp reacts with lignin and produces chlorinated phenolic compounds such as chlorophenols, chloroguaiacols, chlorocatechols etc. The presence of large amounts of chlorophenolics in non wood pulp bleaching effluents, as reported by Xie indicate that grass lignins contain more – hydroxyphenyl units [56]. These organochlorine compounds formed during the conventional CEH bleaching are known to be toxic, mutagenic, persistent and bio-accumulating and causing numerous harmful disturbances in biological system [36,38,43,54]. The presence of potential hazardous organic substances in pulp mill effluent has also been detected by Folke. These low molecular weight organic compounds in the bleach effluent are of great environmental concern as they are highly toxic to aquatic life.

The fresh water requirement in the bleaching is also higher than what is required for wood pulps [32]. The effluents containing these highly toxic compounds are coming under increasing scrutiny and regulation around the word [14,16,36,46]. Studies on the formation of chlorinated organics/phenols have been reported for softwood and hardwood, but very little on nonwoods and agro residue pulps which have a different lignin structure [15,23,50,51,60]. This work is planned to study the formation of different chlorophenolic compounds formed as a function of C stage bleaching condition and to identify and estimate the different chlorophenolic compounds formed and present in different bleaching effluents viz. C, E, H, D etc.

3.2 RESULTS AND DISCUSSION

The Bamboo pulp has been bleached to 80% ISO brightness by CEH sequence under normal bleaching conditions (Table 2.2) and the effluent have been analyzed for different chlorophenolic compounds. The results on different chlorophenolic compounds present in C, E and H stage effluents formed under different condition of C stage bleaching and other bleaching modifications in CEH bleaching are given in Tables 3.2, 3.6, 3.10, 3.14, 3.18, 3.22, 3.26 and 3.30. The results on the impact of the modification in CEH sequence on pulp properties viz CE kappa number, CED viscosity and pulp brightness are shown in Tables 3.5, 3.9, 3.13, 3.17, 3.21, 3.25, 3.29 and 3.33 and on the effluent characteristics viz COD and color are given in Tables 3.3, 3.4, 3.7, 3.8, 3.11, 3.12, 3.15, 3.16, 3.19, 3.20, 3.23, 3.24, 3.27, 3.28, 3.32 and 3.33. Bleach plant effluents have been shown to contain six categories of chlorophenolics [10,14,36,42,56]. These are simple chlorophenols, chlorocatechols (1-2 benzenediols) chloroguaiacols (2 methoxy phenols) chlorosyringols (2,6 dimethoxyphenols), chlorosyringaldehydes (3,5 dimethoxy 4 hydroxybenzaldehydes) and chlorovanillins (4 hydroxy 3 methoxy benzaldehyde). Their structures are shown in Fig. 3.1.

The results on the CEH bleaching show that chlorocatechols, generated in C stage effluent (28.59 g / ton) are about 3 times more than present in E stage effluent (8.93 g / ton), and very little in H stage effluent (0.32 g / ton); chloroguaiacols in E stage effluent (11.92 g / ton) are about 18 times more than in C stage effluent

(0.67 g / ton) and little in H stage effluent (.062 g / ton); chlorophenols (27.56 g / ton) in E stage effluent are more than 4 times in C stage effluent (6.28 g / ton); other chlorophenolic compounds present in E stage effluent (23.08 g /ton) are 8 times more than in C stage effluent (2.87 g / ton) [7].

It has also been reported by various authors that in general chlorocatechols are predominantly present in C stage effluent and chloroguaiacols in E stage effluent [7]. Among the various chlorophenolic compounds 2,4 dichlorophenol, 2,5 dichlorophenol, 3,4 dichlorocatechol, 3,4,5 trichlorocatechol, tetrachlorocatechol are higher in C stage effluent and 2,5 dichlorophenol, 2,6 dichlorophenol, 2,3,5 trichlorophenol, 2,4,6/2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 5,6 dichloroguaiacol, pentachlorophenol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin in E stage effluent.

It is generally believed that pentachlorophenol can also appear in the effluents if the raw material used is contaminated with pesticides. Microgram level of pentachlorophenol has also been detected by Guerre et. al for both C and E stage effluent. The quantity of pentachlorophenol decrease significantly with increase in pH of C stage suggesting that pentachlorophenol is also formed during bleaching. The quantity of different chlorophenolic compounds are much less in H stage effluent as compared to C stage effluent. This is due to the fact that 75 – 80% of the lignin gets removed during C and E stages of pulp bleaching. The quantity of chlorophenolic compounds present in E stage effluent is much higher than in C stage effluent which also holds true in the present case also. The results show that both chlorocatechols and chlorophenols are ~30%, chloroguaiacols are ~11%, and other chlorinated phenolics compounds around are ~23% of the total chlorophenolic compounds.

The impact of bleaching conditions particularly C stage has been studied on the formation of chlorinated phenolics. The effect has been studied by changing one operating parameter and maintaining other parameter constant. The different C stage parameters studied are

- pH
- Temperature
- Pulp consistency
- Distribution of chlorine dosage between C and H stages

- Substitution of chlorine in C stage by chlorine dioxide.
- Splitting of chlorine dose in C stage
    - **(i)** with pulp washing
    - **(ii)** without pulp washing

The different modifications in CEH bleaching sequence studied are

- Replacement of hypochlorite by chlorine dioxide
- Addition of peroxide in E stage (E_P)
- Oxygen delignification stage prior to CEH sequences
- Oxygen delignification stage prior to DED sequences

The modifications in C stage bleaching conditions or amendments in CEH bleaching gives a pulp of different pulp brightness. Efforts have been made to make bleached pulp of 80% brightness through different bleaching routes with a view to reduce the generation of chlorophenolics to make bleached pulp of same brightness.

The different routes investigated are

- D_{50} C_{50} EH
- Splitting of chlorine dose in C stage
- ODED
- By changing the bleaching parameter

The environmental parameters of the bleaching process (COD and Color) and the characteristics of bleached pulp (Brightness and CED viscosity) have also been determined. The quantity of mono, di, tri, tetra and pentachlorophenolic compound is represented by $\sum Cl$, $\sum Cl_2$, $\sum Cl_3$, $\sum Cl_4$, $\sum Cl_5$ respectively and that of chlorinated phenols, catechols, guaiacols and other chlorophenolic compounds (vanillin, syringols and syringaldehydes etc.) by $\sum P$, $\sum C$, $\sum G$ and $\sum O$ respectively.

Part A : Effect of C stage bleaching conditions

(1) pH

The results shown in Table 3.2 and Figs 3.3-3.5 indicate that the quantity of total chlorophenolic compounds formed in CEH sequences decrease with increase in C stage pH from 1.5 – 4. Likewise the quantity of $\sum Cl$, $\sum Cl_2$, $\sum Cl_3$, $\sum Cl_4$, $\sum Cl_5$, $\sum P$, $\sum C$, $\sum G$ and $\sum O$ decrease in C, E and H stage effluent with increase in C stage pH from 1.5 - 4 (Table 3.2, Figs 3.3-3.5). The impact of pH on the formation of few chlorophenolic compounds which are formed in higher amount or those who have high toxicity are shown in Table 3.2. The amount of all these compounds decreases with increase in C stage pH. The different categories of chlorophenolics compounds follow the order

Category of compounds	**Order**
$\Sigma Cl_2, \Sigma Cl_3, \Sigma Cl_5, \Sigma P, \Sigma G, \Sigma O$	E > C > H
$\Sigma Cl, \Sigma Cl_4, \Sigma C$	C > E > H

The principal chlorinated phenolics observed in E stage effluent are chlorophenols, chloroguaiacols and chlorovanillins.

The amount of 2,4 / 2,5 dichlorophenol, 2,3,5 / 2,4,6 / 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,5/3,4 dichlorocatechol, pentachlorophenol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin, tetrachlorocatechol decreases with increase in pH from 1.5 – 4. However 5 chlorovanillin in H stage effluent increases with increase in pH from 1.5 – 4. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig 3.2 at pH 1.5.

There is a decrease in total quantity of chlorophenolic compounds about 50% as pH increases 1.5 – 4 (Table 3.2, Figs 3.3-3.5). C, E, H stage effluent contribute about 37.8 %, 58.5 % and 3.6 % respectively at pH 1.5 to the total chlorophenolic compounds and by increasing pH from 1.5 – 4, there is a reduction of 54 % in C stage, 48% in E stage, 8% in H stage effluent. The amount of mono, di, tri, tetra and penta chlorophenolic compounds is reduced by 56 %, 53%, 44%, 58% and 49% respectively (Table 3.2, Figs 3.3-3.5) and the amount of catechols, phenols, guaiacols, and others chlorophenolic compounds decreases approximately by 50% (Table 3.2, Figs 3.3-3.5) as pH increases from 1.5– 4.

The toxicity of effluent depends upon concentration of individual compounds. The $^{96}LC_{50}$ values given in Table 3.1 indicates that the toxicity of pentachlorophenol, catechols, tri, tetrachloroguaiacol and 2,4,6 trichlorophenol are relatively much higher than 2,4 dichlorophenol and dichloroguaiacol. An appreciable reduction in the quantity of di and trichlorophenolic compounds is observed as pH increases from

1.5 – 4 (Table 3.2, Figs 3.3-3.5).

The presence of different categories of chlorophenolic compounds in bleaching effluents have been reported by Folke, Chhaya, Xie and Lu Zi – Jian, the order being C > E >> H [42,56]. A similar behavior has been reported by Voss et al in the CEH bleaching of hard wood and soft wood pulps, showing that the quantity of total chlorophenolic compounds decrease with increase in end pH in C stage ranging from 1 - 2.5, when bleaching is performed at 25° C and 80% of chlorine demand is charged in C stage [15,50,51].

Chlorinated compounds are formed in chlorination stage of pulp bleaching. Catechols have higher solubility even at lower pH where as guaiacols, phenols and other chlorinated phenolics have low solubility under acidic conditions. These are solublized by alkali treatment performed under E stage. This accounts for higher amount of catechols in C stage and remaining chlorinated phenolics in E stage.

The results further indicate that with the increase in C stage pH from 1.5 - 4, the COD of the combined effluent (CEH) is reduced by 25% (Table 3.3, Figs 3.3-3.5) and effluent color by 28%. (Table 3.4, Figs 3.3-3.5)

A small but constant drop in CE kappa number and brightness is noticed suggesting that there is a minor drop in these values but all these variations are with in the experimental variations thus suggesting that there is not much changes in CE kappa number, CE brightness, and CEH brightness as C stage pH is raised from 1.5 to 4. However a significant drop (~20%) in CED viscosity is observed indicating a drop in pulp strength (Table 3.5, Fig 3.6), which is in agreement with the reported facts that proportion of HOCl, responsible for pulp degradation increases as the chlorination pH is raised. Molecular chlorine leads to the higher formation of chlorinated compounds in comparison to HOCl / OCl^- and chlorine dioxide. As the proportion of molecular chlorine decreases with increase in C stage pH, the formation of chlorinated phenolics is expected to decrease. The results reveal that all categories of chlorinated phenolics are reduced by 50% when pH is raised from 1.5 - 4.

HOCl, OCl^- are stronger oxidizing and bleaching agents than molecular chlorine. With the increased formation of HOCl at higher chlorination pH, lignin is more decolorized and oxidized forming a effluent of lower COD and color.

(2) Temperature

C stage temperature in the range of 35° – 15°C has been chosen for the study of impact of temperature. The results obtained are shown in Table 3.6.

The result indicates that the total chlorophenolic compounds generated in C, E, H stages effluents decrease with decrease in C stage temperature in the range of 35° - 15° C (Table 3.6, Figs 3.8-3.10). At a temperature of 35°C, C stage effluent contributes 33%, E stage effluent contributes 46% and H stage 3% to total chlorophenolic compounds. As temperature decreases from 35° to 15°C, the total chlorophenolic compounds decreases by 54% in C stage effluent, 54 % in E stage effluent and 65% in H stage effluent (Table 3.6, Figs 3.8-3.10).

At temperature of 35°C, the contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig 3.7. As the temperature decreases from 35° to 15° C, the quantity of mono and penta chlorophenolic compound decreases by 49-51% (Table 3.6, Figs 3.8-3.10), di and tri chlorophenolic compounds by 56-58% (Figs 3.8-3.10) and tetrachlorophenolic compounds decreases by 69% (Table 3.6, Figs 3.8-3.10). Likewise the quantity of catechols, phenols and others chlorophenolic compounds also decrease by ~ 55% (Table 3.6, Figs 3.8-3.10) and guaiacols are reduced by 63% (Table 3.6, Figs 3.8-3.10).

The amount of 2,4 dichlorophenol, 2,5 dichlorophenol, 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,5 dichlorocatechol, pentachlorophenol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin, tetrachlorocatechol in C, E, H stage effluents also decrease as the temperature decreases from 35° to 15° C.

The quantity of all categories of chlorinated compounds present in C, E, H and combined CEH effluent decreases by 50% or more when chlorination temperature is reduced from 35° to 15° C. Voss et al. also observed that quantity of total chlorophenolic compounds formed during CEH bleaching of softwood and hard wood pulps was much higher at chlorination temperature of 60°C than at 25°C when 50% or 80% chlorine demand was applied in C stage [15,50,51].

A steady decrease of 22% in COD value is observed when the temperature decrease from 35° to 15° C (Table 3.7, Figs 3.8-3.10). A similar trend is also observed in the case of color, giving 28% reduction (Table 3.8, Figs 3.8-3.10). There is also marginal decrease in the pulp brightness nearly by 4 point after E stage and nearly 2 point after H stage. But the CED pulp viscosity is increased by 28% indicating a decrease in pulp degradation with decrease in C stage bleaching temperature. CE kappa number is found to increase by 4 % showing that the residual lignin increases, as temperature decreases (Table 3.9, Fig 3.11).

At higher temperature the proportion between chlorine and hypochlorous acid responsible for pulp degradation is also enhanced. The reactivity of bleaching agent towards both lignin and carbohydrate is enhanced, leading to the increased formation of chlorinated phenolics which results in the increased pulp degradation as shown by the drop in CED pulp viscosity.

(3) Consistency

Study has been performed at C stage pulp consistency between 2 to 4% and the results of the study are given in Table 3.10.

The total chlorophenolic compounds present in C, E, and H stage effluent increase with increase in C stage consistency (Table 3.10, Figs 3.13-3.15). At 2% consistency, C stage contributes 38%, E stage 59% and H 3% share to total chlorophenolic compound. As consistency increases from 2 to 4%, the quantity of total chlorophenolic compounds increase by 129%, 152%, and 224% in C, E, H stages respectively (Table 3.10, Figs 3.13-3.15).

At 2% consistency, the contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig 3.12. Thus di and trichlorophenolic compounds are major contributor to total chlorophenolic compounds. As consistency increases from 2 to 4%, the amount of mono and trichlorophenolic compounds increases by 156% (Table 3.10, Figs 3.13-3.15), di tetra and pentachlorophenolic compounds increases by 130%, 186%, and 126% respectively (Table 3.10, Figs 3.13-3.15). Similarly the quantities of catechols, phenols, guaiacols and others chlorinated compound also increase with increase in C stage pulp consistency, the increase being 89%, 178%, 210%, and 165% respectively (Table 3.10, Figs 3.13-3.15).

The results are in agreement with that of Earl and Douglas Reeve where the chlorophenolic compounds reported were higher at 10% Cy than 4% Cy. The quantity of di and trichlorophenolic compounds increase where as tetrachlorophenolic compounds decreases when the pulp consistency is raised from 4 - 10% [14,15,50,51].

The amount of 2,4 dichlorophenol, 2,5 dichlorophenol, 2,6 dichlorophenol, 2,3,5 trichlorophenol, 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3–5 dichlorocatechol, 3 chlorocatechol pentachlorophenol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin in C, E, H stage effluents also increases as the consistency is increased.

Increase in C stage pulp consistency increases the total COD by 20% (Table 3.11 and Figs 3.13-3.15) and color by 40% (Table 3.12 and Figs 3.13-3.15). There is about 1% increase in brightness after E and H stages (Table 3.13 and Fig. 3.16). A CED drop of about 17% and increase of about 8% in CE kappa number is also noticed (Table 3.13 and Fig. 3.16).

The increase in pulp consistency at the same bleach chemical charge gives increased concentration of bleach chemicals and increased reaction rates. This is responsible for increased formation of chlorinated phenolic compounds, effluent COD, effluent color and also small increase in pulp brightness.

(4) Distribution of bleaching chemical between C and H stage

The effect of change in the distribution of chlorine dose between C and H stages has been studied at constant total chlorine dose. The results obtained are given in Table 3.14. The results show that the quantity of total chlorinated phenolic compounds increase by 135% in C stage effluent, 96% in E stage effluent and 39% decrease in H stage effluent as distribution of bleach chemical between C and H stages is varied from 45:55 to 65:35 (Table 3.14, Figs. 3.18-3.20) [15,50,51].

At ratio of 45:55, C stage effluent contributes 30%, E stage 65% and H stage 5% to total chlorophenolic compounds. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig 3.17. By varying the proportion of bleach chemical between C and H stage the quantity of mono, di, tri, tetra and pentachlorophenolic compounds increase by 141%, 92%, 101 %,133 %, 62% respectively (Table 3.14, Figs 3.18-3.20).

The results in Figs. 3.18-3.20 shows that there is consistent increase in the quantity of mono, di, tri, tetra and penta chlorophenolic compounds in C and E stage effluent and decrease in H stage effluent as the quantity of chlorine in C stage is increased from 45% to 65%. However in the case of pentachlorophenolic compounds in H stage effluent the quantity first increases then decreases. Similar trend is observed with different categories of chlorophenolic compounds as catechols, phenols, guaiacols, and other chlorophenolic compounds increase by 120%, 102%, 193%, and 55% respectively (Table 3.14, Figs. 3.18-3.20).

The results in Figs 3.18-3.20 show that the amount of different categories of phenolic compounds increases consistently with increase in proportion of chlorine in C stage. The amount of 2,4 dichlorophenol, 2,5 dichlorophenol, 2,3,5 trichlorophenol, 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,4,5 trichlorocatechol, tetrachlorocatechol in C, E and H stage effluents also increase as C:H ratio increases, but 5 chlorovanillin and 5,6 dichlorovanillin decreases but amount of 5 chloroguaiacol, 2,3,5 trichlorophenol, 2,3,6 trichlorophenol, 3,4 dichlorophenol, 5 chlorovanillin, tetrachloroguaiacol, tetra chlorocatechol increase in C and E stage effluents and decrease in the H stage effluent.

The results show that COD of the combined CEH effluent increase by 46% with the increase in proportion of chlorine in C stage (Table 3.15 and Figs. 3.18-3.20). Individually in C stage effluent COD increases by 116%, in E stage effluent increases by 41%, but in H stage effluent decreases by 13% (Table 3.15 and Figs 3.18-3.20). A similar trend is followed by color values. The total color value of CEH effluent increases by 60% (Table 3.16 and Figs. 3.18-3.20). An increase of 67% in C stage, 57 % in E stage and 24% in H stage is observed. There is a small decrease in brightness 0.8 point after E stage and 1 point after H stage and viscosity is increased by 12%, CE kappa number is decreased by 7% (Table 3.17 and Fig. 3.21).

The change in proportion from 45:55 to 65:35 means charging more chlorine in C stage and less hypochlorite in H stage. The action of chlorine on lignin in C stage results in the formation of chlorophenolic compounds. The increased proportion of chlorine will form more chlorinated phenolic compounds in C and E stage effluents. Alkali extraction stage involves the dissolution of undissolved portion of chlorinated phenolic compounds formed during C stage pulp bleaching, thus this stage becomes the major contributor to pollution in terms of COD, color and TOCl. Increased quantity of chlorine in C stage gives more hydrophilic lignin, which is fragmented by hypochlorite and results in increased dissolution of lignin and giving higher effluent COD and color values. The lower quantity of hypochlorite charged in H stage will give lower amount of chlorinated phenolics in H stage effluent.

(5) Substitution of chlorine by chlorine dioxide in C stage

The study has been performed by substituting 25 to 100% of chlorine by chlorine dioxide in C stage. The results obtained are given in Table 3.18. The results show that the formation of total chlorophenolic compounds decrease substantially (82%) at 100% replacement of chlorine by chlorine dioxide in C stage [3,4,17,25,28, 33,35,44,49,52,53,57,58,59]. Some reports indicate that the amount of total chlorinated phenolics formed increases with increase in chlorine dioxide substitution, pass through a maxima at 50% substitution and then decreases rapidly to low levels at 100% chlorine dioxide substitution [2,15,50].

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 3.22 at $C_{75}D_{25}EH$ sequence. The results in Figs. 3.23-3.25 show that quantity of the total chlorophenolic compounds formed decreases up to 82%. A decrease of 88% in C stage effluent, 79% in E stage effluent and 85% in H stage effluent is observed when chlorine in C stage is completely replaced by ClO_2 (Table 3.18, Figs. 3.23-3.25). The formation of mono, di, tri, tetra, and penta chlorophenolic compounds decrease up to 79%, 77%, 83%, 90%, and 100% at 100% chlorine substitution by chlorine dioxide (Table 3.18, Figs. 3.23-3.25). Likewise the formation of catechols, phenols, guaiacols and other chlorophenolic compounds decrease up to 91%, 78%, 65%, and 82% respectively at 100% substitution of chlorine by ClO_2 in C stage (Table 3.18, Figs. 3.23-3.25). The quantity of some mono, di and trichlorophenolic compounds in C stage effluent increases up to 50% replacement and then decrease gradually up to 100% substitution (Table 3.18, Figs. 3.23-3.25).

The amount of 3,4 dichlorocatechol, 3,5 dichlorocatechol, 3 chlorocatechol, 6 chlorovanillin, pentachlorophenol, 3,4,5 trichlorocatechol, 2,6 dichlorosyringaldehyde, tetrachlorocatechol in C and E stage effluent decrease with increase in chlorine dioxide substitution. But the amount of 2,4/ 2,5 dichlorophenol, 2,6 dichlorophenol, 3 chlorophenol, 4 chlorophenol, 2,3,5 trichlorophenol, 2 chlorophenol, 2,3,6 trichlorophenol, and 4 chloroguaiacol in C and E stage effluent increase up to 50% substitution and fall rapidly to zero at 100% chlorine dioxide substitution.

A 40% reduction in effluent COD (Table 3.19 and Figs 3.23-3.25) and 79% reduction in color value of CEH effluent (Table 3.20 and Figs 3.23-3.25) indicate a significant drop in pollution load [25,37,49]. Under same conditions the viscosity of pulp is improved by 33% and brightness of pulp is improved by 16.8 point after E stage and 8 point after H stage and CE kappa number is reduced by 4% (Table 3.21 and Fig. 3.26).

Chlorine dioxide is a highly selective bleaching agent as it attacks only lignin and it is a strong decolorization agent. Increased substitution of chlorine by chlorine dioxide reduces the attack on cellulose that reduces the drop in pulp viscosity very significantly i.e. higher pulp viscosity and lower dissolution of cellulose fragments giving much lower effluent COD and color. The chlorine dioxide can give a pulp of higher brightness and cleanliness without impairing its strength.

High level of ClO_2 has been substituted for chlorine in the traditional first bleaching stage. 40 – 60% substitution has been practiced because this is the normal optimum condition for full delignification. The change to 100% substitution with chlorine dioxide is a response of market pressure [29]. The greatest economic consideration in the use of chlorine dioxide in delignification is the chemical cost. The relatively high cost of bleaching chemicals is basically a function of present of chlorine dioxide and the price ratio of chlorine dioxide and chlorine. This is typical of many studies in which the lowest cost is obtained in the range of 30 – 50% substitution with the cost being relatively insensitive over this range. As 100% substitution is approached, the chemical cost increases sharply [12].

(6) Splitting of chlorine dose in C stage

(a) Without pulp washing

The chlorine dose in C stage has been divided into two equal parts. Firstly chlorination has been performed with half the dose and then chlorination with the next half dose is performed. No washing of pulp has been done between two chlorine stages. The extraction and hypochlorite stages are performed under same conditions as performed with out chlorine splitting. The results are given in Table 3.22.

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 3.27. The results shown in Figs. 3.28–3.30 indicates that quantity of mono, di, tri, tetra, penta chlorophenolic compounds, phenols, catechols, guaiacols and other chlorinated compound in C, E, H stage effluents, all decrease with the use of split chlorine dose in C stage. Lieber Gott has also reported a decrease in the formation of chlorinated compounds when chlorine dose was split into two portions [19,20].

The results shown in Figs 3.28–3.30 indicates that splitting of chlorine dose gives 47% lower formation of chlorinated phenolic compounds in CEH stage effluent [19,20] 50% reduction in chlorinated phenolic compounds in C stage effluent, 44% reduction in E stage effluent and 51% reduction in H stage effluent. The reduction of 41%, 46%, 45%, 36% and 67% of mono, di, tri, tetra and pentachlorophenolic compounds respectively is observed (Table 3.22, Figs. 3.28–3.30). Similarly the formation of phenol, catechol, guaiacol and other chlorinated compounds is reduced by 51%, 45%, 33%, and 48% respectively (Table 3.22, Figs. 3.28–3.30).

A very large decrease in 2,4 dichlorophenol, 2,5 dichlorophenol, 2,4,6 trichlorophenol, 3,4 dichlorocatechol, 5 chlorovanillin, 4 chlorocatechol, 3,5 dichlorocatechol, 2,3,4,6 tetrachlorocatechol is observed when chlorine dose in C stage is splitted into two equal doses and no washing between chlorination stages has been done. A reduction of 13% in effluent COD (Table 3.23 and Figs. 3.28–3.30) and 19% in effluent color was also observed (Table 3.24 and Figs. 3.28–3.30). The pulp brightness is improved by 0.5 point after E stage and 0.4 point after H stage and appreciable increase in pulp viscosity (23%) (Table 3.25 and Fig. 3.31) is observed. So splitting of chlorine dose reduces the pollution load and gives a stronger and brighter pulp.

The splitting of chlorine dose means applying lower concentration of chlorine over longer period making mild attack on cellulose and hemicellulose giving lower dissolution of carbohydrate fraction giving lower effluent COD and color. Mild attack on cellulose gives lower pulp degradation and will yield stronger pulp of higher viscosity.

(b) With pulp washing

As the chlorine dose in C stage has been divided into two equal parts, pulp washing has been done after applying first chlorine dose. The rest half dose is applied on the pulp after first chlorination stage and after completion of second chlorination stage again pulp washing has been done. Both C_1 and C_2 effluents are collected, mixed and used for further analysis. The results are given in Table 3.22. The results show that the amount of chlorophenolic compounds decrease more when pulp is washed after the first split chlorination stage.

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 3.27.The total chlorophenolic compounds decrease by 54% which is 7% more in comparison to chlorination stage (*Dosage being splitted into two equal parts and no in between washing has taken place*). A reduction of 54% in C stage, 48% in E stage and 54% in H stage effluent in total chlorophenolic compounds is observed (Table 3.22, Figs. 3.28–3.30). The reduction of 44%, 50%, 51%, 46%, and 68% in mono, di, tri, tetra, and penta chlorophenolic compounds respectively is also observed (Table 3.22, Figs. 3.28–3.30) [19,20]. A similar trend has also been shown by phenols, catechols, guaiacols and other chlorophenolic compounds, the respective reductions being 55%, 50%, 37%, and 50% (Table 3.22, Figs. 3.28–3.30).

The effluent COD is reduced by 16% and color is reduced by 22% (Tables 3.23-3.24 and Figs 3.28–3.30). There is an increase in brightness of 0.6 point after E stage and 0.5 point after H stage; viscosity is improved by 24% and CE kappa number is reduced by 4% (Table 3.25 and Fig 3.31). Washing of pulp after first chlorination stage removes the water soluble fraction of the lignin and other color constituents which consumes a portion of chlorine when fresh chlorine is charged in second split chlorination stage. The lignin and other colored constituents are attacked better, forming a lower CE kappa number and gives some improvement in pulp brightness after E and H stages.

Part – B : Modifications in CEH bleaching sequences

(1) Replacement of hypochlorite by ClO_2 in H stage

The complete replacement of hypochlorite by chlorine dioxide will change the bleaching sequence from CEH to CED. The results of this replacement are given in Table 3.26.

The results show that there is practically no change in the quantity of various chlorophenolic compounds in combined CEH effluent because main contribution in total chlorophenolic compounds is from C and E stage effluents. The contribution from H stage is minor.

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 3.32-3.33. There is a reduction of 3% in total chlorophenolic compounds (Table 3.26, Figs. 3.34-3.36) as there is decrease in the quantity of 2,4 dichlorophenol, 2,5 dichlorophenol, 2,3,6 trichlorophenol, trichlorosyringol, and tetrachlorocatechol in H stage effluent [31].

Nearly 2% reduction in mono, di, tri chlorophenolic compounds, 3 – 5% in tetra, penta chlorophenolic compounds, phenol and other chlorophenolic compounds and negligible reduction in catechol & guaiacol is observed (Table 3.26, Figs. 3.34-3.36). In C and E stage effluents the bleaching results and environmental loads remain nearly unchanged. The contribution of H stage effluent to the bleaching sequence in terms of chlorinated phenolic compounds, effluent COD and color is very small i.e. 3%, 4% and 1% respectively. The replacement of H by D reduces the formation of chlorophenolic compounds, effluent COD and color in D stage but the overall impact remains small because the improvement is small 1 – 4% (Tables 3.27 – 3.28 and Figs. 3.34-3.36).

Pulp viscosity and brightness is the biggest gain in this replacement. The improvement in pulp viscosity is 32% and in brightness by 1.8 point after H stage (Table 3.29 and Fig. 3.37). Hypochlorite is strongly pulp degrading where as ClO_2 is inert to pulp thus giving a stronger pulp. Chlorine dioxide is also known to give lower PC number – pulp with lower color reversion tendency.

(2) Addition of peroxide in E stage (E_p)

Reinforced extraction stage with peroxide has been performed i.e. E_p. The results are given in the Table 3.26. The total chlorophenolic compounds decrease appreciably when E stage changes to E_p stage; there is no change in the conditions of chlorination and hypochlorite stage [8,31].

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 3.32-3.33. There is a reduction of 54% in total chlorophenolic compound in the CEH effluent, when E stage is changed to E_p. A reduction of 81% in E stage effluent and 90% in H stage effluent in the amount of chlorophenolic compounds is obtained (Table 3.26, Figs. 3.34-3.36). Mono, di, tri, tetra chlorophenolic compound also decrease by 34%, 51%, 62%, 27% respectively, pentachlorophenolic compound was not detected in E and H stage effluents (Table 3.26, Figs. 3.34-3.36). A similar trend is shown by phenols, catechols, guaiacols and other chlorophenolic compounds as they are reduced by 66%, 19%, 79% and 76% respectively (Table 3.26, Figs. 3.34-3.36).

There is a appreciable reduction in the amount of 2,4 dichlorophenol, 2,5 dichlorophenol, 5 chloroguaiacol, 2,3,5 trichlorophenol, 2,3,6 trichlorophenol, 2,4,6 trichlorophenol, 3,4 dichloroguaiacol, 5 chlorovanillin, 5,6 dichloroguaiacol, 3,5 dichlorosyringol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin, tetrachlorocatechol.

The effluent COD and color value are reduced by 35% and 33% respectively as E stage is changed to E_p stage (Table 3.29, Figs. 3.34-3.36). The pulp brightness is improved by 10.1 point after E stage and 0.9 point after H stage, the pulp viscosity is increased by 9% and the CE kappa number is decreased by 5% (Table 3.29, Fig. 3.37).

Peroxide is an oxidizing and decolouring agent. The chlorophenolic compounds are oxidized and thus reducing the quantity of chlorophenolics in E_p stage effluent. The oxidation reaction results in increased dissolution of lignin fragments giving a lower effluent COD and small reduction in CE kappa number of pulp. The bleaching action of peroxide also slightly improves the brightness of the pulp.

(3) Oxygen delignification stage followed by sequential CEH (OCEH)

Oxygen delignified pulp was bleached by CEH sequence; the results obtained are given in Table 3.26. Oxygen delignification stage (prebleaching stage) reduced the formation of chlorophenolic compounds by 74% [8-11,13,17,21,22,24,48]. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 3.32-3.33. A reduction of total chlorophenolic compounds by 75% in C stage, 73% in E stage and 77% in H stage effluent is observed (Table 3.26, Figs 3.34-3.36) [5,45]. In case of mono, di, tri, tetra and penta chlorophenolic compound, a reduction of 65%, 76%, 72%, 67%, 89% respectively is also being observed (Table 3.26, Figs. 3.34-3.36). The similar trend has shown by phenols, catechols, guaiacols and others chlorophenolic compounds. These are reduced by 79%, 73%, 71%, and 68% respectively (Table 3.26, Figs. 3.34-3.36).

On using Oxygen delignification stage, there is a large reduction in the quantities of 2,4 dichlorophenol, 2,5 dichlorophenol, 2 chlorophenol, 2,3,6 trichlorophenol, 3,4 dichlorocatechol, 3,5 dichlorocatechol, 3 chlorocatechol, pentachlorophenol, 3,4,5 trichlorocatechol, 2,3,5 trichlorophenol, 3,5 dichloroguaiacol, 3,4,6 trichloroguaiacol, trichloroguaiacol, 5,6 dichlorovanillin and 2,6 dichlorosyringaldehyde.

The effluent COD is reduced by 30% and the color value is reduced by 46% (Tables 3.27 and 3.28, Figs. 3.34-3.36). There is major improvement of brightness by 6.6 points after H stage but viscosity drop by 8% and the CE kappa number is reduced by 12% (Table 3.29, Fig. 3.37).

The process of oxygen delignification is another way to reduce the amount of chlorophenolic compounds. This procedure is used to reduce the pulp kappa number by 40 – 50% which in turn reduces the bleach chemical demand in the following C, E, and H stages to nearly the same extent which reduces the environmental loads – chlorophenolic compounds, COD and color very significantly.

(4) Oxygen delignification stage followed DED i.e. (ODED)

After oxygen delignification stage, the bleach liquor is replaced by chlorine dioxide in chlorination and hypochlorite stage i.e. ODED. The results are given in Table 3.26.

The results indicate that the total chlorophenolic compounds are reduced by 86% as the sequence changes from CEH to ODED and corresponding reduction in C stage effluent is by 92%, in E stage effluent by 82% and in H stage effluent by 88% (Table 3.26, Figs. 3.34-3.36) [17,30,58]. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 3.32-3.33.

Mono, di, tri and tetra chlorophenolic compounds are reduced by 84%, 81%, 86% and 92% respectively (Table 3.26, Figs. 3.34-3.36) and no penta chlorophenolic compound has been found (Table 3.26, Figs. 3.34-3.36). In case of phenols, catechols, guaiacols and other chlorophenolic compounds, there is a reduction of 86%, 92%, 75%, 81% respectively (Table 3.26, Figs. 3.34-3.36).

The quantity of 2,4 dichlorophenol, 2,5 dichlorophenol, 3 chloroguaiacol, 5 chloroguaiacol, 2,3,5 trichlorophenol, 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 5 chlorovanillin, 5,6 dichloroguaiacol, pentachlorophenol, 2,3,4,6 tetrachlorophenol, tetrachlorocatechol, 5,6 dichlorovanillin, trichlorosyringol, 2,6 dichlorosyringaldehyde decrease as CEH changes to ODED.

The COD values and color values are reduced by 59% (Tables 3.27 and 3.28 and Figs. 3.34-3.36). The CEH brightness is improved by 9.3 point and CE kappa number is also reduced by 2%. The viscosity drops by 4% (Table 3.29, Fig. 3.37).

Part C : 80% brightness pulp by different routes

The results on the studies shown in Part A and Part B indicate that various C stage bleaching conditions and changes in bleaching sequence can give effluent of lower chlorophenolic compounds but the final brightness is different. In order to make comparative study, a target pulp bright of 80% ISO was chosen. A few modified bleaching sequences as given below have been tried.

(1) $D_{50}C_{50}EH$

To get the target brightness i.e. 80% the bleach chemical demand has been changed. In sequential bleaching (i.e. CEH), the bleach chemical demand is 6.87%, but when the sequence changed to $D_{50}C_{50}EH$, the bleach chemical demand drops to 4.50%. All other parameters remain same. The results are given in Table 3.30.

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 3.38-3.39. The results show that there is a substantial decrease in the amount of total chlorophenolic compounds i.e. 53%. In C, E and H stage effluent there is reduction of 45%, 56% and 65% respectively in the formation of chlorophenolic compounds (Table 3.30, Figs. 3.40-3.42). In mono, di, tri, tetra and penta chlorophenolic compounds, there is a reduction of 48%, 49%, 49%, 59%, 86% respectively (Table 3.30, Figs. 3.40-3.42). A similar trend of reduction has shown by catechols (55%), phenols (58%), guaiacols (38%) and others chlorophenolic compounds (54%), as bleach chemical demand decrease from 6.87 to 4.50% (Table 3.30, Figs. 3.40-3.42) except some chlorophenolic compounds in C stage effluent whose concentration are increased.

The results indicate that all individual chlorophenolic compounds decreases, and there is large reduction in the quantity of 2,5 dichlorophenol, 4 chlorophenol, 3,4 dichloroguaiacol, 3,5 dichlorocatechol, 3,4,6 trichloroguaiacol, pentachlorophenol, tetrachlorocatechol, 5,6 dichlorovanillin.

The effluent COD and color reduce by 48% and 67% respectively (Tables 3.31 and 3.32, Figs. 3.40-3.42). The brightness is increased to 80.6%. There is also a gain of 24% in viscosity. The CE kappa number remains nearly unchanged (Table 3.33, Fig. 3.43).

(2) Splitting of chlorine dose in C stage (without washing)

The other sequence to get the 80% brightness is the splitting of chlorine dose. The bleach chemical demand decreases from 6.87 to 5.61%. However, there was no change in the conditions in the extraction and hypochlorite stages. The results are shown in Table 3.30.

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs 3.38-3.39. The results show that there is a reduction of 57% in the amount of total chlorophenolic compounds. There is reduction in the amount of total chlorophenolic compounds in C stage effluent 57%, in E stage effluent 57% and 67% reduction in H stage effluent (Table 3.30, Figs. 3.40-3.42). In mono, di, tri, tetra and pentachlorophenolic compounds, there is a reduction of 51%, 58%, 55%, 69%, 74% respectively (Table 3.30, Figs. 3.40-3.42). A similar trend has shown by catechols, phenols, guaiacols and others chlorophenolic compounds, the reduction being 55%, 63%, 48%, and 58% respectively (Table 3.30, Figs. 3.40-3.42).

The results show a large reduction in the quantity of 2,5 dichlorophenol, 4 chloroguaiacol, 3,4 dichlorocatechol, 3,5 dichlorocatechol, 5,6 dichloroguaiacol, tetrachlorocatechol, pentachlorophenol and trichlorosyringol.

The splitting of chlorine dose reduces the pollution load in terms of effluent COD and color values by 28% and 35% respectively (Tables 3.31 and 3.32, Figs. 3.40-3.42). Along this, a gain of 21% in viscosity is also observed at the target brightness (80%) (Table 3.33, Fig. 3.43).

(3) Oxygen delignification followed by DED (ODED)

In this bleaching, the bleach chemical demand is reduced very sharply from 6.87 – 3.50 %. The results are shown in Table 3.30.

The result shows a very large reduction in the concentration of total chlorophenolic compounds i.e. 90%. In C stage effluent there is a reduction of 94%, 87% in E stage effluent and 92% reduction in H stage effluent (Table 3.30, Figs. 3.40-3.42). The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 3.38-3.39. In case of mono, di, tri, and tetrachlorophenolic compounds there is a reduction of 84%, 89%, 90%, 95% respectively (Figs. 3.40-3.42). The concentration of penta chloro phenolic compounds is nil (Table 3.30, Figs. 3.40-3.42). The amount of catechols, phenols, guaiacols and other chlorophenolic compounds are reduced by 94%, 90%, 79%, and 87% respectively (Table 3.30, Figs. 3.40-3.42). This sequence gives a very large reduction in the amount of chlorophenolic compounds. But the viscosity drops down by 3% (Table 3.33 and Figs. 3.40-3.43).

The result shows a large reduction in the quantity of 2,4 dichlorophenol, 2,5 dichlorophenol, 4 chloroguaiacol, 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,5 dichlorocatechol, 3,4 dichlorocatechol, 5,6 dichloroguaiacol, 2,3,4,6 tetrachlorophenol, tetrachlorocatechol, trichlorosyringol and 5,6 dichlorovanillin. The concentration of pentachlorophenol is observed nil.

The effluent COD and color values are reduced by 68% and 70% respectively (Tables 3.31 – 3.32, Figs. 3.40-3.42). There is nearly no change in CE kappa number and the brightness remains the target brightness (80%) (Table 3.33, Fig. 3.43).

(4) Modified CEH bleaching

By changing all the C stage bleaching parameters the target brightness has been achieved by new bleaching, the temperature is 30° C, pH 2.5, consistency 2.5 and the bleach chemical demand remain unchanged. The results are shown in the Table 3.30.

The result shows a reduction of 21% in total chlorophenolic compounds. The similar trend was observed in C, E, and H stage effluents i.e. 16%, 23%, 22% respectively (Table 3.30, Figs. 3.40-3.42). In the case of mono, di, tri, tetra and penta chlorophenolic compound, the result shows a reduction of 15%, 20%, 22%, 28% and 22% respectively (Table 3.30, Figs. 3.40-3.42). The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 3.38-3.39.

The amount of catechols, phenols, guaiacols, and other chlorophenolic compounds reduced to 23%, 22%, 21%, and 26% respectively (Figs 3.40-3.42). The effluent COD and color value is reduced by 16% and 18% respectively (Tables 3.31 and 3.32, Figs. 3.40-3.42). But the main draw back of this sequence is pulp strength. The viscosity drops down by 15% and the brightness remains the target brightness (80%) (Table 3.33, Fig. 3.43).

Summary of results

Part – A : (Changes in C stage bleaching conditions)

(a) pH

(1) Increasing pH from 1.5 – 4, gives about 25% drop in effluent COD and 28% drop in effluent color.

(2) The total amount of total chlorophenolic compounds reduce by 50% and the di and tri chlorophenolic compounds decrease by 53% and 44% respectively.

(3) There is not much change in the pulp brightness and CE kappa number, but a drop of 20% is observed in CED viscosity.

(b) Temperature

1. As the temperature decreases from 35 – 15°C, the total chlorophenolic compounds reduce by 55% and di, tri and tetra chlorophenolic compounds decrease by 56%, 58% and 69% respectively.
2. The effluent COD and color reduce by 22% and 28% respectively.
3. The CEH brightness decrease by 2 point, but the pulp viscosity is improved by 28%.

(c) Consistency

1. Increasing pulp consistency from 2 to 4%, the COD and effluent color value increase by 20% and 40% respectively.
2. Only 1 point increment in brightness is observed after H stage.
3. CE kappa number increase by 8%.
4. 17% drop in pulp viscosity is an indication of increased pulp degradation.
5. Chlorophenolic compounds increase by 145%.

(d) Distribution of bleaching chemical between C and H stage

1. By changing the proportion of chlorine from 45:55 to 65:35, the total chlorophenolic compounds increase by 100%. And 135% and 96% increase in C and E stages effluent respectively, but 39% reduction in H stage effluent.
2. COD and color of combined CEH effluent increase by 46% and 60%.
3. Brightness decrease by 1 point.
4. CE kappa number decrease by 7%.
5. Pulp viscosity improves by 12%.

(e) Chlorine dioxide substitution

1. Total chlorophenolic compounds reduce by 82% when chlorine is substituted by chlorine dioxide.
2. COD and color reduced by 40% and 79%.
3. Gain of 33% in viscosity is an indication of protective action of chlorine dioxide.
4. Brightness improves by 8.3 points.

(f) Splitting of chlorine dose

- *Without pulp washing*
  1. 47% reduction in the chlorophenolic compounds.
  2. 13% and 19% reduction in effluent COD and color.
  3. 23% improvement in CED pulp viscosity.
  4. A minor improvement of 0.4 point in brightness.
- *With pulp washing*
  1. 54% reduction in the chlorophenolic compounds.
  2. 16% and 22% reduction in effluent COD and color.
  3. 24% improvement in CED pulp viscosity.
  4. A minor improvement of 0.5 point in brightness.

Part – B : (Modifications in CEH bleaching sequences)

(a) Replacement of hypochlorite by chlorine dioxide

(1) Small reduction (3%) in chlorophenolic compounds.
(2) Small reduction (1 – 4%) in effluent color and COD.
(3) A very significant improvement in pulp viscosity (32%).
(4) A minor improvement (1.8 point) in pulp brightness.

(b) Addition of peroxide in E stage

(1) 54% reduction in chlorophenolic compounds.
(2) Effluent COD and color reduce by 35% and 33% respectively.
(3) Pulp viscosity improves by 9%.
(4) Pulp brightness increases by 0.9 point.

(c) Oxygen delignification followed by CEH (OCEH)

(1) 74 % reduction in chlorophenolic compounds.
(2) 30% reduction in COD and 46% reduction in color.
(3) Viscosity drops by 8%.
(4) 6.6 point improvement in brightness

(d) Oxygen delignification followed by DED (ODED)

(1) Chlorophenolic compounds reduce by 86%.
(2) Effluent COD and color reduce by 59%.

(3) Pulp brightness improves by 9.3 point.

(4) Viscosity drops by 4%.

Part – C : (80% target brightness by different routes)

(a) $D_{50}C_{50}EH$

(1) 56% reduction in chlorophenolic compounds.

(2) Effluent COD and color reduce by 48% and 67%.

(3) Gain of 24% in pulp viscosity.

(4) 80.6% brightness achieved

(b) **Splitting of chlorine dose in C stage (Without pulp washing)**

(1) Chlorophenolic compounds reduce by 57%.

(2) 28% and 35% reduction in effluent COD and color.

(3) 21% improvement in pulp viscosity

(c) **Oxygen delignification followed by DED (ODED)**

(1) Reduction of 90% in chlorophenolic compounds.

(2) Effluent COD and color reduce by 68% and 70%.

(3) Viscosity drops by 3%.

(d) **Modified CEH bleaching**

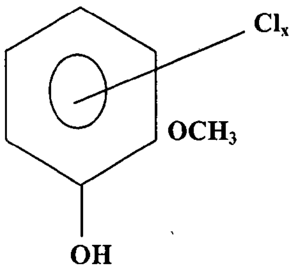
(1) 21% reduction in chlorophenolic compounds.

(2) 16 – 18% reduction in effluent COD and color values.

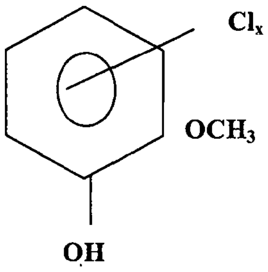
(3) Pulp viscosity drop by 15%.

Table 3.1 LC_{50} values for various Chlorophenols

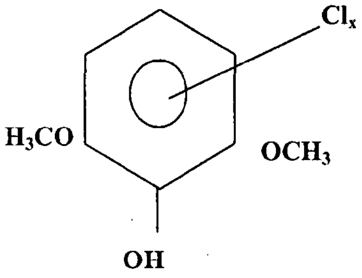
Sl. No.	Compounds	$^{96}L_{50}$ (mg/l)
1	Dichlorocatechol	0.5 – 1.0
2	Dichloroguaiacol	2.3
3	2,4-dichlorophenol	2.8
4	Pentachlorophenol	0.047 – 0.106
5	2,4,6- trichlorophenol	0.45 – 2.6
6	Tetrachlorocatechol	0.25 – 1.5
7	3,4,5- trichlorocatechol	0.89 – 1.5
8	Trichloroguaiacol	0.7 – 1.0
9	Tetrachloroguaiacol	0.2 – 1.7



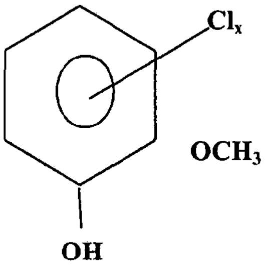
Chlorophenols



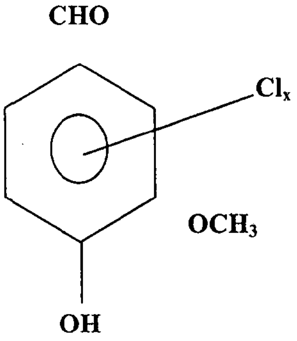
Chloroguaiacols



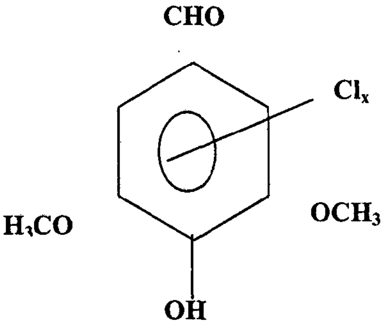
Chlorosyringols



Chlorovanillins



Chlorocatechol



Chlorosyringaldehydes

Fig. 3.1 Structures of different chlorophenolic compounds

Table 3.2 Effect of C stage pH on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at pH values of														
	1.5			2.0			2.5			3.0			4.0		
	C	E	H	C	E	H	C	E	H	C	E	H	C	E	H
2,4 Dichlorophenol	2.43	1.34	0.25	0.80	0.39	0.14	0.78	0.67	0.13	0.67	0.34	0.09	0.43	0.25	0.09
2,5 Dichlorophenol	1.50	2.40	0.23	1.43	2.89	0.21	1.27	2.54	0.19	1.02	1.44	0.11	0.91	1.23	0.09
2,3 Dichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3-Chloroguaiacol		0.25	-	-	0.25	-	-	0.24	-	-	0.19	-	-	0.17	-
2,6 Dichlorophenol	0.32	1.59	-	0.11	2.56	-	0.08	2.31	-	0.08	2.02	-	0.07	1.59	-
4-Chlorophenol	0.30	-	-	0.23	-	-	0.21	-	-	0.13	-	-	0.10	-	-
3-Chlorophenol	0.60	1.98	-	0.49	1.94	-	0.37	1.79	-	0.28	1.30	-	0.24	1.12	-
4-Chloroguaiacol	0.03	-	-	0.02	-	-	-	-	-	-	-	-	-	-	-
5-Chloroguaiacol	-	1.54	0.07	-	1.46	0.06	0.02	1.32	.053	0.02	1.12	0.05	0.01	0.99	0.03
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-chlorophenol	0.35	-	-	0.11	-	-	0.09	-	-	0.07	-	-	0.07	-	-
2,3,5-Trichlorophenol	0.20	2.15	0.38	0.16	3.12	0.33	-	2.98	0.29	-	2.71	0.22	-	2.06	0.16
2,4,6-Trichlorophenol	0.31	3.05	-	0.22	2.01	-	0.18	1.93	-	0.12	1.36	-	0.09	1.04	-
2,4,5-Trichlorophenol	-	-	0.28	-	-	-	0.13	0.11	-	0.10	0.07	-	0.08	0.06	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	0.06	0.03	-	0.04	0.02	-	0.03	0.01	-
2,3,6 Trichlorophenol	0.98	6.03	0.39	0.80	5.88	0.34	0.25	4.94	0.33	1.19	3.02	0.29	1.27	2.34	0.25
3,6 Dichloroguaiacol	0.16	-	-	0.10	-	-	0.07	-	-	0.06	-	-	0.04	-	-
3,4 Dichloroguaiacol	0.20	5.01	-	0.18	4.93	-	0.17	4.61	-	0.13	3.15	-	0.09	2.85	-
3,4-Dichlorocatechol	4.69	1.11	-	3.78	1.06	-	3.32	0.98	-	2.17	0.83	-	2.02	0.38	-
3,4-Dicholorophenol	0.69	-	0.65	0.65	-	0.65	0.54	-	0.54	0.43	-	0.43	0.31	-	0.38
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.07	-	-	0.06	-	-	0.06	-	-	0.03	-	-	0.03	-
5-Chlorovanillin	2.78	2.98	0.40	1.95	2.69	0.15	1.67	2.53	0.19	1.38	1.33	0.16	1.09	1.22	0.13
5,6 Dichloroguaiacol	-	2.47	-	-	2.39	-	-	1.99	-	-	1.28	-	-	0.99	-

4-Chlorocatechol	3.68	-	-	2.65	-	-	2.53	-	-	2.20	-	-	2.01	-	-
3,5-Dichlorocatechol	5.99	-	-	5.85	-	-	4.32	-	-	3.13	0.08	-	2.99	0.06	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.68	0.63	-	0.28	0.51	-	0.23	0.48	-	0.17	0.45	-	0.16	0.32	-
3,5,6-Trichloroguaiacol	-	0.22	-	-	0.21	-	-	0.19	-	-	0.13	-	-	0.09	-
3,4,6-Trichloroguaiacol	-	2.18	-	-	2.11	-	-	2.01	-	-	1.84	-	-	1.57	-
3,5-Dichlorosyringol	-	2.63	0.62	-	1.32	0.11	-	1.23	0.09	-	1.01	0.08	-	0.93	0.08
3,4,5-Trichloroguaiacol	0.03	-	-	0.01	-	-	0.01	-	-	0.01	-	-	0.01	-	-
3-Chlorocatechol	5.93	0.09	-	4.54	-	-	4.38	-	-	3.08	-	-	2.34	-	-
6-Chlorovanillin	1.03	1.81	-	0.02	1.75	-	0.02	1.66	-	0.02	1.26	-	0.01	1.06	-
3,6-Dichlorocatechol	0.85	0.30	-	0.79	0.38	-	0.71	0.38	-	0.69	0.10	-	0.57	0.08	-
4,5,6-Trichloroguaiacol	0.37	0.44	-	0.35	0.40	-	0.26	0.34	-	0.29	0.23	-	0.22	0.13	-
2-Chlorosyringaldehyde	0.29	-	-	0.26	-	-	0.18	-	-	0.15	-	-	0.07	-	-
4,5-Dichlorocatechol	0.98	-	-	0.65	-	-	0.62	-	-	0.53	-	-	0.35	-	-
Pentachlorophenol	2.09	9.05	0.35	1.00	8.26	0.34	0.93	7.75	0.27	0.84	6.99	0.22	0.69	5.06	0.13
3,4,5-Trichlorocatechol	6.92	6.07	-	6.78	5.92	-	6.09	5.03	-	5.38	4.31	-	4.05	3.37	-
Tetrachloroguaiacol	0.01	0.13	-	0.01	0.11	-	0.01	0.09	-	0.01	0.06	-	0.01	0.06	-
Trichlorosyringol	0.48	8.42	0.69	0.47	7.44	0.67	0.43	6.85	0.53	0.33	5.39	0.43	0.21	4.35	0.49
3,4,6-Trichlorocatechol	0.78	-	-	0.55	-	-	0.51	-	-	0.50	-	-	0.45	-	-
2,6-Dichlorosyringaldehyde	0.23	6.73	-	0.17	6.72	-	0.17	5.92	-	0.13	4.82	-	0.50	3.98	-
5,6-Dichlorovanillin	-	4.23	-	-	3.16	-	-	2.93	-	-	1.79	-	-	1.47	-
Tetrachlorocatechol	3.75	1.68	0.37	3.00	1.57	0.32	2.98	1.56	0.32	1.67	1.23	0.21	1.34	1.02	0.12
Total	**49.63**	**76.58**	**4.68**	**38.41**	**71.49**	**3.32**	**33.59**	**65.45**	**2.93**	**27.02**	**49.9**	**2.29**	**22.83**	**39.88**	**1.95**

C stage bleaching conditions: Temperature 30°C and Consistency 3%.

Table 3.3 Effect of C stage pH on COD generation

Stage/pH	COD (kg/t) at different pH values of				
	1.5	**2.0**	**2.5**	**3.0**	**4.0**
C	31.3	29.6	27.9	25.5	23.6
E	61.7	59.7	55.1	49.9	47.6
H	22.8	19.2	18.4	17.3	16.0
Total	**115.8**	**108.5**	**101.4**	**92.7**	**87.2**

Table 3.4 Effect of C stage pH on color generation

Stage/pH	Color (kg/t) at different pH values of				
	1.5	**2.0**	**2.5**	**3.0**	**4.0**
C	34.7	32.7	30.5	28.7	26.3
E	74.3	71.5	65.4	59.7	52.3
H	1.9	1.2	1.2	1.2	1.1
Total	**110.9**	**105.4**	**97.1**	**89.6**	**79.7**

Table 3.5 Effect of C stage pH on CE kappa no, brightness and CED viscosity

Parameter/pH	Different parameter at different pH values of				
	1.5	**2.0**	**2.5**	**3.0**	**4.0**
CE Kappa no	5.5	5.4	5.1	5.3	5.2
CE Brightness (%ISO)	46.7	45.6	45.4	45.1	45.1
CEH Brightness (%ISO)	81.3	80.5	79.4	79.0	78.9
Viscosity (cp)	10.3	9.9	9.1	8.9	8.0

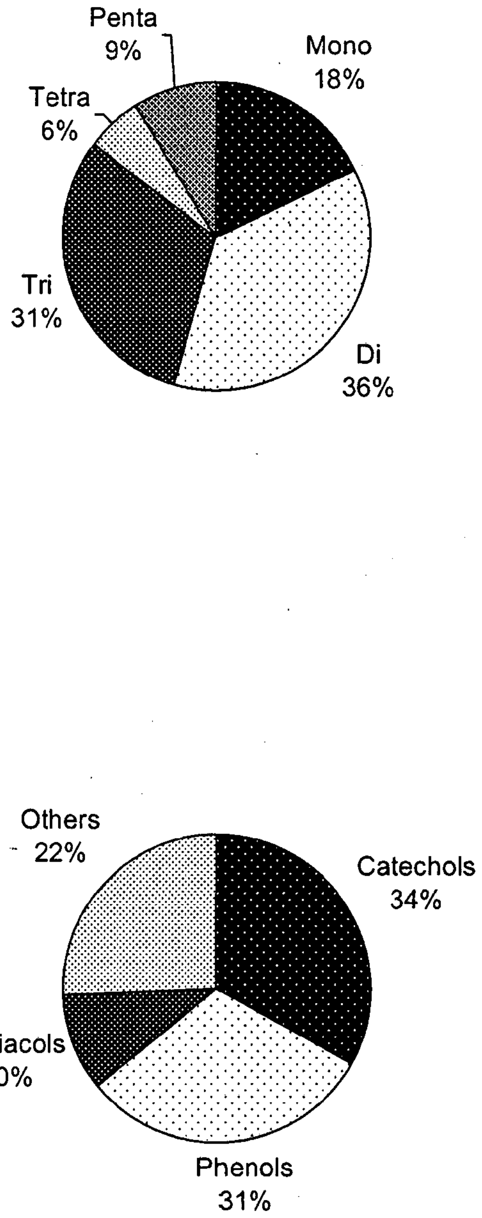


Fig. 3.2 The contribution of different chlorophenolic compounds at pH 1.5

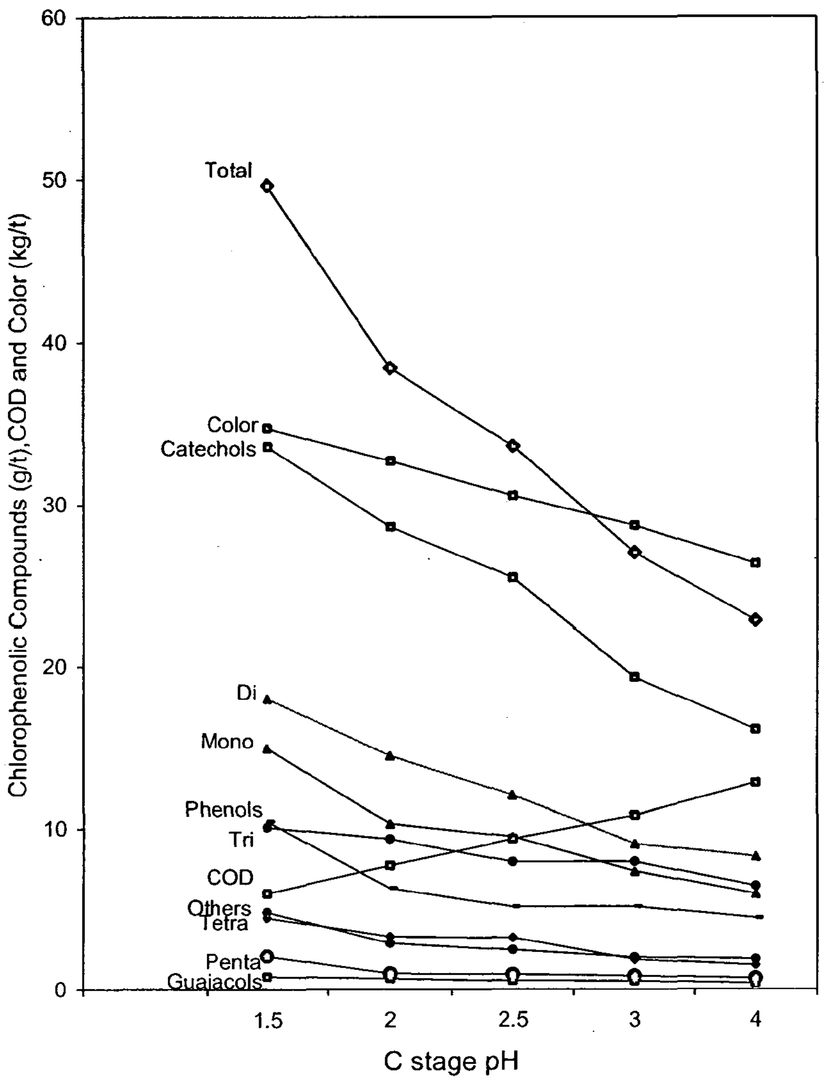


Fig 3.3 Effect of C stage pH on the generation of chlorophenolics, COD and color in C stage effluent.

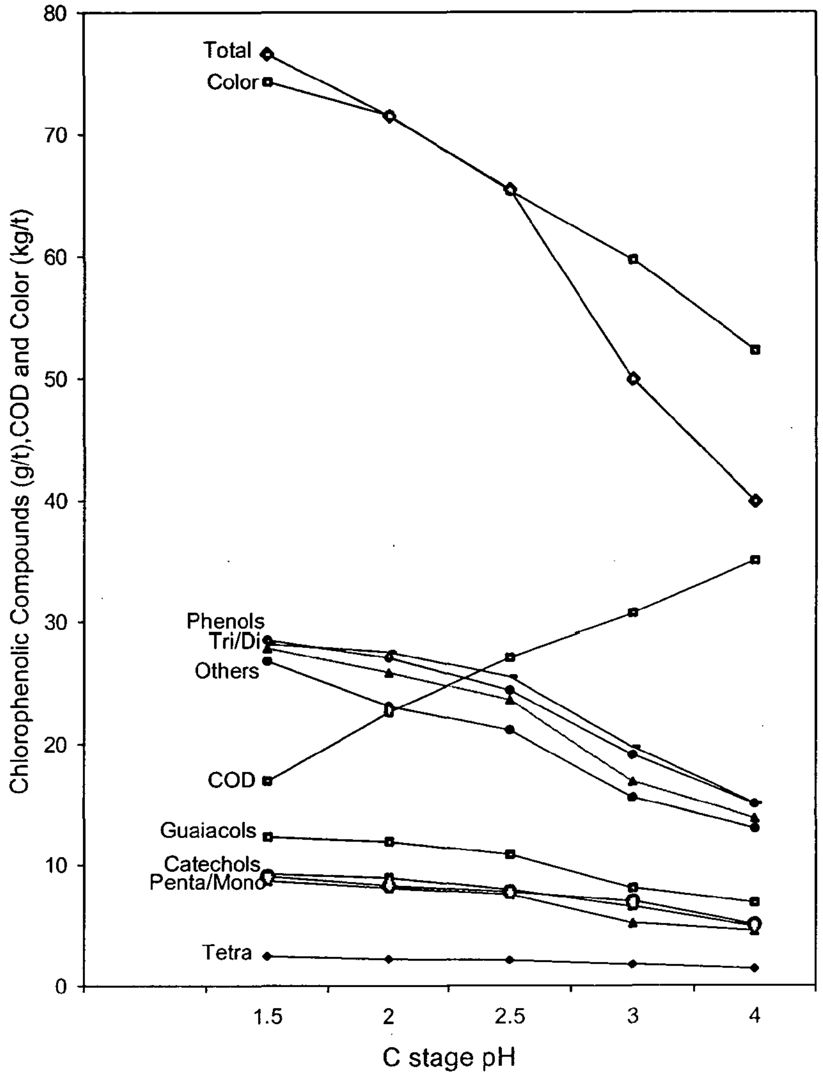


Fig 3.4 Effect of C stage pH on the generation of chlorophenolics, COD and color in E stage effluent.

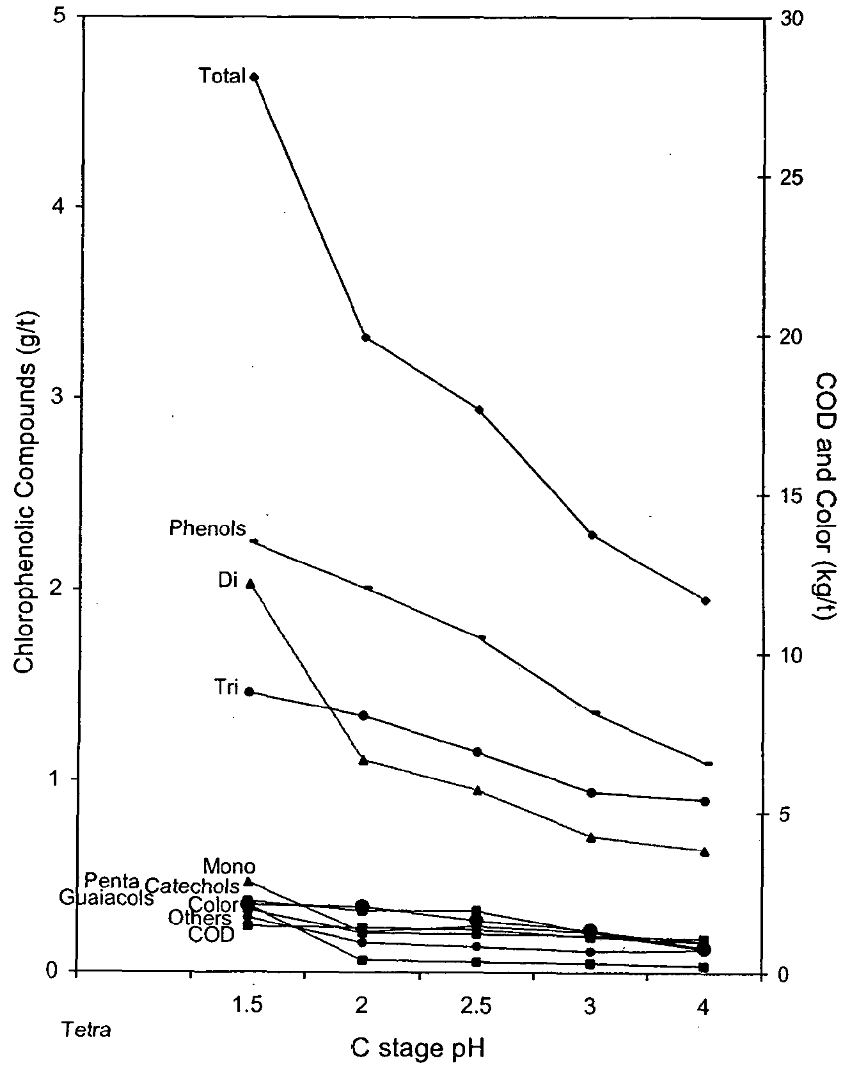


Fig 3.5 Effect of C stage pH on the generation of chlorophenolics, COD and color in H stage effluent.

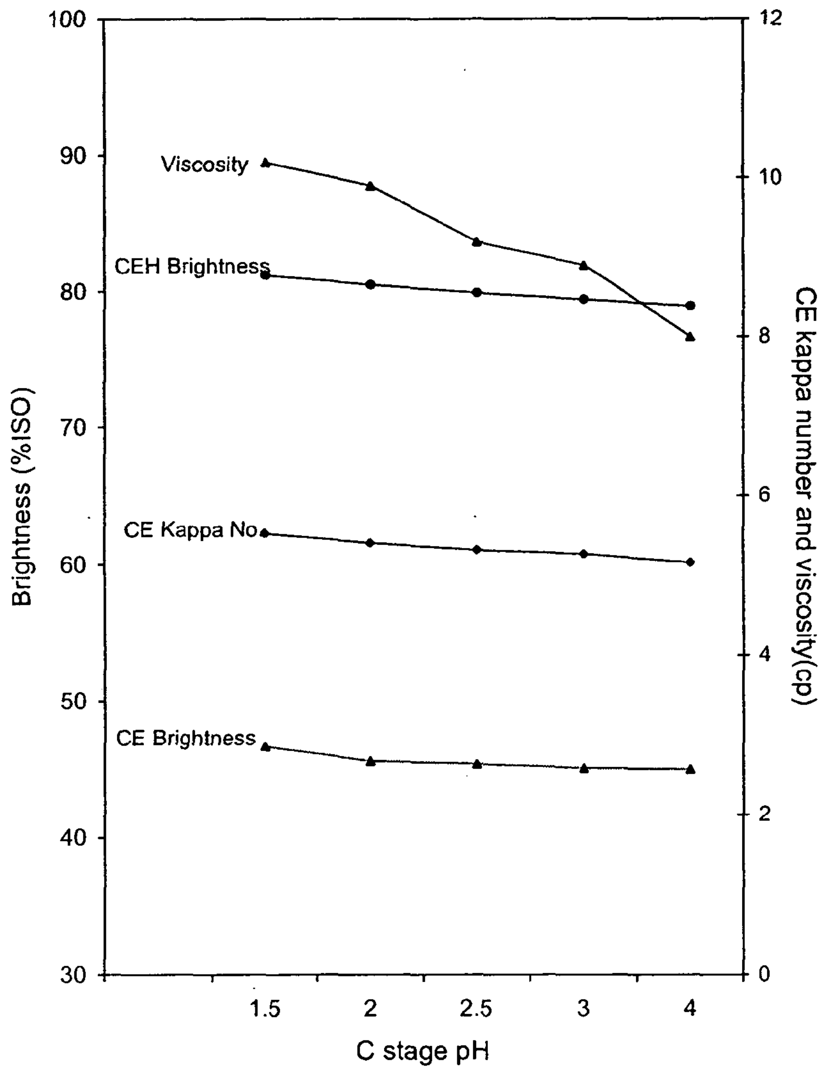


Fig 3.6 Effect of C stage pH on brightness, viscosity and CE kappa number.

Table 3.6 Effect of temperature in C stage on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at temperature														
	35° C			30° C			25° C			20° C			15° C		
	C	E	H	C	E	H	C	E	H	C	E	H	C	E	H
2,4 Dichlorophenol	1.05	1.73	0.19	0.80	0.39	0.14	0.68	-	-	0.54	-	-	0.48	-	-
2,5 Dichlorophenol	1.56	3.01	0.32	1.43	2.89	0.21	1.21	2.53	0.19	1.01	2.03	0.16	0.92	1.95	0.13
2,3 Dichlorophenol	-	-	-	-	-	-	-	0.32	0.12	-	0.29	0.10	-	0.22	0.10
3-Chloroguaiacol	-	0.34	-	-	0.25	-	-	0.20	-	-	0.14	-	-	0.11	-
2,6 Dichlorophenol	0.13	2.97	-	0.11	2.56	-	0.09	2.06	-	0.07	1.85	-	0.03	1.53	-
4-Chlorophenol	0.30	-	-	0.23	-	-	0.19	-	-	0.12	-	-	0.08	-	-
3-Chlorophenol	0.51	1.99	-	0.49	1.94	-	0.32	1.74	-	0.28	1.56	-	0.21	1.31	-
4-Chloroguaiacol	0.03	-	-	0.02	-	-	0.02	-	-	0.02	-	-	0.02	-	-
5-Chloroguaiacol	-	1.68	0.08	-	1.46	0.06	-	1.05	0.05	-	0.97	0.05	-	0.64	0.03
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.27	-	-	0.11	-	-	0.09	-	-	0.07	-	-	0.06	-	-
2,3,5-Trichlorophenol	0.39	4.08	0.46	0.16	3.12	0.33	0.13	2.73	0.26	0.10	2.08	0.19	0.09	1.85	0.12
2,4,6-Trichlorophenol	1.24	3.78	-	0.22	2.01	-	0.19	1.96	-	0.15	1.71	-	0.11	1.32	-
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.95	6.76	0.63	0.80	5.88	0.34	0.67	4.98	0.28	0.56	4.02	0.23	0.43	3.36	0.14
3,6 Dichloroguaiacol	0.38	-	-	0.10	-	-	0.10	-	-	0.07	-	-	0.09	-	-
3,4 Dichloroguaiacol	0.29	5.04	-	0.18	4.93	-	0.15	3.34	-	0.12	2.78	-	0.09	1.99	-
3,4-Dichlorocatechol	3.97	1.75	-	3.78	1.06	-	2.69	1.01	-	2.27	0.99	-	1.99	0.78	-
3,4-Dicholorophenol	0.74	-	0.68	0.65	-	0.65	0.58	-	0.56	0.41	-	0.35	0.30	-	0.26
4,5 Dichloroguaiacol	0.26	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.08	-	-	0.06	-	-	0.06	-	-	0.05	-	-	0.03	-
5-Chlorovanillin	2.77	2.97	0.16	1.95	2.69	0.15	1.63	2.04	0.11	1.54	1.83	0.09	1.31	1.52	0.07
5,6 Dichloroguaiacol	-	2.56	-	-	2.39	-	-	1.99	-	-	1.52	-	-	1.04	-

4-Chlorocatechol	3.25	-	-	2.65	-	-	2.21	-	-	1.92	-	-	1.64	-	-
3,5-Dichlorocatechol	6.99	-	-	5.85	-	-	5.24	-	-	4.30	-	-	3.15	-	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.31	0.78	-	0.28	0.51	-	0.25	0.43	-	0.19	0.37	-	0.13	0.26	-
3,5,6-Trichloroguaiacol	-	0.33	-	-	0.21	-	-	0.19	-	-	0.17	-	-	0.15	-
3,4,6-Trichloroguaiacol	-	3.32	-	-	2.11	-	-	2.03	-	-	1.86	-	-	1.53	-
3,5-Dichlorosyringol	1.05	2.79	0.25	-	1.32	0.11	-	1.15	0.10	-	1.05	0.09	-	0.98	0.05
3,4,5-Trichloroguaiacol	0.02	-	-	0.01	-	-	0.01	-	-	0.01	-	-	-	-	-
3-Chlorocatechol	4.78	-	-	4.54	-	-	3.78	-	-	3.03	-	-	2.76	-	-
6-Chlorovanillin	0.03	2.05	-	0.02	1.75	-	0.02	1.67	-	0.02	1.34	-	-	1.17	-
3,6-Dichlorocatechol	0.98	0.48	-	0.79	0.38	-	0.65	0.33	-	0.54	0.28	-	0.49	0.21	-
4,5,6-Trichloroguaiacol	1.45	0.67	-	0.35	0.40	-	0.33	0.36	-	0.27	0.23	-	0.22	0.19	-
2-Chlorosyringaldehyde	0.37	-	-	0.26	-	-	0.24	-	-	0.19	-	-	0.14	-	-
4,5-Dichlorocatechol	0.73	-	-	0.65	-	-	0.59	-	-	0.43	-	-	0.40	-	-
Pentachlorophenol	1.05	9.05	0.69	1.00	8.26	0.34	0.94	7.18	0.29	0.89	6.06	0.24	0.73	4.34	0.19
3,4,5-Trichlorocatechol	6.96	6.64	-	6.78	5.92	-	5.67	4.41	-	4.32	3.25	-	3.09	2.07	-
Tetrachloroguaiacol	0.03	0.26	-	0.01	0.11	-	0.01	0.10	-	0.01	0.08	-	0.01	0.07	-
Trichlorosyringol	0.54	7.79	0.75	0.47	7.44	0.67	0.36	6.27	0.53	0.29	5.04	0.46	0.21	4.38	0.38
3,4,6-Trichlorocatechol	0.79	-	-	0.55	-	-	0.47	-	-	0.38	-	-	0.25	-	-
2,6-Dichlorosyringaldehyde	0.31	7.09	-	0.17	6.72	-	0.15	5.34	-	0.12	4.09	-	0.09	3.49	-
5,6-Dichlorovanillin	0.25	3.54	-	-	3.16	-	-	2.56	-	-	2.13	-	-	1.86	-
Tetrachlorocatechol	4.05	2.78	0.45	3.00	1.57	0.32	2.72	1.45	0.26	2.01	1.28	0.23	1.39	1.07	0.16
Total	**48.78**	**86.31**	**4.66**	**38.41**	**71.49**	**3.32**	**32.38**	**59.48**	**2.75**	**26.25**	**49.05**	**2.19**	**20.91**	**39.42**	**1.63**

C stage bleaching conditions: $C_{end\ pH} \geq 2$ and Consistency 3%.

Table 3.7 Effect of C stage temperature on COD generation

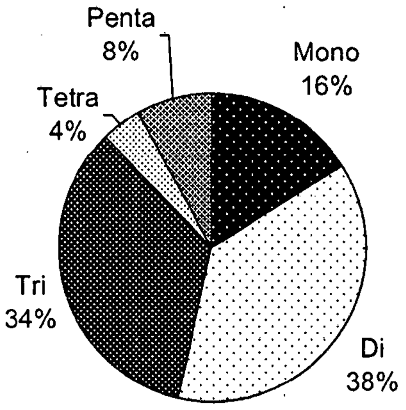
Stage/temperature	COD (kg/t) at different temperature				
	35°C	30°C	25°C	20°C	15°C
C	30.6	29.6	28.9	28.0	24.4
E	61.0	59.7	52.3	50.1	45.6
H	20.1	19.2	18.9	17.8	16.9
Total	**111.7**	**108.5**	**100.1**	**95.9**	**86.9**

Table 3.8 Effect of C stage temperature on color generation

Stage/temperature	Color (kg/t) at different temperature				
	35°C	30°C	25°C	20°C	15°C
C	36.8	32.7	30.3	25.7	21.3
E	75.9	71.5	68.8	63.5	60.3
H	2.4	1.2	1.1	1.1	1.1
Total	**115.1**	**105.4**	**100.2**	**90.2**	**82.7**

Table 3.9 Effect of C stage temperature on CE kappa no, brightness and CED viscosity

Parameters/temperature	Different parameter at different temperature				
	35°C	30°C	25°C	20°C	15°C
CE Kappa no	5.4	5.1	5.5	5.1	5.6
CE Brightness(%ISO)	47.3	45.6	44.2	43.5	43.1
CEH Brightness(%ISO)	81.0	80.5	79.8	79.2	79.0
Viscosity(cp)	8.4	9.9	10.3	10.4	10.8



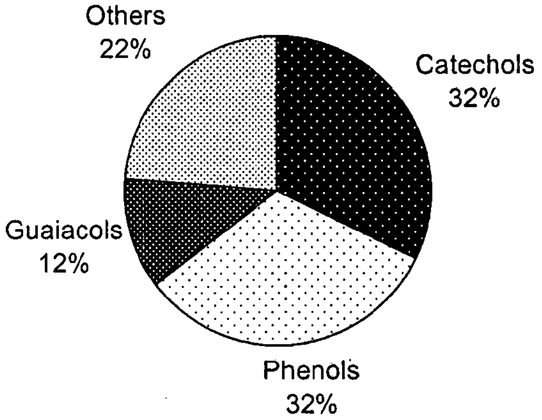


Fig. 3.7 **The contribution of different chlorophenolic compounds at 35°C temperature**

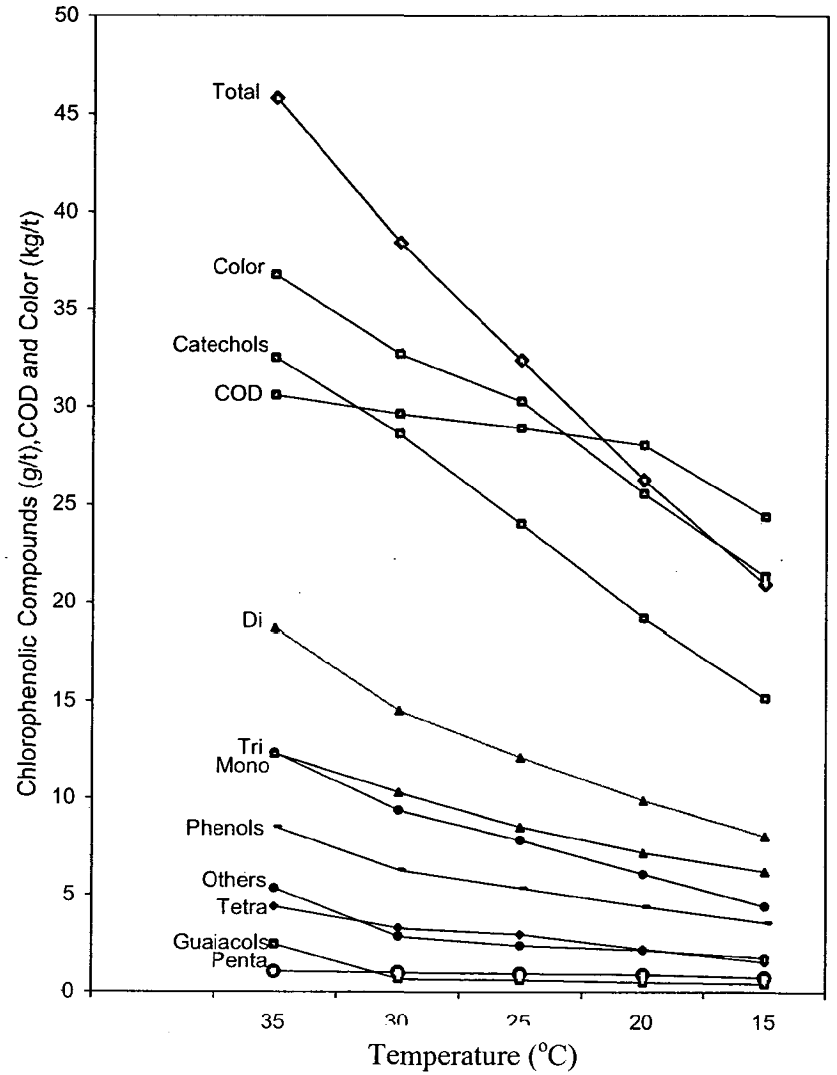


Fig 3.8 **Effect of C stage temperature on the generation of chlorophenolics, COD and color in C stage effluent.**

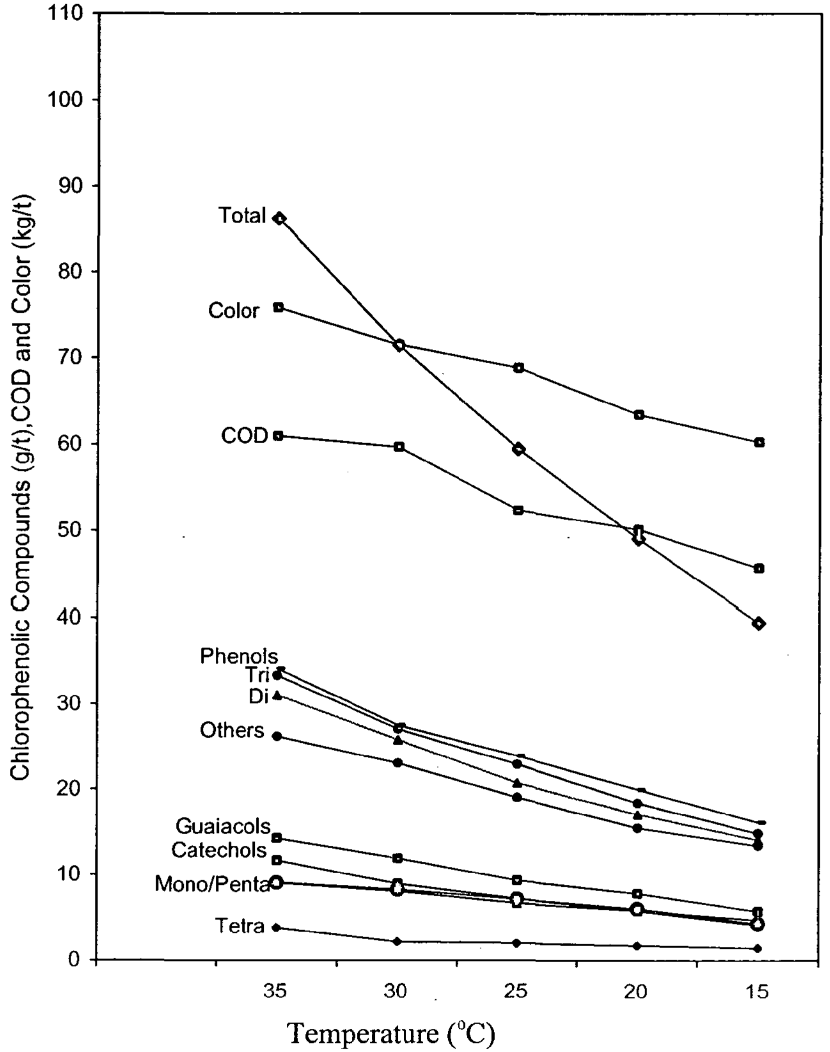


Fig 3.9 **Effect of C stage temperature on the generation of chlorophenolics, COD and color in E stage effluent.**

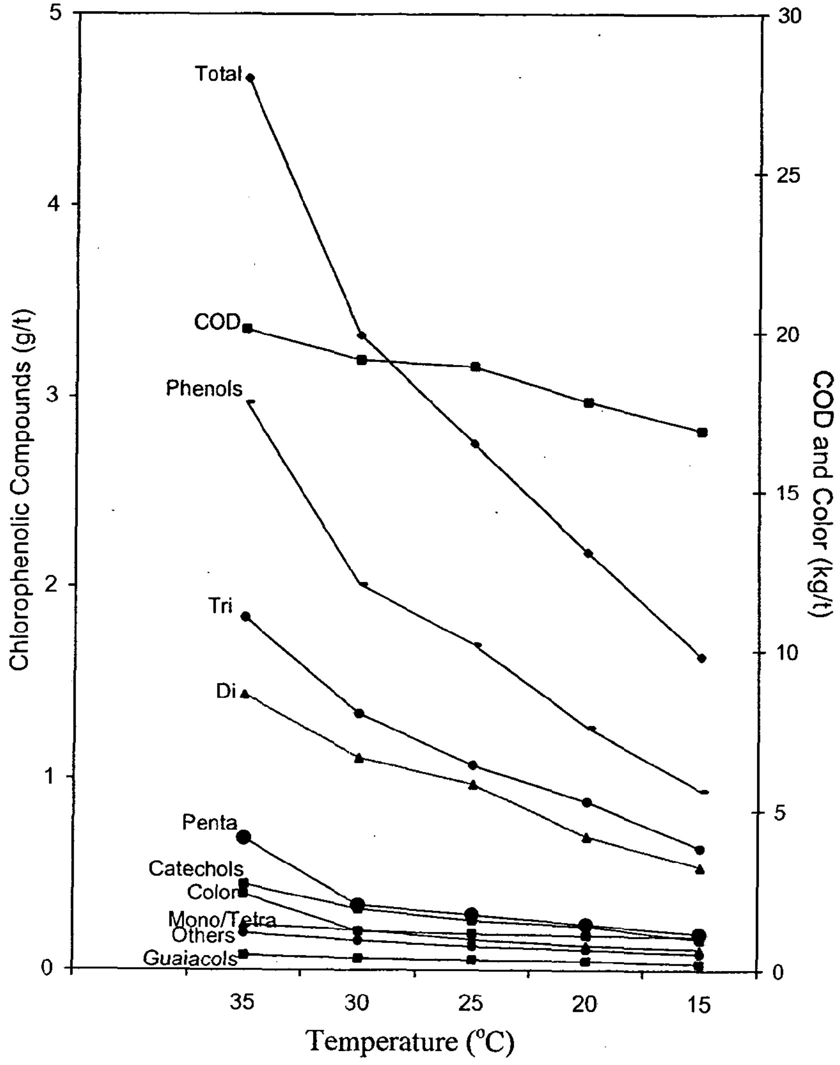


Fig 3.10 Effect of C stage temperature on the generation of chlorophenolics, COD and color in H stage effluent.

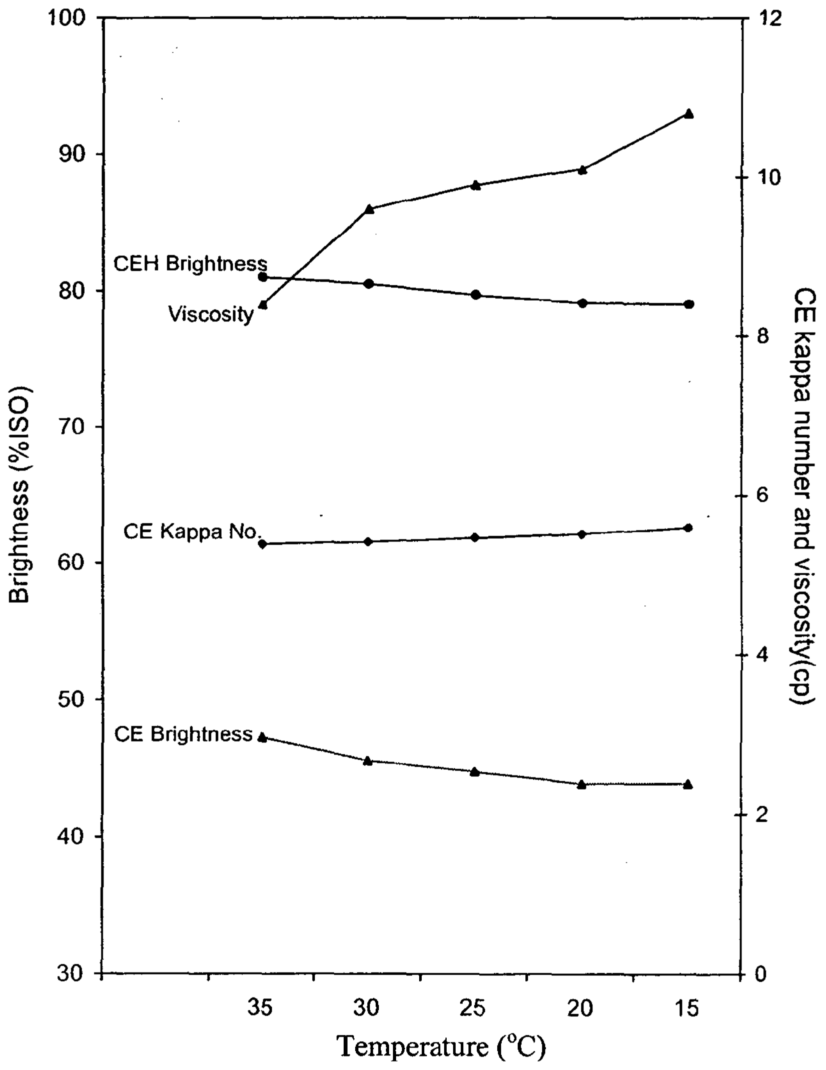


Fig 3.11 Effect of C stage temperature on brightness, viscosity and CE kappa number.

Table 3.10 Effect of consistency in C stage on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at consistency														
	2%			2.5%			3%			3.5%			4%		
	C	E	H	C	E	H	C	E	H	C	E	H	C	E	H
2,4-Dichlorophenol	0.31	-	0.15	0.67	-	0.19	0.80	0.39	0.14	1.02	-	0.32	1.68	-	0.36
2,5-Dichlorophenol	1.09	2.32	0.11	1.12	2.01	0.12	1.43	2.89	0.21	1.79	3.37	0.18	2.05	3.65	0.21
2,3-Dichlorophenol	-	0.25	-	-	0.18	-	-	-	-	-	0.68	-	-	0.98	-
3-Chloroguaiacol	0.06	0.18	-	0.11	0.12	-	-	0.25	-	-	0.33	-	-	0.53	-
2,6-Dichlorophenol	0.02	2.03	-	0.09	1.64	-	0.11	2.56	-	0.34	3.19	-	0.69	3.79	-
4-Chlorophenol	0.10	-	-	0.15	-	-	0.23	-	-	0.46	-	-	0.68	-	-
3-Chlorophenol	0.26	1.03	-	0.32	1.14	-	0.49	1.94	-	2.13	2.26	-	2.86	2.93	-
4-Chloroguaiacol	0.01	-	-	0.01	-	-	0.02	-	-	0.07	-	-	0.14	-	-
5-Chloroguaiacol	-	0.95	0.03	-	1.07	0.05	-	1.46	0.06	-	1.88	0.09	-	1.96	0.09
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.05	-	-	0.08	-	-	0.11	-	-	0.65	-	-	1.07	-	-
2,3,5-Trichlorophenol	0.05	1.78	0.18	0.10	2.96	0.23	0.16	3.12	0.33	0.58	4.54	0.53	0.69	5.07	0.58
2,4,6-Trichlorophenol	0.12	1.06	-	0.19	1.51	-	0.22	2.01	-	1.01	3.76	-	1.14	4.13	-
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5-Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6-Trichlorophenol	0.36	3.11	0.23	0.68	4.39	0.30	0.80	5.88	0.34	1.28	6.37	0.42	1.99	7.21	0.59
3,6 Dichloroguaiacol	0.06	-	-	0.07	-	-	0.10	-	-	0.87	-	-	0.95	-	-
3,4 Dichloroguaiacol	0.14	2.52	-	0.15	3.78	-	0.18	4.93	-	0.54	5.89	-	0.68	6.18	-
3,4-Dichlorocatechol	2.03	0.64	-	2.53	0.95	-	3.78	1.06	-	3.06	2.32	-	2.72	2.96	-
3,4-Dicholorophenol	0.31	-	0.14	0.54	-	0.31	0.65	-	0.65	0.98	-	0.76	1.07	-	0.78
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.04	-	-	0.05	-	-	0.06	-	-	0.08	-	-	0.01	-
5-Chlorovanillin	1.27	1.76	0.09	1.47	2.33	0.10	1.95	2.69	0.15	2.69	3.55	0.23	2.89	4.02	0.41
5,6 Dichloroguaiacol	-	0.99	-	-	1.25	-	-	2.39	-	-	3.60	-	-	3.94	-

4-Chlorocatechol	1.99	-	-	2.32	-	-	2.65	-	-	3.77	-	-	3.92	-	-
3,5-Dichlorocatechol	4.23	-	-	5.19	-	-	5.85	-	-	6.31	-	0.14	0.43	-	0.18
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.01	0.27	-	0.16	0.32	-	0.28	0.51	-	0.33	0.68	-	0.68	0.83	-
3,5,6-Trichloroguaiacol	-	0.16	-	-	0.19	-	-	0.21	-	-	0.46	-	-	0.57	-
3,4,6-Trichloroguaiacol	-	1.11	-	-	1.34	-	-	2.11	-	-	3.33	-	-	3.89	-
3,5-Dichlorosyringol	-	0.84	0.03	-	1.03	0.07	-	1.32	0.11	-	2.64	0.21	-	2.98	0.23
3,4,5-Trichloroguaiacol	0.01	-	-	0.01	-	-	0.01	-	-	0.03	-	-	0.08	-	-
3-Chlorocatechol	3.35	-	-	4.18	-	-	4.54	-	-	5.18	-	-	5.25	-	-
6-Chlorovanillin	0.01	0.79	-	0.02	1.12	-	0.02	1.75	-	0.09	2.49	-	0.17	3.39	-
3,6-Dichlorocatechol	0.58	0.13	-	0.60	0.27	-	0.79	0.38	-	1.09	0.27	-	1.23	0.36	-
4,5,6-Trichloroguaiacol	0.23	0.28	-	0.29	0.38	-	0.35	0.40	-	0.78	0.48	-	1.08	0.52	-
2-Chlorosyringaldehyde	0.11	-	-	0.15	-	-	0.26	-	-	0.35	-	-	0.56	-	-
4,5-Dichlorocatechol	0.54	-	-	0.61	-	-	0.65	-	-	0.86	-	-	0.99	-	-
Pentachlorophenol	0.88	4.11	0.23	0.94	6.23	0.31	1.00	8.26	0.34	1.27	9.17	0.44	1.65	9.68	0.48
3,4,5-Trichlorocatechol	4.97	2.95	-	5.59	4.41	-	6.78	5.92	-	7.13	6.33	0.23	7.23	6.46	0.30
Tetrachloroguaiacol	0.01	0.06	-	0.01	0.09	-	0.01	0.11	-	0.06	0.24	-	0.09	0.38	-
Trichlorosyringol	0.25	3.24	0.28	0.36	5.15	0.47	0.47	7.44	0.67	0.88	8.01	0.78	1.03	8.77	0.85
3,4,6-Trichlorocatechol	0.32	-	-	0.47	-	-	0.55	-	-	0.65	-	-	0.87	-	-
2,6-Dichlorosyringaldehyde	0.11	3.98	-	0.13	5.27	-	0.17	6.72	-	0.92	7.08	-	1.14	7.89	-
5,6-Dichlorovanillin	-	1.76	-	-	2.02	-	-	3.16	-	-	3.52	0.03	-	4.12	0.04
Tetrachlorocatechol	1.69	0.97	0.25	2.07	1.16	0.30	3.00	1.57	0.32	4.86	1.85	0.43	5.06	2.06	0.48
Total	**25.53**	**39.31**	**1.72**	**31.38**	**52.36**	**2.45**	**38.41**	**71.49**	**3.32**	**52.03**	**88.37**	**4.79**	**52.76**	**99.26**	**5.58**

C stage bleaching conditions: $C_{end\ pH} \geq 2$ and Temperature 30°C.

Table 3.11 Effect of C stage consistency on COD generation

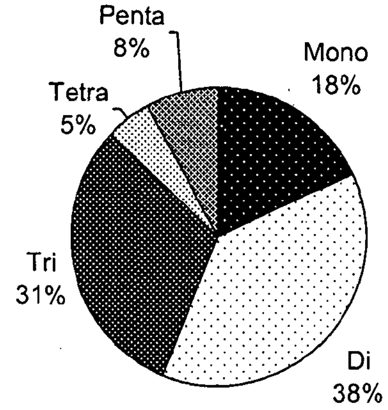
Stage/consistency	**COD (kg/t) at different consistency**				
	2.0%	**2.5%**	**3.0%**	**3.5%**	**4.0%**
C	27.4	29.1	29.6	32.0	34.5
E	55.9	57.9	59.7	61.6	65.9
H	17.4	18.5	19.2	19.9	20.5
Total	**100.7**	**105.5**	**108.5**	**113.5**	**121.9**

Table 3.12 Effect of C stage consistency on color generation

Stage/consistency	**Color (kg/t) at different consistency**				
	2.0%	**2.5%**	**3.0%**	**3.5%**	**4.0%**
C	26.6	29.4	32.7	35.8	38.9
E	57.9	63.6	71.5	75.4	79.4
H	1.0	1.1	1.2	1.3	1.3
Total	**85.5**	**94.1**	**105.4**	**112.5**	**119.6**

Table 3.13 Effect of C stage consistency on CE kappa no, brightness and CED viscosity

Parameter/consistency	**Different parameter at different consistency**				
	2.0%	**2.5%**	**3.0%**	**3.5%**	**4.0%**
CE Kappa no	5.1	5.3	5.4	5.3	5.6
CE Brightness(%ISO)	44.9	45.4	45.6	45.9	46.0
CEH Brightness(%ISO)	79.9	80.2	80.5	80.1	80.9
Viscosity(cp)	10.1	9.8	9.9	8.8	8.4



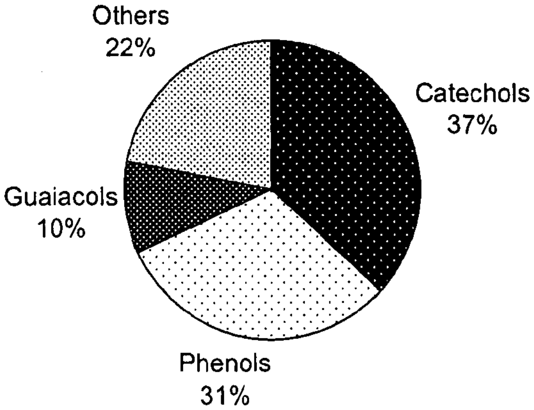


Fig. 3.12 The contribution of different chlorophenolic compounds at 2% consistency

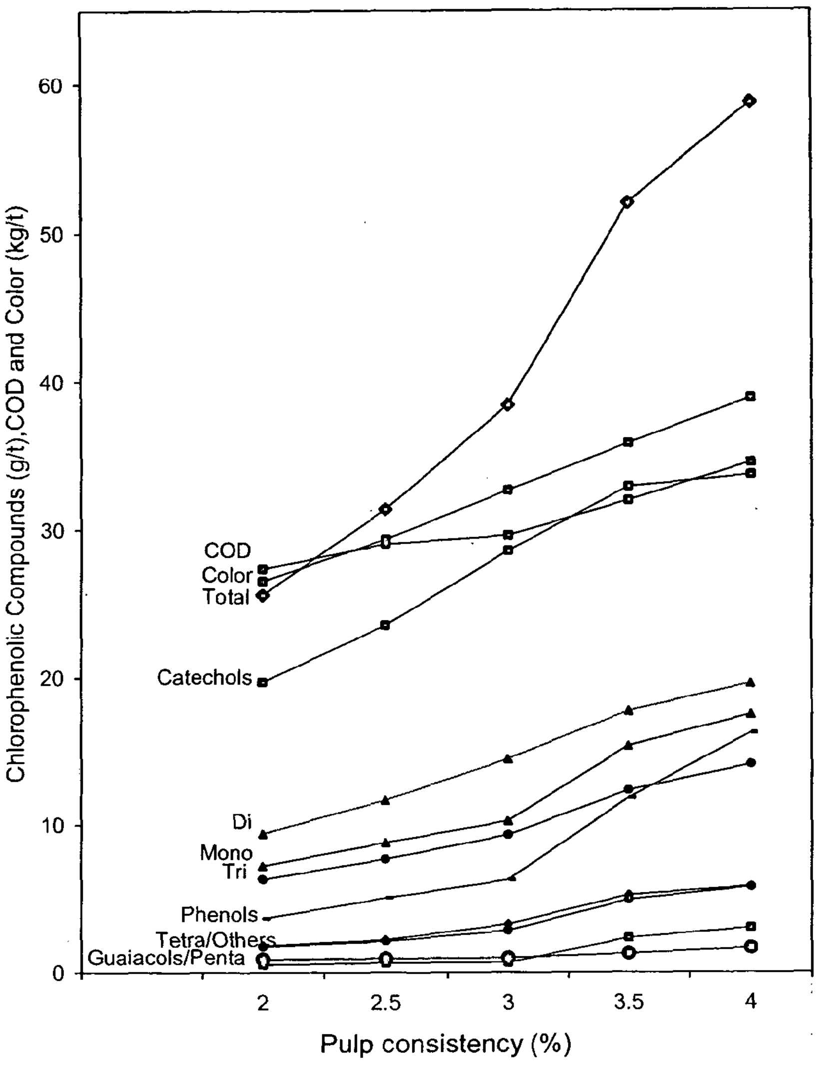


Fig 3.13 **Effect of C stage consistency on the generation of chlorophenolics, COD and color in C stage effluent.**

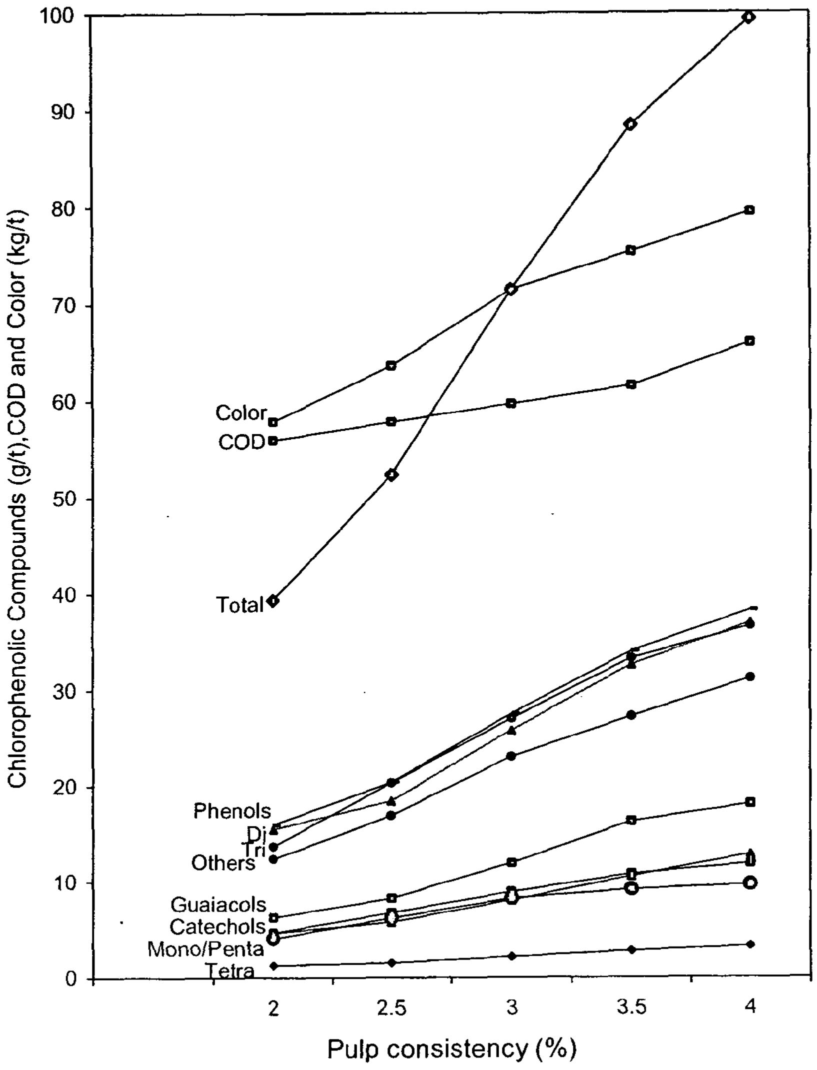


Fig 3.14 **Effect of C stage consistency on the generation of chlorophenolics, COD and color in E stage effluent.**

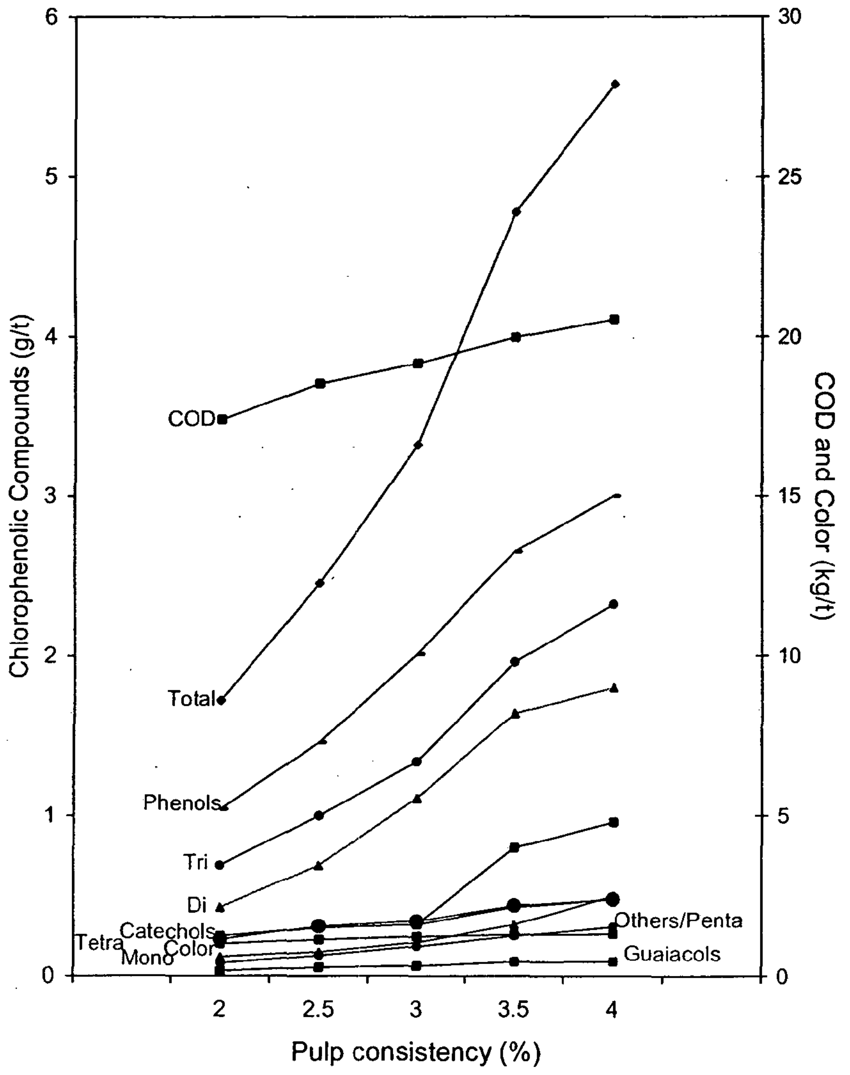


Fig 3.15 Effect of C stage consistency on the generation of chlorophenolics, COD and color in H stage effluent.

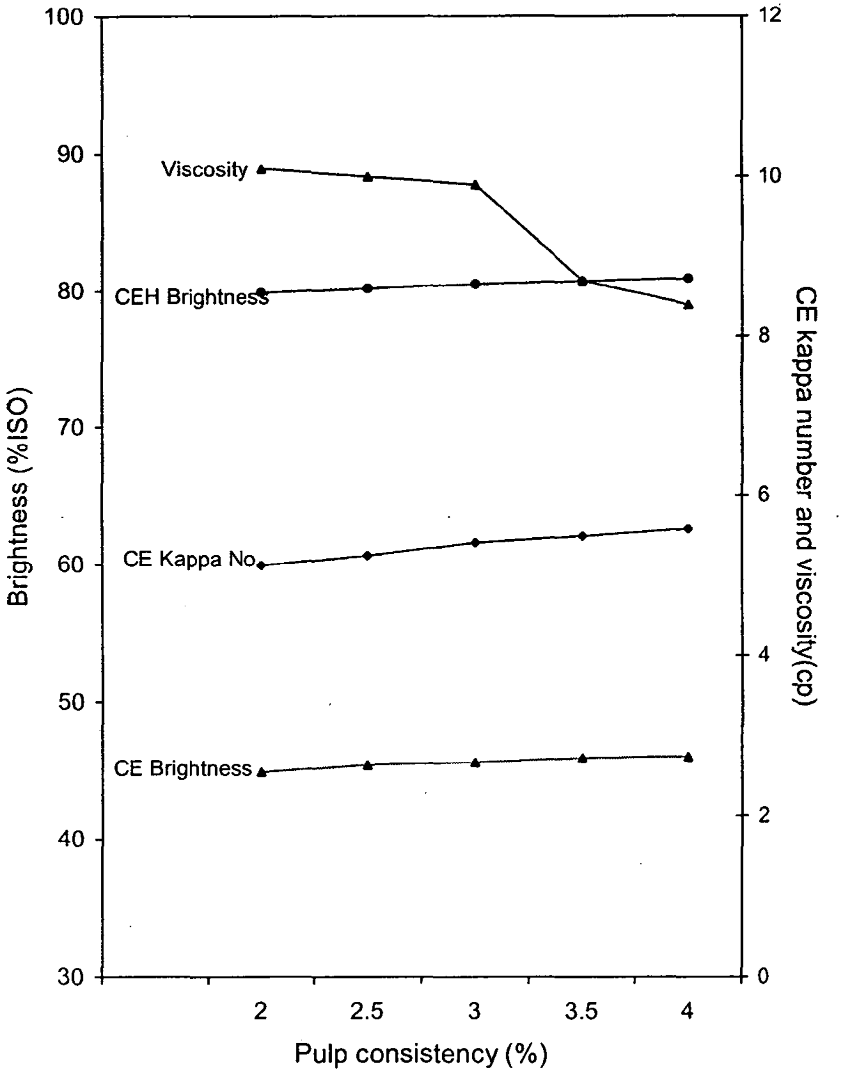


Fig 3.16 Effect of C stage consistency on brightness, viscosity and CE kappa number.

Table 3.14 Effect of distribution of bleach chemical between C and H stage on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at different distribution between C:H stages														
	45:55			50:50			55:45			60:40			65:35		
	C	E	H	C	E	H	C	E	H	C	E	H	C	E	H
2,4 Dichlorophenol	0.54	0.32	0.11	0.68	0.36	0.13	0.80	0.39	0.14	0.93	0.57	0.14	1.27	0.78	0.16
2,5 Dichlorophenol	1.06	1.97	0.10	1.23	2.12	0.12	1.43	2.89	0.21	1.89	3.02	0.13	2.04	3.89	0.15
2,3 2,4 Dichlorophenol	-	0.25	-	-	0.28	-	-	-	-	-	-	-	-	-	-
3-Chloroguaiacol	-	0.14	-	-	0.18	-	-	0.25	-	-	0.33	-	-	0.54	-
2,6 2,4 Dichlorophenol	0.05	1.32	-	0.08	1.77	-	0.11	2.56	-	0.24	3.12	-	0.38	3.86	-
4-Chlorophenol	0.12	-	-	0.16	-	-	0.23	-	-	0.56	-	-	0.67	-	-
3-Chlorophenol	0.28	1.28	-	0.37	1.53	-	0.49	1.94	-	0.63	2.21	-	0.93	2.93	-
4-Chloroguaiacol	0.02	-	-	0.02	-	-	0.02	-	-	0.04	-	-	0.08	-	-
5-Chloroguaiacol	-	0.93	0.08	-	1.04	0.07	-	1.46	0.06	-	1.89	0.06	-	2.34	0.04
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.08	-	-	0.09	-	-	0.11	-	-	0.23	-	-	0.37	-	-
2,3,5-Trichlorophenol	0.09	2.06	0.42	0.12	2.96	0.34	0.16	3.12	0.33	0.28	3.29	0.23	0.41	4.15	0.19
2,4,6-Trichlorophenol	0.13	1.15	-	0.19	1.61	-	0.22	2.01	-	0.35	3.07	-	0.68	3.56	-
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.62	3.35	0.49	0.77	4.96	0.48	0.80	5.88	0.34	1.02	6.14	0.29	1.68	6.92	0.16
3,6 Dichloroguaiacol	-	-	-	0.10	-	-	0.10	-	-	0.25	-	-	0.54	-	-
3,4 Dichloroguaiacol	0.12	2.27	-	0.15	3.62	-	0.18	4.93	-	0.29	5.38	-	0.46	5.63	-
3,4-Dichlorocatechol	2.76	0.76	-	3.13	0.97	-	3.78	1.06	-	4.33	1.56	-	5.23	2.45	-
3,4-Dicholorophenol	0.35	-	0.76	0.42	-	0.70	0.65	-	0.65	0.71	-	0.52	0.92	-	0.35
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	-	-	-	-	-	-	0.06	-	-	0.08	-	-	0.10	-
5-Chlorovanillin	2.04	1.78	0.38	1.99	2.32	0.24	1.95	2.69	0.15	2.08	3.00	0.13	2.98	3.37	0.09
5,6 Dichloroguaiacol	-	1.04	-	-	1.76	-	-	2.39	-	-	2.98	-	-	3.08	-

4-Chlorocatechol	1.83	-	-	2.05	-	-	2.65	-	-	3.17	-	-	3.37	-	-
3,5-Dichlorocatechol	3.68	-	-	4.34	-	-	5.85	-	-	6.09	-	-	6.35	-	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	0.44	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.13	0.32	-	0.17	0.45	-	0.28	0.51	-	0.36	0.68	-	0.15	0.97	-
3,5,6-Trichloroguaiacol	-	0.16	-	-	0.19	-	-	0.21	-	-	0.34	-	-	0.58	-
3,4,6-Trichloroguaiacol	-	1.28	-	-	1.83	-	-	2.11	-	-	2.91	-	-	3.14	-
3,5-Dichlorosyringol	0.15	0.84	0.09	-	1.07	0.10	-	1.32	0.11	-	2.56	0.10	-	2.93	0.13
3,4,5-Trichloroguaiacol	-	-	-	0.01	-	-	0.01	-	-	0.03	-	-	0.07	-	-
3-Chlorocatechol	-	-	-	-	-	-	4.54	-	-	5.31	-	-	5.56	-	-
6-Chlorovanillin	0.03	1.79	-	0.02	1.78	-	0.02	1.75	-	0.02	2.05	-	0.01	2.65	-
3,6-Dichlorocatechol	0.54	0.25	-	0.78	0.36	-	0.79	0.38	-	0.98	0.47	-	1.03	0.82	-
4,5,6-Trichloroguaiacol	0.19	0.18	-	0.25	0.29	-	0.35	0.40	-	0.67	0.58	-	0.84	0.96	-
2-Chlorosyringaldehyde	0.21	-	-	0.24	-	-	0.26	-	-	0.45	-	-	0.56	-	-
4,5-Dichlorocatechol	0.32	-	-	0.46	-	-	0.65	-	-	0.82	-	-	1.08	-	-
Pentachlorophenol	0.53	6.57	0.19	0.63	7.13	0.28	1.00	8.26	0.34	1.13	9.07	0.26	1.76	9.89	0.19
3,4,5-Trichlorocatechol	4.37	3.43	-	5.52	4.55	-	6.78	5.92	-	7.01	6.22	-	7.13	6.78	-
Tetrachloroguaiacol	0.01	0.08	0.03	0.01	0.08	0.02	.012	0.11	-	0.04	0.21	-	0.05	0.67	-
Trichlorosyringol	0.16	5.31	0.52	0.38	6.21	0.57	0.47	7.44	0.67	0.74	8.13	0.59	0.95	8.93	0.60
3,4,6-Trichlorocatechol	0.39	-	-	0.46	-	-	0.55	-	-	0.69	-	-	1.08	-	-
2,6-Dichlorosyringaldehyde	0.08	4.86	-	0.13	5.03	-	0.17	6.72	-	0.38	7.04	-	0.59	7.56	-
5,6-Dichlorovanillin	-	3.98	-	-	3.87	-	-	3.16	-	-	3.11	-	-	3.04	-
Tetrachlorocatechol	1.97	1.01	0.51	2.12	1.16	0.45	3.00	1.57	0.32	3.69	2.32	0.28	4.02	2.97	0.15
Total	**22.85**	**46.68**	**3.68**	**27.07**	**59.48**	**3.5**	**38.41**	**71.49**	**3.32**	**45.41**	**82.33**	**2.73**	**53.68**	**95.49**	**2.21**

C stage bleaching conditions: Temperature 30°C, Consistency 3% and $C_{end\ pH} \geq 2$

Table 3.15 Effect of distribution of bleach chemical between C and H stage on COD generation

Stage/distribution	COD (kg/t) at different distribution between C:H stages				
	45:55	50:50	55:45	60:40	65:35
C	20.5	29.6	33.2	38.9	44.3
E	50.9	59.7	62.4	68.5	71.7
H	20.2	19.2	18.3	18.2	17.6
Total	**91.6**	**108.5**	**113.9**	**125.6**	**133.6**

Table 3.16 Effect of distribution of bleach chemical between C and H stage on color generation

Stage/distribution	Color (kg/t) at different distribution between C:H stages				
	45:55	50:50	55:45	60:40	65:35
C	29.2	32.7	39.5	41.3	48.7
E	56.9	67.5	77.8	83.4	89.7
H	1.0	1.2	1.3	1.3	1.4
Total	**87.1**	**101.4**	**118.6**	**126.0**	**139.8**

Table 3.17 Effect of distribution of bleach chemical between C and H stage on CE kappa no, brightness and CED viscosity

Parameters/distributions	Different parameter at different at different distribution between C:H stages				
	45:55	50:50	55:45	60:40	65:35
CE Kappa no	5.5	5.4	5.1	5.2	5.1
CE Brightness(%ISO)	45.9	45.2	45.7	45.1	45.1
CEH Brightness(%ISO)	80.7	80.5	80.0	80.1	79.7
Viscosity(cp)	9.2	9.9	10.0	10.1	10.2

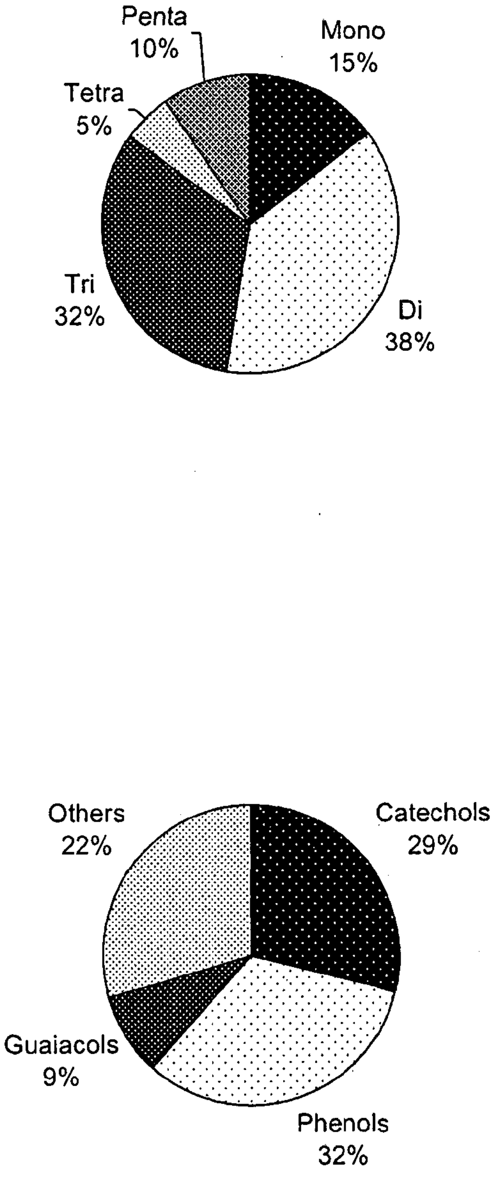


Fig. 3.17 The contribution of different chlorophenolic compounds at distribution of bleach chemical between C and H stage.

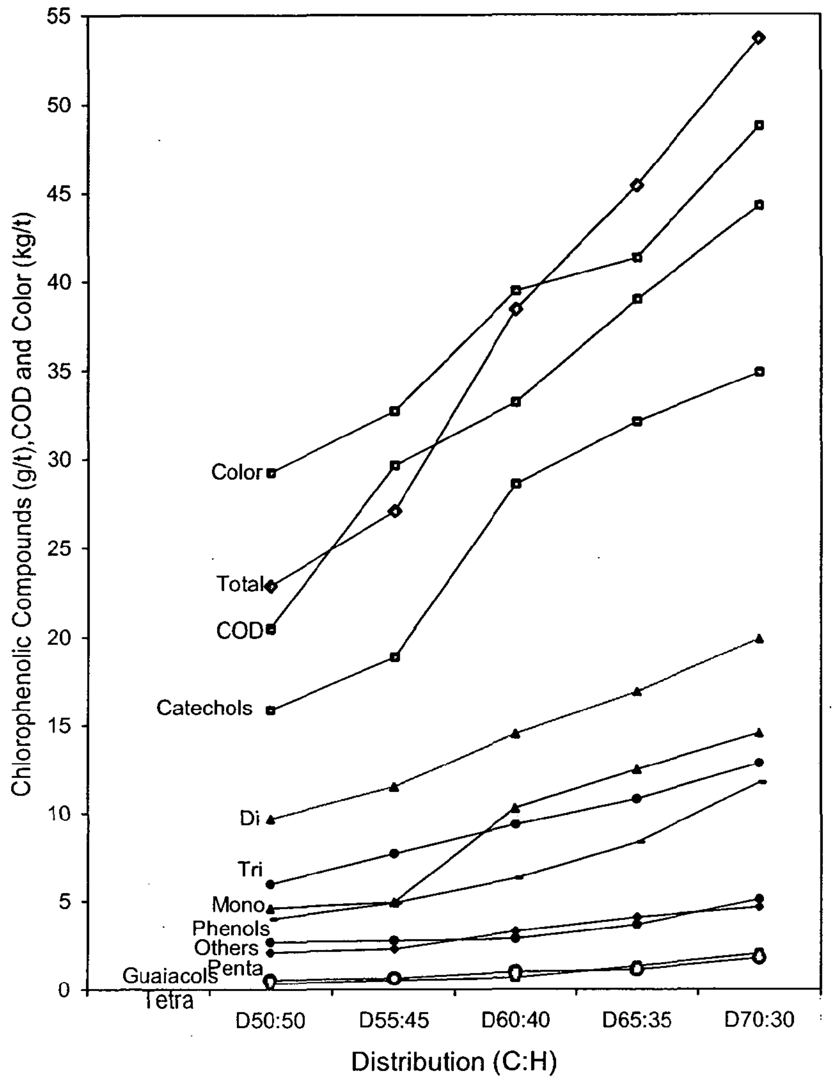


Fig 3.18 **Effect of distribution of bleach chemical between C and H stage on the generation of chlorophenolics, COD and color in C stage effluent.**

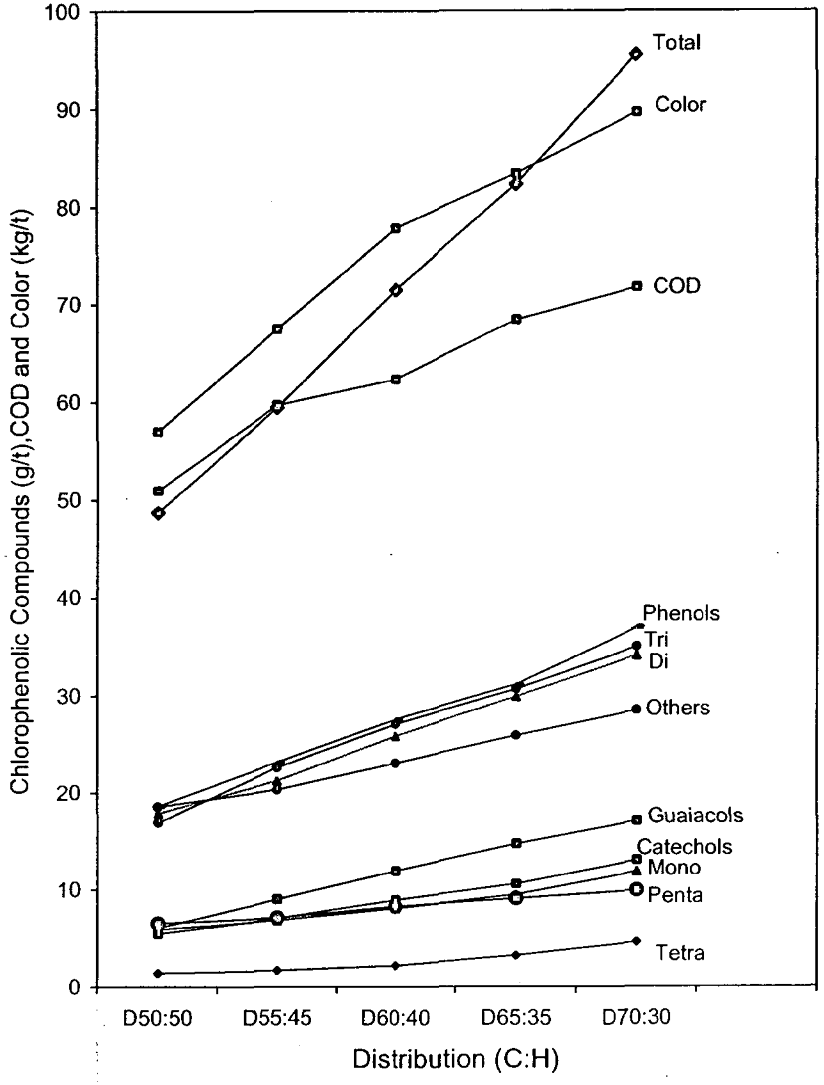


Fig 3.19 **Effect of distribution of bleach chemical between C and H stage on the generation of chlorophenolics, COD and color in E stage effluent.**

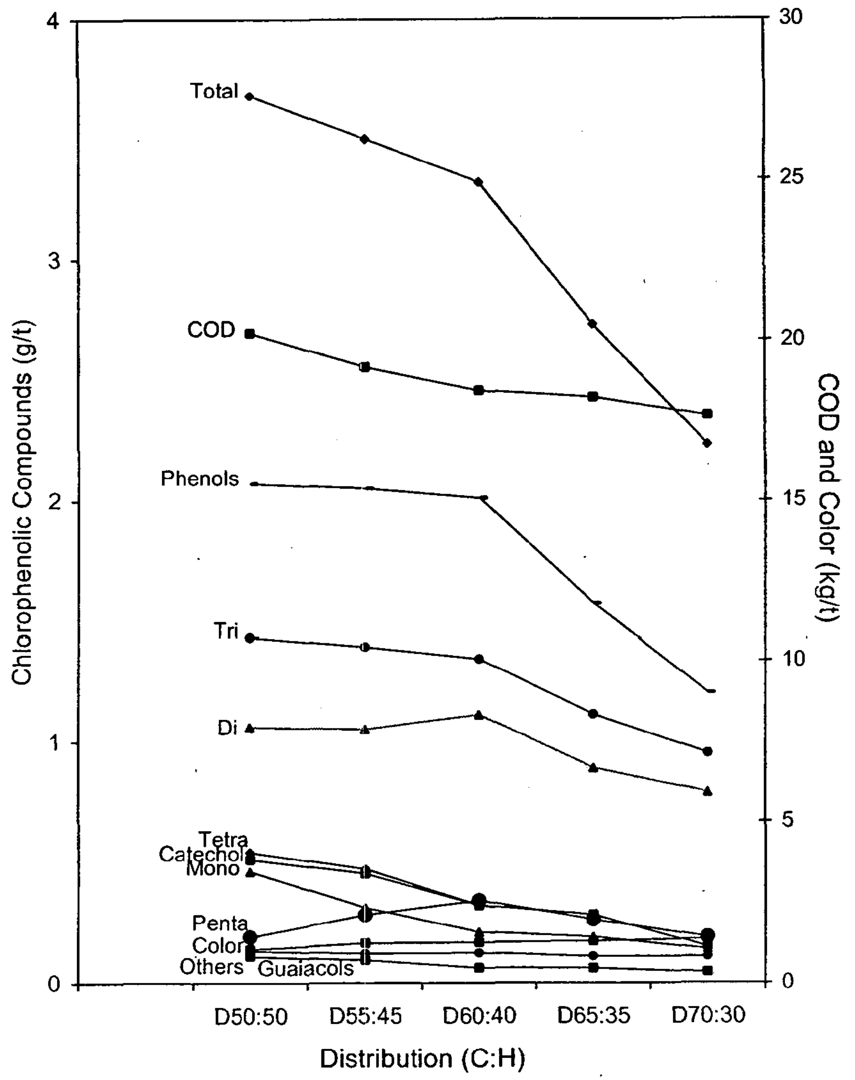


Fig 3.20 Effect of distribution of bleach chemical between C and H stage on the generation of chlorophenolics, COD and color in H stage effluent.

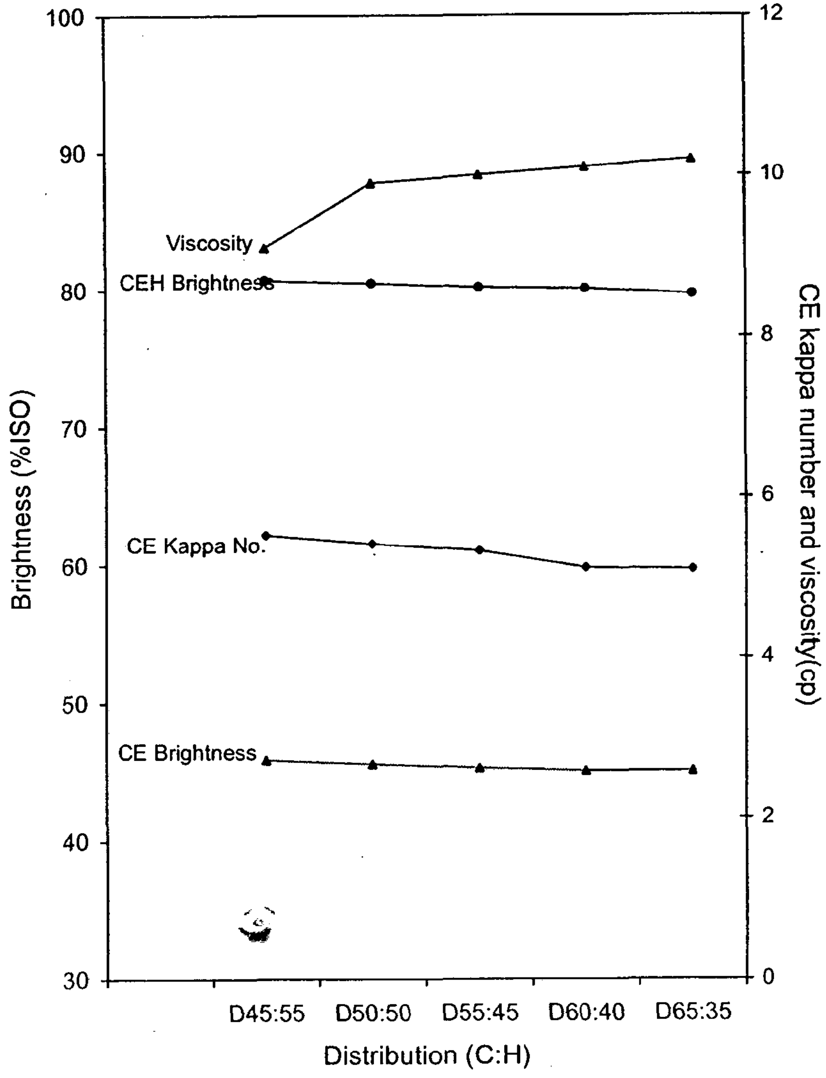


Fig 3.21 Effect of distribution of bleach chemical between C and H stage on brightness, viscosity and CE kappa number.

Table 3.18 Effect of replacement of chlorine by chlorine dioxide in C stage on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at chlorine dioxide substituted sequences														
	Normal CEH			$C_{75}D_{25}EH$			$C_{50}D_{50}EH$			$C_{25}D_{75}EH$			DEH		
	C	E	H	$C_{75}D_{25}$	E	H	$C_{50}D_{50}$	E	H	$C_{25}D_{75}$	E	H	D	E	H
2,4 Dichlorophenol	0.80	0.39	0.14	0.96	0.33	0.09	1.05	0.26	0.05	0.63	0.19	0.03	0.21	0.12	-
2,5 Dichlorophenol	1.43	2.89	0.21	1.60	2.54	0.13	1.68	2.01	0.09	1.03	1.77	0.06	0.78	1.01	0.02
2,3 Dichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3-Chloroguaiacol	-	0.25	-	-	0.19	-	-	0.17	-	-	0.11	-	-	0.08	-
2,6 Dichlorophenol	0.11	2.56	-	0.27	2.32	-	0.31	2.03	-	0.11	1.68	-	0.01	0.95	-
4-Chlorophenol	0.23	-	-	0.38	-	-	0.42	-	-	0.24	-	-	0.09	-	-
3-Chlorophenol	0.49	1.94	-	0.74	1.58	-	0.83	1.46	-	0.65	0.94	-	0.01	0.78	-
4-Chloroguaiacol	0.02	-	-	0.04	-	-	0.05	-	-	0.01	-	-	-	-	-
5-Chloroguaiacol	-	1.46	0.06	-	1.26	0.02	-	1.15	0.01	-	1.03	0.01	-	0.99	-
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.11	-	-	0.23	-	-	0.29	-	-	0.17	-	-	0.06	-	-
2,3,5-Trichlorophenol	0.16	3.12	0.33	0.25	2.05	0.25	0.34	1.98	0.16	0.26	1.19	0.08	0.08	1.00	0.06
2,4,6-Trichlorophenol	0.22	2.01	-	0.85	1.73	-	0.93	1.64	-	0.53	1.01	-	0.15	0.84	-
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.80	5.88	0.34	0.91	4.86	0.22	0.98	3.82	0.18	0.57	1.34	0.12	0.16	1.13	0.09
3,6 Dichloroguaiacol	0.10	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-
3,4 Dichloroguaiacol	0.18	4.93	-	0.10	3.69	-	0.09	2.57	-	0.04	1.27	-	-	1.02	-
3,4-Dichlorocatechol	3.78	1.06	-	2.58	0.94	0.93	2.05	0.78	-	1.13	0.64	-	0.74	0.33	-
3,4-Dicholorophenol	0.65	-	0.65	0.72	-	-	0.81	-	0.56	0.68	-	0.27	0.19	-	0.18
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.06	-	-	0.05	-	-	0.02	-	-	-	-	-	-	-
5-Chlorovanillin	1.95	2.69	0.15	1.36	1.21	-	1.16	1.01	-	0.76	0.96	-	0.18	0.65	-
5,6 Dichloroguaiacol	-	2.39	-	-	1.19	-	-	1.23	-	-	1.07	-	-	0.99	-

4-Chlorocatechol	2.65	-	-	1.88	-	-	1.63	-	-	0.99	-	-	0.32	-	-
3,5-Dichlorocatechol	5.85	-	-	4.23	-	-	3.74	-	-	1.38	-	-	0.64	-	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.28	0.51	-	0.30	0.37	-	0.46	0.16	-	0.25	0.12	-	0.08	0.08	-
3,5,6-Trichloroguaiacol	-	0.21	-	-	0.11	-	-	0.08	-	-	0.06	-	-	0.02	-
3,4,6-Trichloroguaiacol	-	2.11	-	-	1.92	0.02	-	1.52	0.03	-	1.24	0.04	-	1.13	0.03
3,5-Dichlorosyringol	-	1.32	0.11	-	1.03	0.09	-	0.93	0.07	-	0.61	0.04	-	0.15	-
3,4,5-Trichloroguaiacol	0.01	-	-	0.01	-	-	.023	-	-	0.01	-	-	-	-	-
3-Chlorocatechol	4.54	-	-	3.84	-	-	3.01	-	-	1.21	-	-	0.23	-	-
6-Chlorovanillin	0.02	1.75	-	0.02	1.27	-	0.01	1.08	-	-	0.97	-	-	0.49	-
3,6-Dichlorocatechol	0.79	0.38	-	0.56	0.34	-	0.45	0.25	-	0.32	0.15	-	0.13	0.09	-
4,5,6-Trichloroguaiacol	0.35	0.40	-	0.58	0.36	-	0.64	0.28	-	0.54	0.19	-	0.06	0.12	-
2-Chlorosyringaldehyde	0.26	-	-	0.13	-	-	0.10	-	-	0.02	-	-	-	-	-
4,5-Dichlorocatechol	0.65	-	-	0.48	-	-	0.38	-	-	0.16	-	-	0.08	-	-
Pentachlorophenol	1.00	8.26	0.34	0.93	3.03	0.05	0.76	1.68	-	-	1.05	-	-	-	-
3,4,5-Trichlorocatechol	6.78	5.92	-	5.36	4.53	-	4.62	3.03	-	1.31	-	-	0.23	-	-
Tetrachloroguaiacol	0.01	0.11	-	0.01	0.07	-	0.01	0.03	-	-	0.01	-	-	0.01	-
Trichlorosyringol	0.47	7.44	0.67	0.41	6.14	0.32	0.38	4.14	0.23	0.22	3.34	0.11	0.07	1.12	0.09
3,4,6-Trichlorocatechol	0.55	-	-	0.45	-	-	0.37	-	-	0.23	-	-	0.02	-	-
2,6-Dichlorosyringaldehyde	0.17	6.72	-	0.11	5.22	-	0.09	4.93	-	0.02	2.36	-	-	1.06	-
5,6-Dichlorovanillin	-	3.16	-	-	2.05	-	-	1.78	-	-	1.08	-	-	0.93	-
Tetrachlorocatechol	3.00	1.57	0.32	1.53	1.11	0.14	1.35	1.02	0.12	0.42	0.99	0.07	0.11	0.28	0.03
Total	**38.41**	**71.49**	**3.32**	**31.87**	**51.49**	**2.26**	**29.01**	**41.04**	**1.51**	**13.89**	**25.37**	**0.83**	**4.63**	**15.37**	**0.5**

C stage bleaching conditions: $C_{end\ pH} \geq 2 - 4.25$, Temperature 30 - 70°C and Consistency 3- 10%.

Table 3.19 Effect of replacement of chlorine by ClO_2 in C stage on COD generation

Stage/Replacement	COD (kg/t) at different chlorine dioxide substituted sequences				
	Normal CEH	$C_{75}D_{25}EH$	$C_{50}D_{50}EH$	$C_{25}D_{75}EH$	DEH
C	29.6	21.4	18.8	15.4	11.5
E	59.7	50.1	48.4	46.8	42.5
H	19.2	17.7	15.9	13.2	11.6
Total	**108.5**	**89.2**	**83.1**	**75.4**	**65.6**

Table 3.20 Effect of replacement of chlorine by ClO_2 in C stage on color generation

Stage/Replacement	Color (kg/t) at different chlorine dioxide substituted sequences				
	Normal CEH	$C_{75}D_{25}EH$	$C_{50}D_{50}EH$	$C_{25}D_{75}EH$	DEH
C	32.7	23.4	19.9	15.3	9.5
E	71.5	68.2	39.7	20.3	12.0
H	1.2	1.1	1.1	0.8	0.4
Total	**105.4**	**92.7**	**60.7**	**36.4**	**21.9**

Table 3.21 Effect of replacement of bleach chemical by ClO_2 on CE kappa no, brightness and CED viscosity

Parameters/Replacement	Different parameters at chlorine dioxide substituted sequences				
	Normal CEH	$C_{75}D_{25}EH$	$C_{50}D_{50}EH$	$C_{25}D_{75}EH$	DEH
CE kappa no	5.4	5.4	5.1	5.3	5.2
CE Brightness (%ISO)	45.6	50.8	55.9	60.3	62.4
CEH Brightness (%ISO)	80.5	83.4	85.8	87.6	88.8
Viscosity (cp)	9.9	11.8	12.2	14.0	14.8

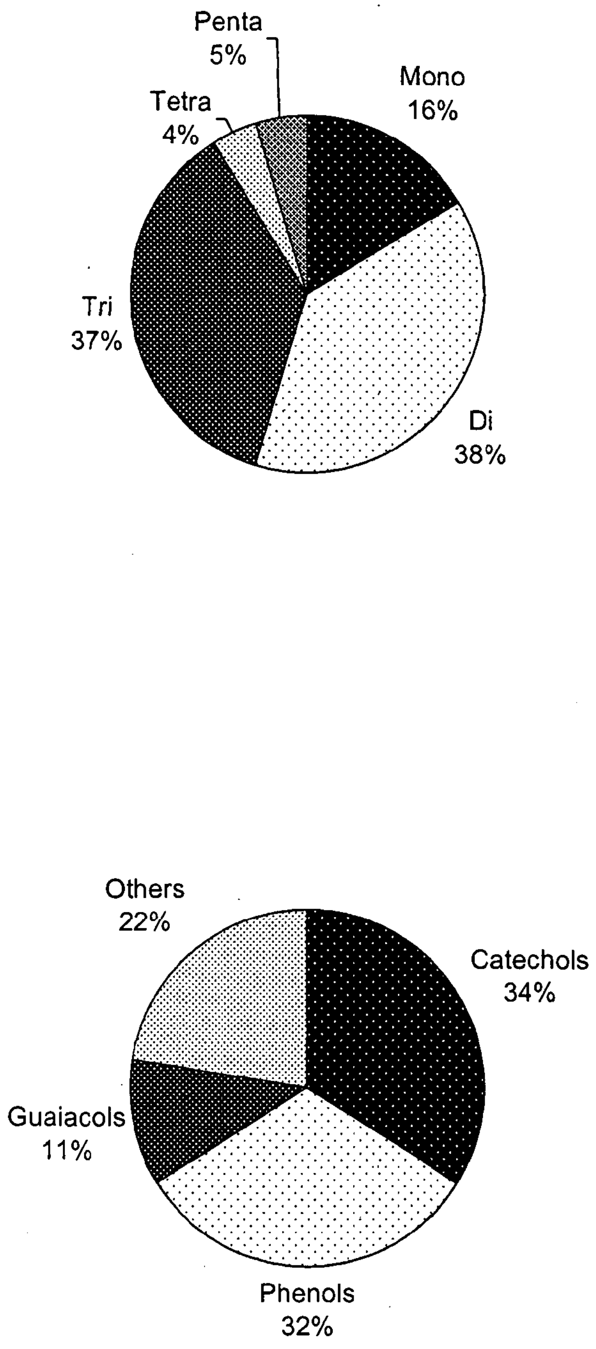


Fig. 3.22 The contribution of different chlorophenolic compounds at 25% substitution of chlorine by chlorine dioxide in C stage.

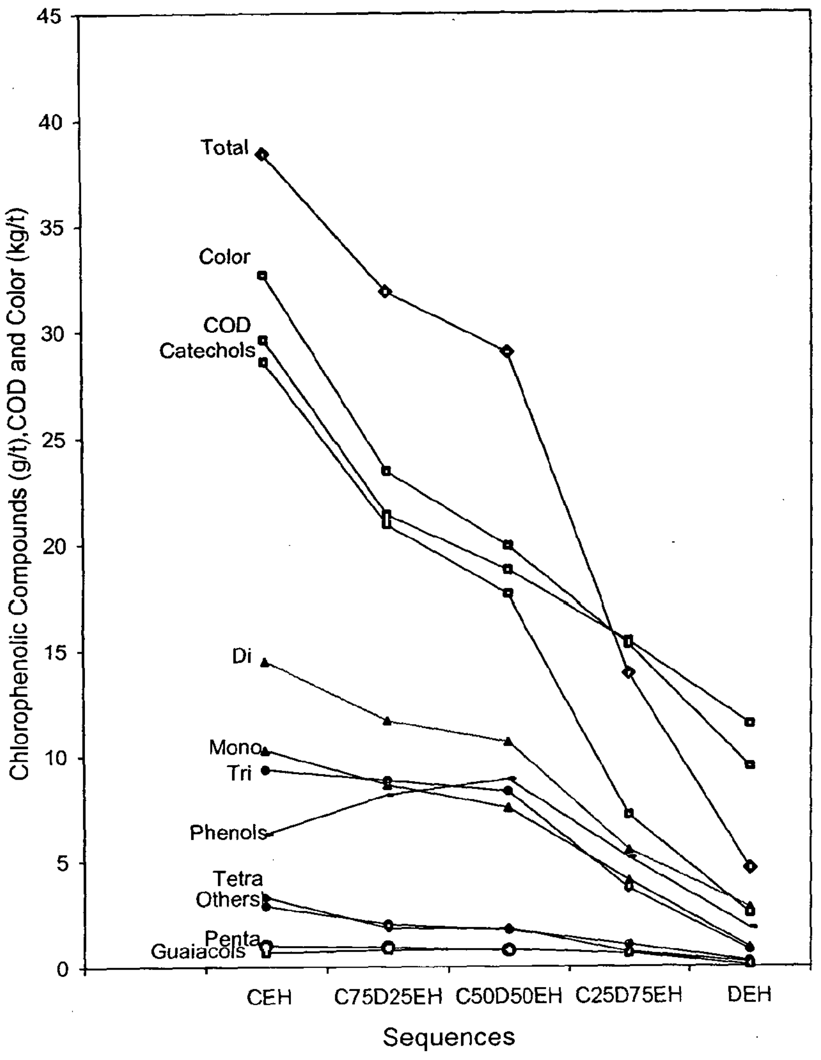


Fig 3.23 **Effect of replacement of chlorine by chlorine dioxide on the generation of chlorophenolics, COD and color in C stage effluent.**

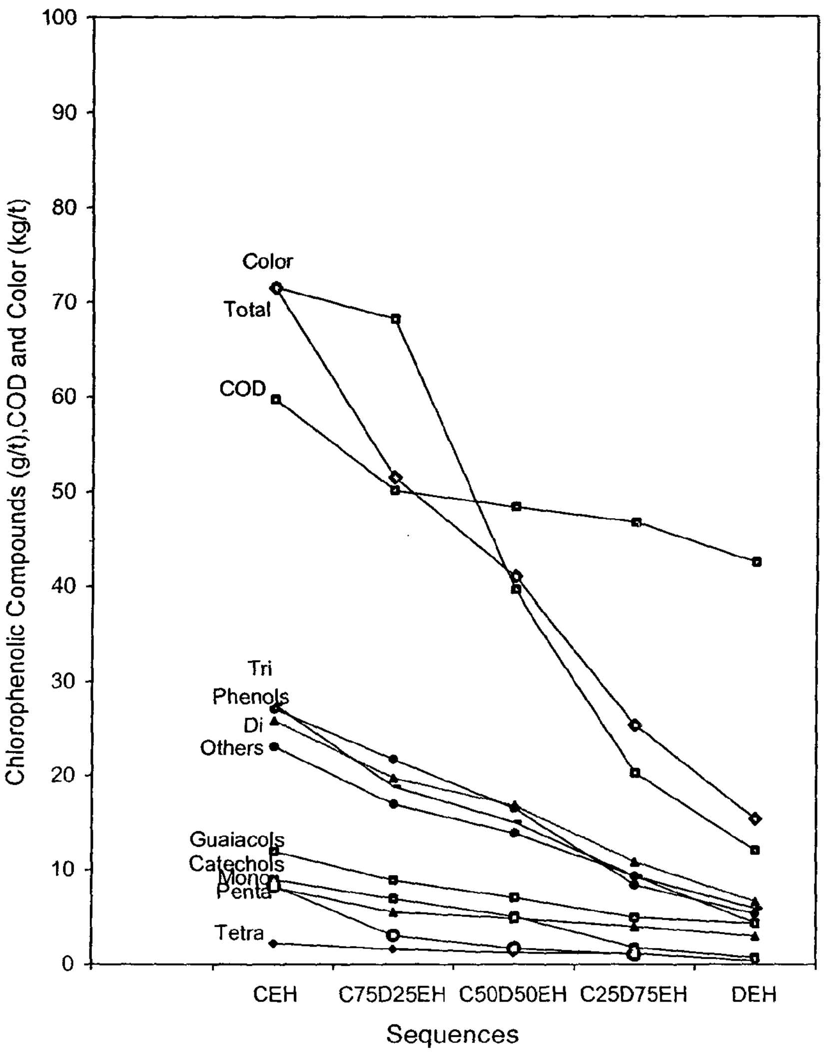


Fig 3.24 **Effect of replacement of chlorine by chlorine dioxide on the generation of chlorophenolics, COD and color in E stage effluent.**

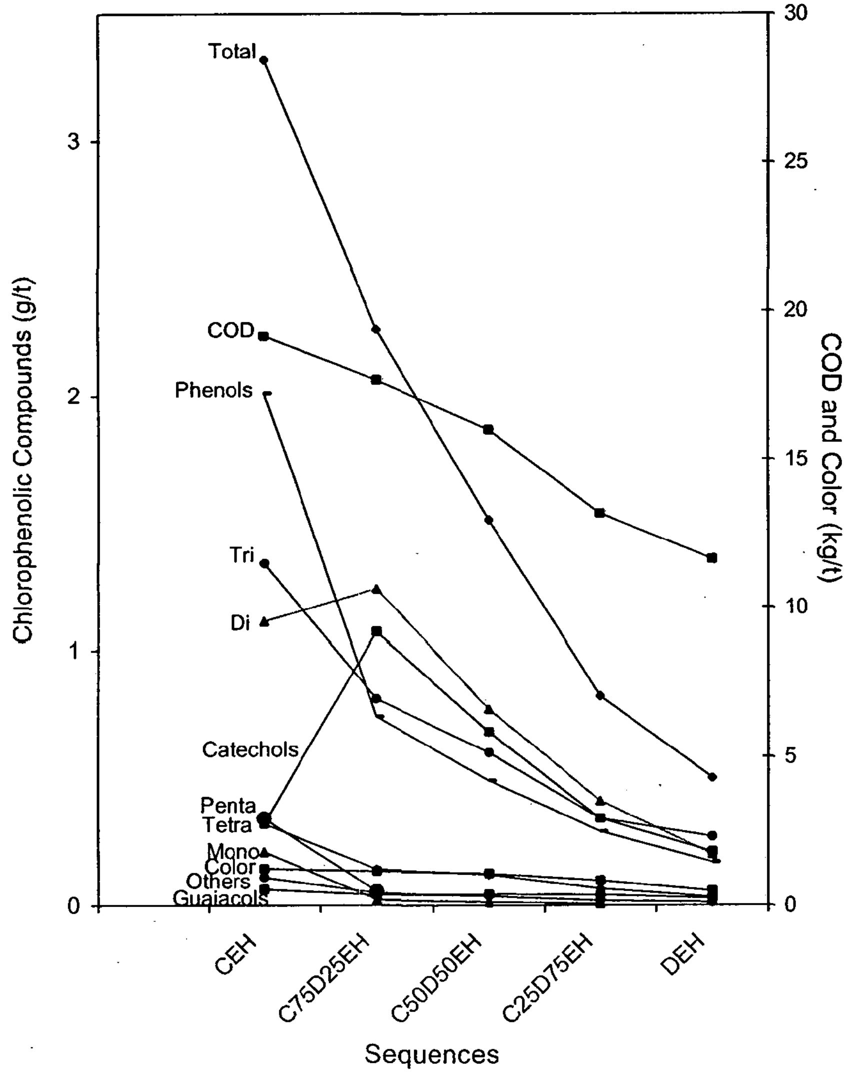


Fig 3.25 **Effect of replacement of chlorine by chlorine dioxide on the generation of chlorophenolics, COD and color in H stage effluent.**

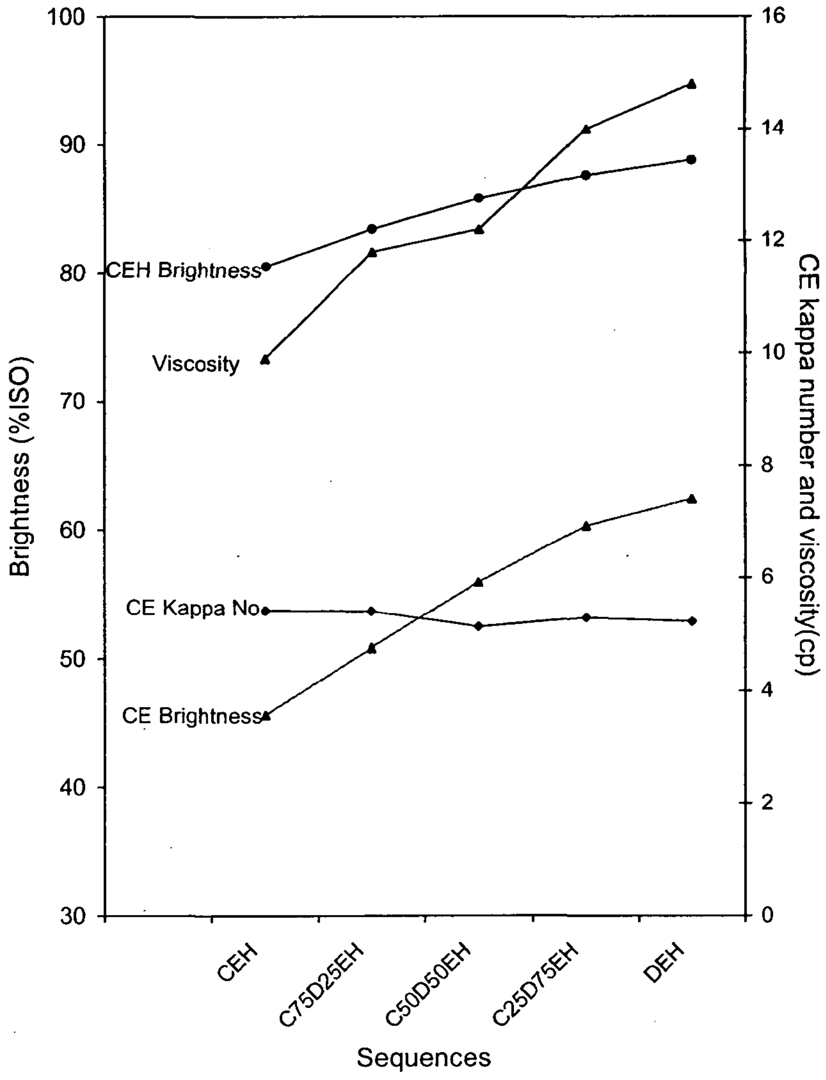


Fig 3.26 **Effect of replacement of chlorine by chlorine dioxide on brightness, viscosity and CE kappa number.**

Table 3.22 Effect of splitting of chlorine dose in C stage (with and without washing) on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Normal CEH			C (splitting) EH					
				Without pulp washing			With pulp washing		
	C	E	H	C	E	H	C	E	H
2,4 Dichlorophenol	0.80	0.39	0.14	0.24	0.21	0.09	0.23	0.21	0.09
2,5 Dichlorophenol	1.43	2.89	0.21	0.33	1.43	0.15	0.31	1.41	0.15
2,3 2,4 Dichlorophenol	-	-	-	-	-	-	-	-	-
3-Chloroguaiacol	-	0.25	-	-	0.13	-	-	0.12	-
2,6 2,4 Dichlorophenol	0.11	2.56	-	0.04	1.87	-	0.03	1.87	-
4-Chlorophenol	0.23	-	-	0.23	-	-	0.20	-	-
3-Chlorophenol	0.49	1.94	-	0.31	0.97	-	0.29	0.89	-
4-Chloroguaiacol	0.02	-	-	0.02	-		0.01	-	-
5-Chloroguaiacol	-	1.46	0.06	-	0.89	0.04	-	0.85	0.04
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.11	-	-	0.09	-	-	0.09	-	-
2,3,5-Trichlorophenol	0.16	3.12	0.33	0.11	1.86	0.21	0.09	1.58	0.19
2,4,6-Trichlorophenol	0.22	2.01	-	0.03	1.39	-	0.02	1.36	-
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.80	5.88	0.34	0.65	2.97	-	0.55	2.51	-
3,6 Dichloroguaiacol	0.10	-	-	0.05	-	-	0.03	-	-
3,4 Dichloroguaiacol	0.18	4.93	-	0.15	2.65	-	0.12	2.33	-
3,4-Dichlorocatechol	3.78	1.06	-	2.12	0.71	-	1.96	0.68	-
3,4-Dicholorophenol	0.65	-	0.65	0.30	-	0.39	0.26	-	0.38
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.06	-	-	0.05	-	-	0.05	-

5-Chlorovanillin	1.95	2.69	0.15	1.06	1.36	0.13	1.01	1.34	0.11
5,6 Dichloroguaiacol	-	2.39	-	-	1.78	-	-	1.72	-
4-Chlorocatechol	2.65	-	-	1.23	-	-	1.16	-	-
3,5-Dichlorocatechol	5.85	-	-	2.44	-	-	2.28	-	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.28	0.51	-	0.14	0.28	-	0.12	0.25	-
3,5,6-Trichloroguaiacol	-	0.21	-	-	0.09	-	-	0.09	-
3,4,6-Trichloroguaiacol	-	2.11	-	-	1.96	-	-	1.76	-
3,5-Dichlorosyringol	-	1.32	0.11	-	0.88	0.05	-	0.79	0.04
3,4,5-Trichloroguaiacol	0.01	-	-	-	-	-	-	-	-
3-Chlorocatechol	4.54	-	-	3.18	-	-	3.11	-	-
6-Chlorovanillin	0.02	1.75	-	0.02	1.17	-	0.02	1.08	-
3,6-Dichlorocatechol	0.79	0.38	-	0.57	0.24	-	0.43	0.22	-
4,5,6-Trichloroguaiacol	0.35	0.40	-	0.22	0.36	-	0.22	0.33	-
2-Chlorosyringaldehyde	0.26	-	-	0.18	-	-	0.16	-	-
4,5-Dichlorocatechol	0.65	-	-	0.43	-	-	0.40	-	-
Pentachlorophenol	1.00	8.26	0.34	0.12	3.05	-	0.09	2.99	-
3,4,5-Trichlorocatechol	6.78	5.92	-	2.34	3.95	-	2.34	3.15	-
Tetrachloroguaiacol	0.01	0.11	-	0.01	0.10	-	0.01	0.08	-
Trichlorosyringol	0.47	7.44	0.67	0.25	3.72	0.45	0.21	3.56	0.40
3,4,6-Trichlorocatechol	0.55	-	-	0.36	-	-	0.32	-	-
2,6-Dichlorosyringaldehyde	0.17	6.72	-	0.02	3.36	-	0.02	3.07	-
5,6-Dichlorovanillin	-	3.16	-	-	1.67	-	-	1.58	-
Tetrachlorocatechol	3.00	1.57	0.32	1.98	1.05	0.13	1.53	1.03	0.13
Total	**38.41**	**71.49**	**3.32**	**19.22**	**40.15**	**1.64**	**17.62**	**36.9**	**1.53**

C stage bleaching conditions: $C_{end\ pH} \geq 2$, Temperature 30°C and Consistency 3%.

Table 3.23 Effect of splitting of chlorine dose in C stage on COD generation

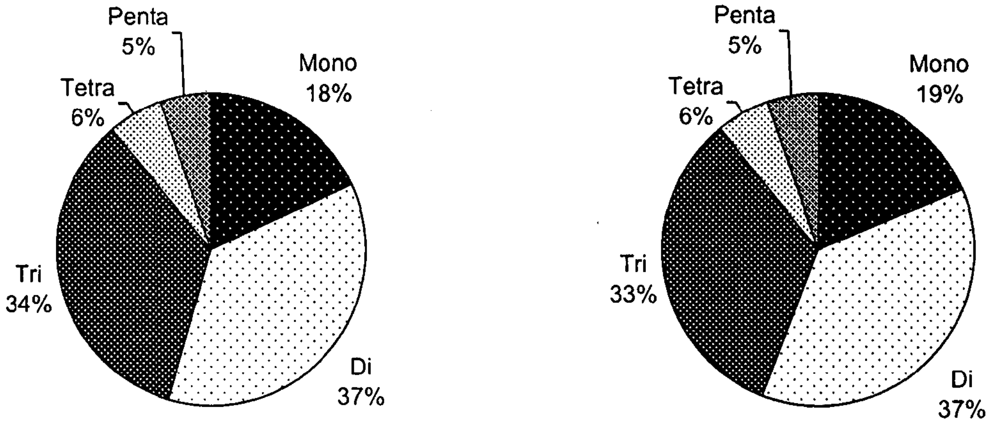
Stage/sequences	COD (kg/t) at different sequences		
	Normal CEH	C (splitting) EH	
		Without pulp washing	With pulp washing
C	29.6	22.8	21.9
E	59.7	55.3	52.9
H	19.2	16.3	16.0
Total	**108.5**	**94.4**	**90.8**

Table 3.24 Effect of splitting of chlorine dose in C stage on color generation

Stage/sequences	Color (kg/t) at different sequences		
	Normal CEH	C (splitting) EH	
		Without pulp washing	With pulp washing
C	32.7	23.0	20.2
E	71.5	62.6	61.9
H	1.2	0.3	0.2
Total	**105.4**	**85.9**	**82.3**

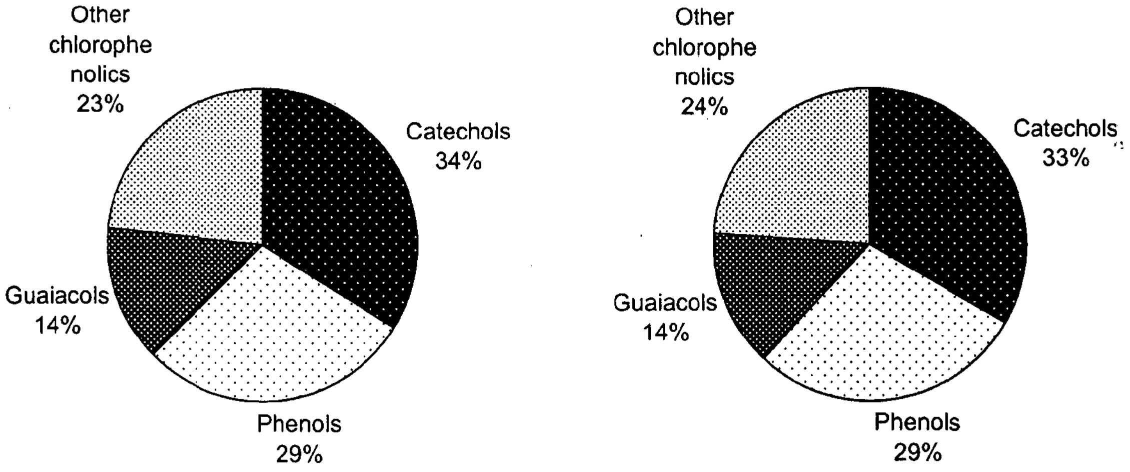
Table 3.25 Effect of splitting of chlorine dose in C stage on CE kappa no, brightness and CED viscosity

Parameter/sequences	Different parameters at different sequences		
	Normal CEH	C (splitting) EH	
		Without pulp washing	With pulp washing
CE kappa no	5.4	5.3	5.2
CE Brightness(%ISO)	45.6	46.1	46.3
CEH Brightness(%ISO)	80.5	80.9	81.0
Viscosity(cp)	9.9	11.8	12.3



C(splitting without washing)EH

C(splitting with washing)EH



C(splitting without washing)EH

C(splitting with washing)EH

Fig 3.27 The contribution of different chlorophenolic compounds at splitting of chlorine dose in C stage (with and without washing).

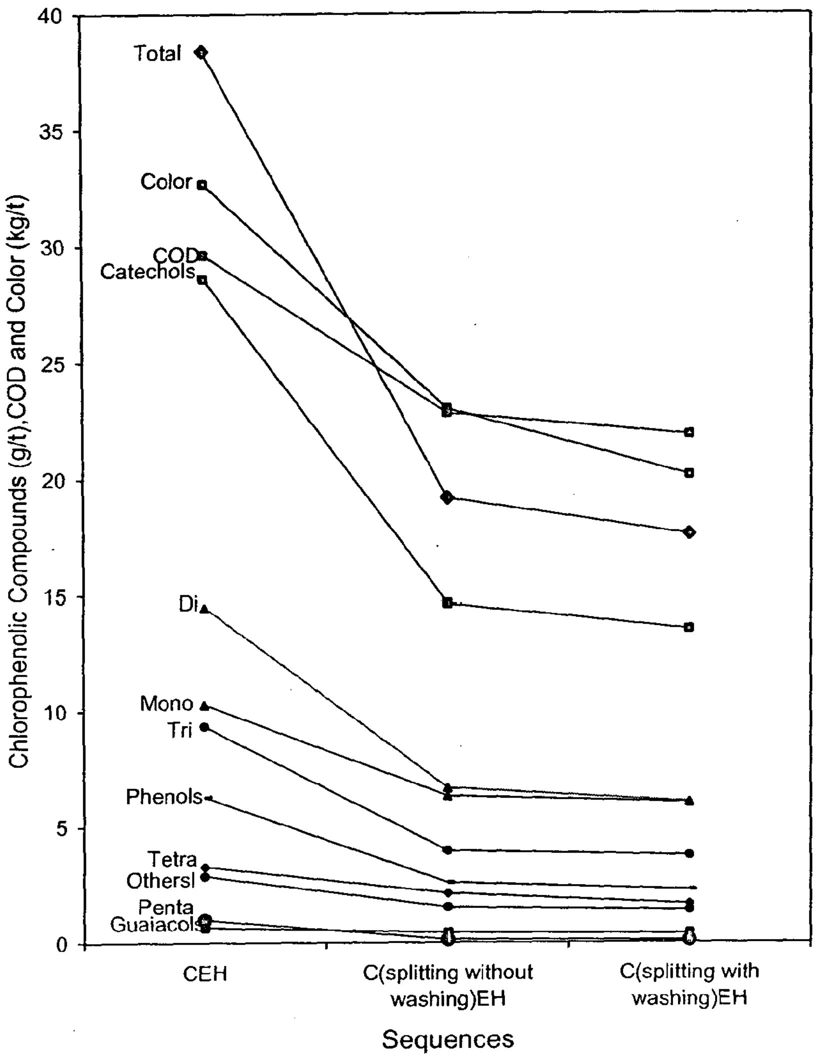


Fig 3.28 Effect of splitting of chlorine dose in C stage (with and without washing) on the generation of chlorophenolics, COD and color in C stage effluent.

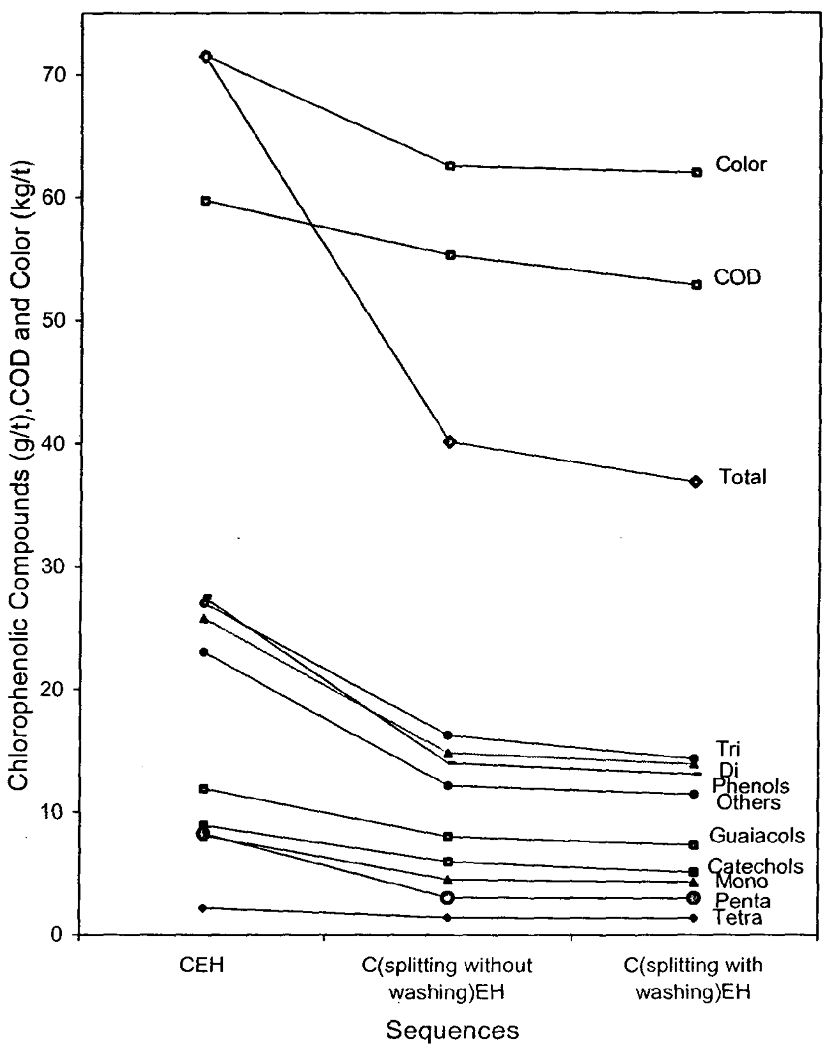


Fig 3.29 Effect of splitting of chlorine dose in C stage (with and without washing) on the generation of chlorophenolics, COD and color in E stage effluent.

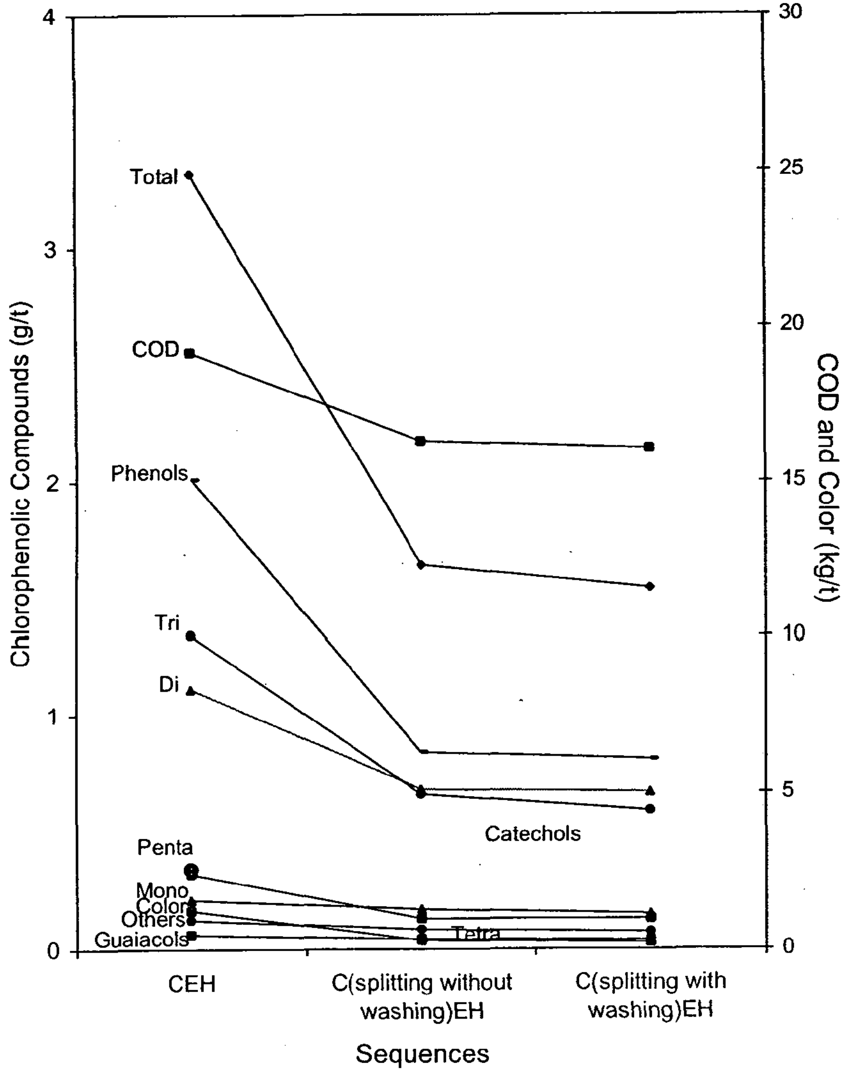


Fig 3.30 **Effect of splitting of chlorine dose in C stage (with and without washing) on the generation of chlorophenolics, COD and color in H stage effluent.**

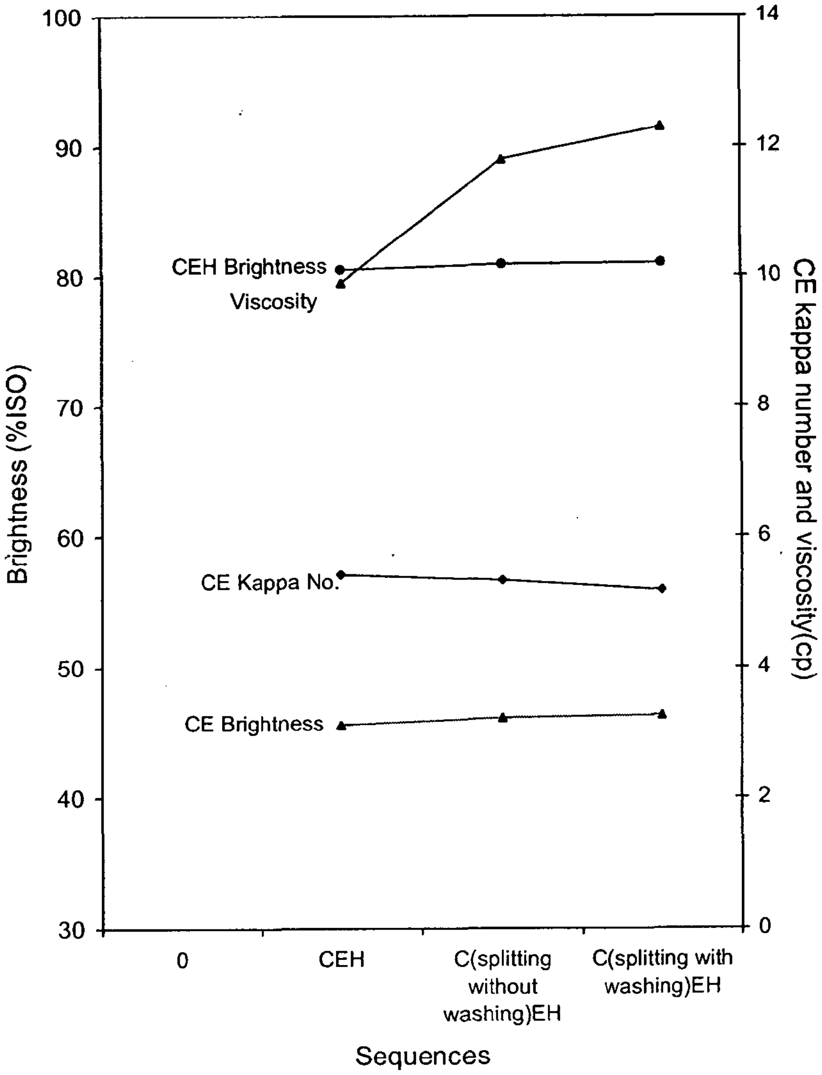


Fig 3.31 **Effect of splitting of chlorine dose in C stage (with and without washing) on brightness, viscosity and CE kappa number.**

Table 3.26 Effect of changed sequence on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at different sequences														
	Normal CEH			CED			CE_pH			OCEH			ODED		
	C	E	H	C	E	D	C	E_p	H	C	E	H	D	E	D
2,4 Dichlorophenol	0.80	0.39	0.14	0.80	0.39	0.01	0.80	0.44	0.01	0.11	0.06	-	0.02	0.04	-
2,5 Dichlorophenol	1.43	2.89	0.21	1.43	2.89	0.09	1.43	0.49	0.06	0.42	0.20	0.04	0.33	0.16	0.02
2,3 2,4 Dichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3-Chloroguaiacol	-	0.25	-	-	0.25	-	-	0.01	-	-	0.06	-	-	0.05	-
2,6 2,4 Dichlorophenol	0.11	2.56	-	0.11	2.56	-	0.11	1.58	-	0.01	1.02	-	0.01	0.98	-
4-Chlorophenol	0.23	-	-	0.23	-	-	0.23	-	-	0.13	-	-	0.09	-	-
3-Chlorophenol	0.49	1.94	-	0.49	1.94	-	0.49	1.22	-	0.18	0.78	-	0.01	0.74	-
4-Chloroguaiacol	0.02	-	-	0.02	-	-	0.02	-	-	0.01	-	-	-	-	-
5-Chloroguaiacol	-	1.46	0.06	-	1.46	0.01	-	0.19	0.01	-	0.32	0.01	-	0.30	-
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.11	-	-	0.11	-	-	0.11	-	-	0.03	-	-	0.02	-	-
2,3,5-Trichlorophenol	0.16	3.12	0.33	0.16	3.12	.016	0.16	1.23	0.01	0.01	0.77	0.17	0.01	0.74	0.05
2,4,6-Trichlorophenol	0.22	2.01	-	0.22	2.01	-	0.22	0.58	-	0.04	0.49	-	0.04	0.38	-
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.80	5.88	0.34	0.80	5.88	0.01	0.80	0.18	0.01	0.49	1.18	0.09	0.10	1.03	0.08
3,6 Dichloroguaiacol	0.10	-	-	0.10	-	-	0.10	-	-	0.01	-	-	-	-	-
3,4 Dichloroguaiacol	0.18	4.93	-	0.18	4.93	-	0.18	1.34	-	0.03	0.74	-	-	0.69	-
3,4-Dichlorocatechol	3.78	1.06	-	3.78	1.06	-	3.78	0.04	-	0.58	0.37	-	0.52	0.28	0.11
3,4-Dicholorophenol	0.65	-	0.65	0.65	-	0.14	0.65	-	0.10	0.13	-	0.16	0.17	-	-
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.06	-	-	0.06	-	-	0.23	-	-	1.05	-	-	-	-
5-Chlorovanillin	1.95	2.69	0.15	1.95	2.69	-	1.95	0.13	-	0.65	1.01	0.04	0.15	0.65	-
5,6 Dichloroguaiacol	-	2.39	-	-	2.39	-	-	-	-	-	-	-	-	0.93	-

4-Chlorocatechol	2.65	-	-	2.65	-	-	2.65	-	-	1.14	-	-	0.29	-	-
3,5-Dichlorocatechol	5.85	-	-	5.85	-	-	5.85	-	-	1.46	-	-	0.61	-	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.28	0.51	-	0.28	0.51	-	0.28	0.01	-	0.01	0.10	-	0.07	0.01	-
3,5,6-Trichloroguaiacol	-	0.21	-	-	0.21	-	-	-	-	-	0.07	-	-	0.02	-
3,4,6-Trichloroguaiacol	-	2.11	-	-	2.11	0.01	-	0.15	-	-	1.05	-	-	1.03	-
3,5-Dichlorosyringol	-	1.32	0.11	-	1.32	0.01	-	0.08	0.01	-	0.78	0.03	-	0.75	0.03
3,4,5-Trichloroguaiacol	0.01	-	-	0.01	-	-	0.01	-	-	-	-		-	-	-
3-Chlorocatechol	4.54	-	-	4.54	-	-	4.54	-	-	1.14	-		0.22	-	-
6-Chlorovanillin	0.02	1.75	-	0.02	1.75	-	0.02	0.36	-	0.01	0.89		-	0.49	-
3,6-Dichlorocatechol	0.79	0.38	-	0.79	0.38	-	0.79	0.05		0.26	0.13		0.11	0.08	-
4,5,6-Trichloroguaiacol	0.35	0.40	-	0.35	0.40	-	0.35	0.06	-	0.09	0.16		0.06	0.11	-
2-Chlorosyringaldehyde	0.26	-	-	0.26	-	-	0.26	-	-	0.07	-		-	-	-
4,5-Dichlorocatechol	0.65	-	-	0.65	-	-	0.65	-	-	0.16	-		0.08	-	-
Pentachlorophenol	1.00	8.26	0.34	1.00	8.26	0.01	1.00	-	-	-	1.03		-	-	-
3,4,5-Trichlorocatechol	6.78	5.92	-	6.78	5.92	-	6.78	1.12	-	1.59	1.32		0.23	-	-
Tetrachloroguaiacol	0.01	0.11	-	0.01	0.11	-	0.01	-	-	0.01	0.06		-	0.01	-
Trichlorosyringol	0.47	7.44	0.67	0.47	7.44	0.11	0.47	1.40	0.11	0.12	2.48	0.17	0.06	1.09	0.08
3,4,6-Trichlorocatechol	0.55	-	-	0.55	-	-	0.55	-	-	0.16	-	-	0.02	-	-
2,6-Dichlorosyringaldehyde	0.17	6.72	-	0.17	6.72	-	0.17	1.31	-	0.04	1.14	-	-	1.04	-
5,6-Dichlorovanillin	-	3.16	-	-	3.16	-	-	0.22	-	-	1.06	-	-	0.88	-
Tetrachlorocatechol	3.00	1.57	0.32	3.00	1.57	0.02	3.00	0.94	0.01	0.67	0.98	0.07	0.08	0.27	0.02
Total	**38.41**	**71.49**	**3.32**	**38.41**	**71.49**	**0.44**	**38.41**	**13.36**	**0.33**	**9.76**	**19.3**	**0.78**	**3.3**	**12.75**	**0.39**

C stage bleaching conditions: Temperature 30 - 70°C, Consistency 3 - 10% and $C_{end\ pH} \geq 2-4$.

Table 3.27 Effect of changed sequences on COD generation

Stage/sequences	COD (kg/t) at different sequences				
	Normal CEH	CED	CE_pH	OCEH	ODED
C	29.6	29.6	29.6	16.9	6.5
E	59.7	59.7	30.5	47.2	34.1
H	19.2	14.6	10.8	11.3	4.3
Total	**108.5**	**103.9**	**70.9**	**75.4**	**44.9**

Table 3.28 Effect of changed sequences on color generation

Stage/sequences	Color (kg/t) at different sequences				
	Normal CEH	CED	CE_pH	OCEH	ODED
C	32.7	32.7	32.7	20.5	18.2
E	71.5	71.5	36.8	35.9	25.0
H	1.2	0.1	0.8	0.3	0.2
Total	**105.4**	**104.3**	**70.3**	**56.7**	**43.4**

Table 3.29 Effect of changed sequence on CE kappa no, brightness and CED viscosity

Parameter/sequences	Different parameters at different sequences				
	Normal CEH	CED	CE_pH	OCEH	ODED
CE Kappa No	5.4	5.4	5.1	4.5	4.3
CE Brightness (%ISO)	45.6	45.6	55.7	60.3	62.7
CEH Brightness (%ISO)	80.5	82.3	81.4	87.1	89.8
Viscosity (cp)	9.9	14.6	10.9	9.1	9.5

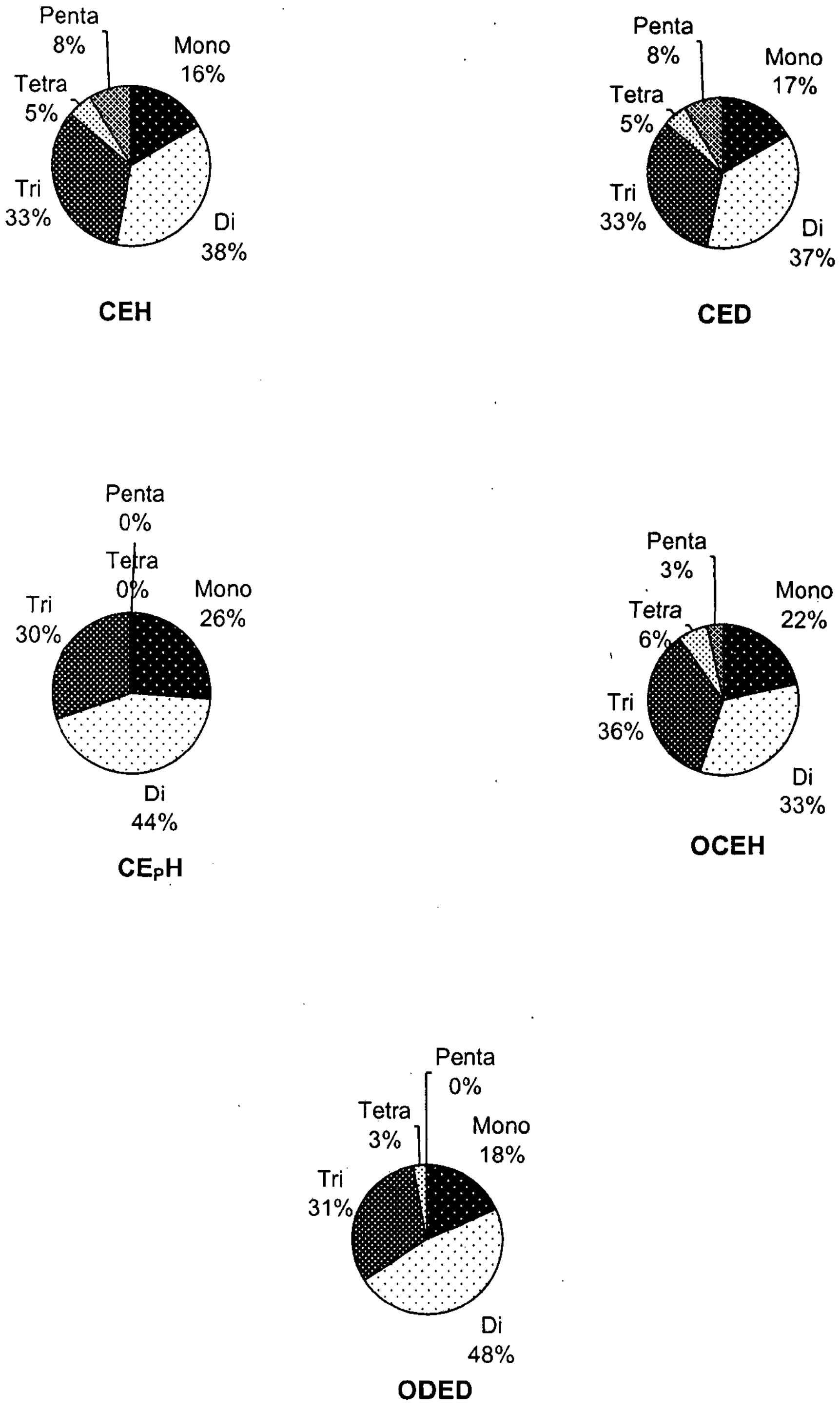


Fig. 3.32 The contribution of different chlorophenolic compounds in different sequences

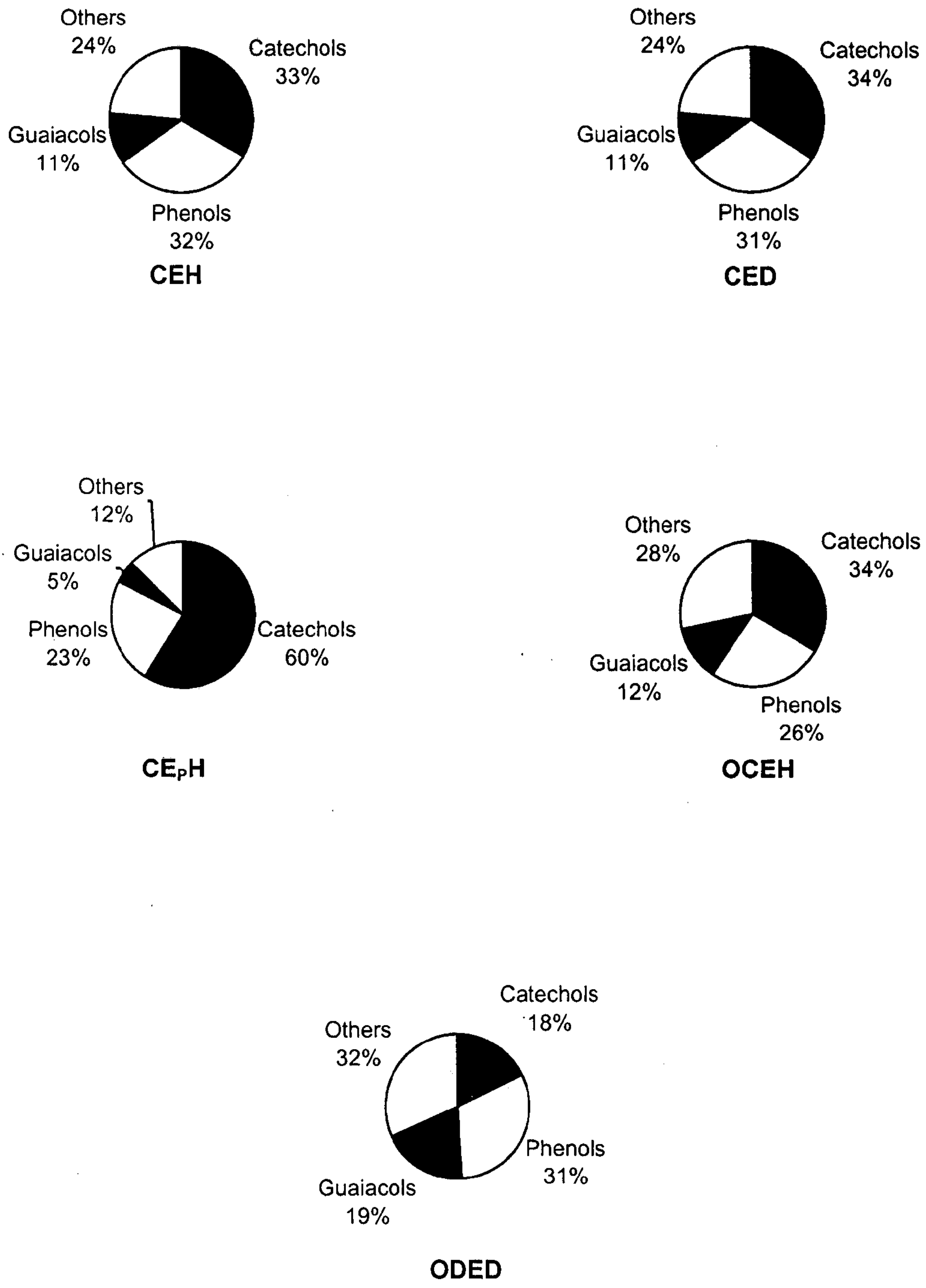


Fig. 3.33 The contribution of different chlorophenolic compounds in different sequences

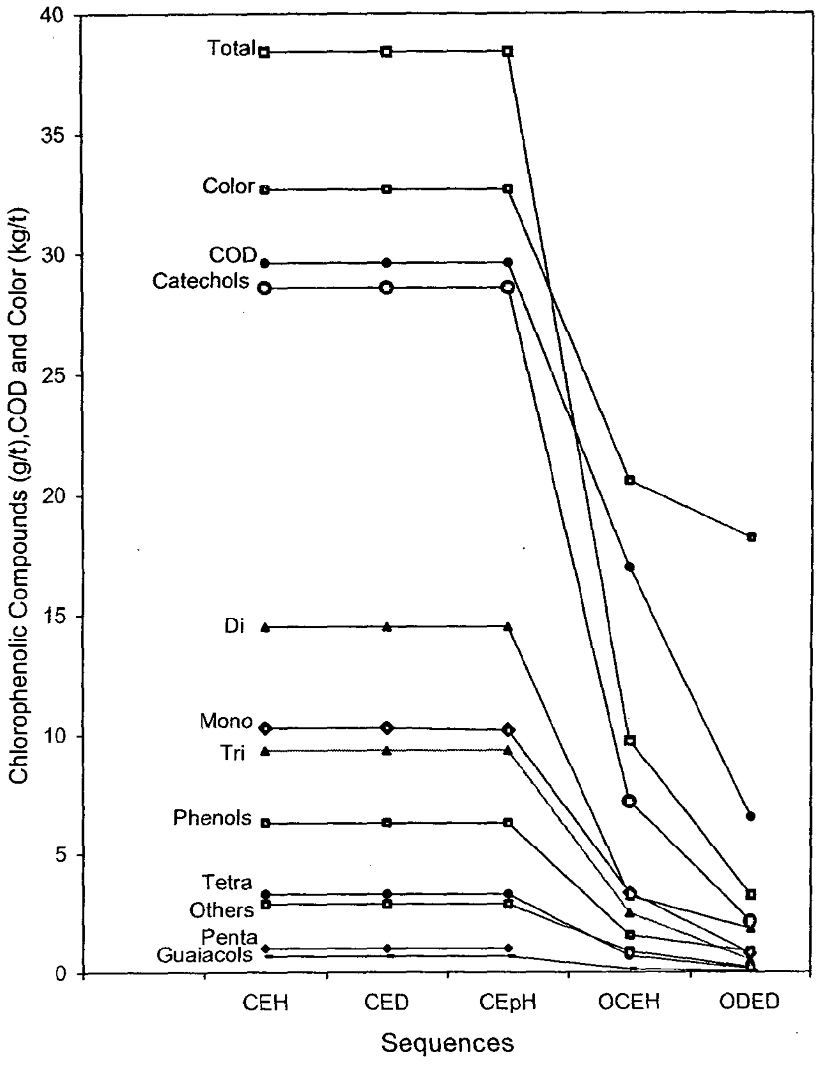


Fig 3.34 Effect of changed sequences on the generation of chlorophenolics, COD and color in C stage effluent.

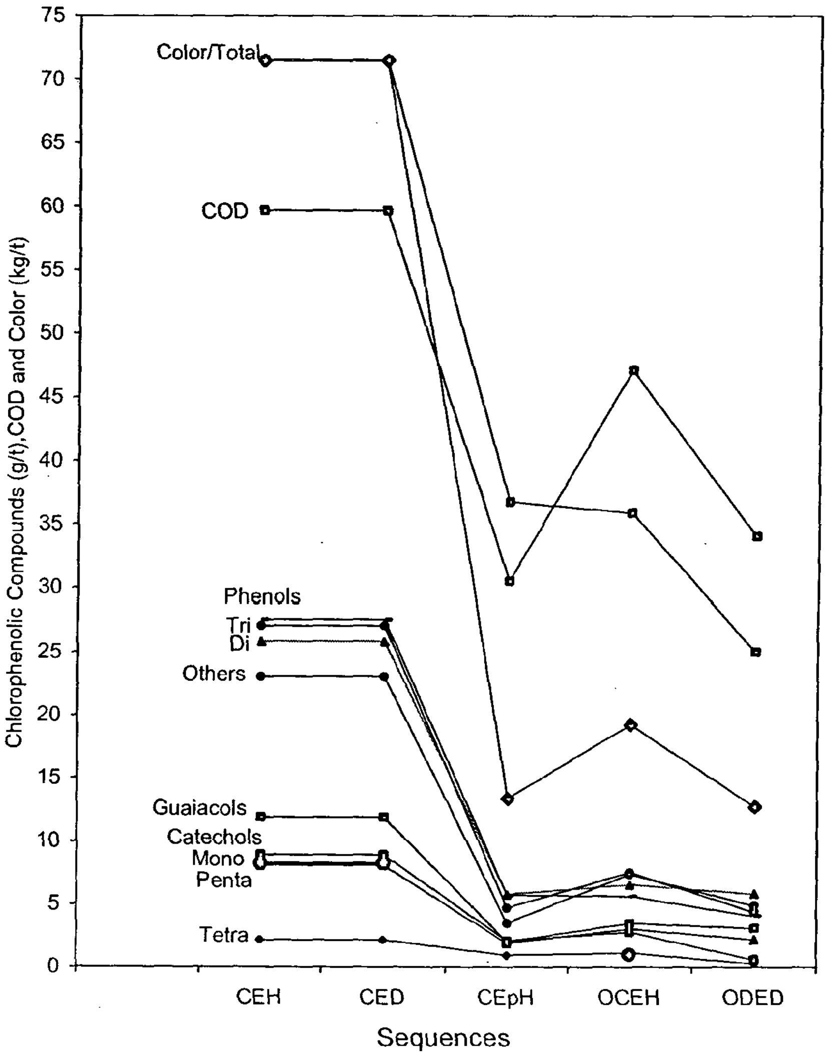


Fig 3.35 Effect of changed sequences on the generation of chlorophenolics, COD and color in E stage effluent.

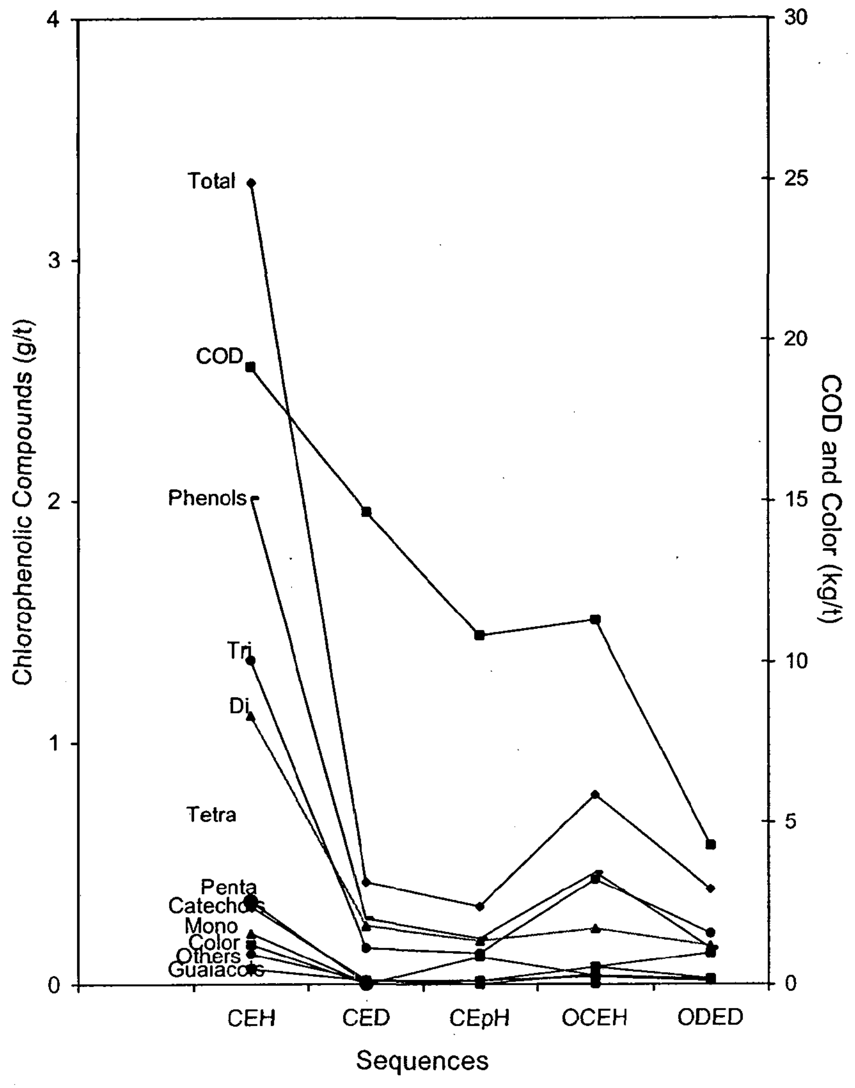


Fig 3.36 Effect of changed sequences on the generation of chlorophenolics, COD and color in H stage effluent.

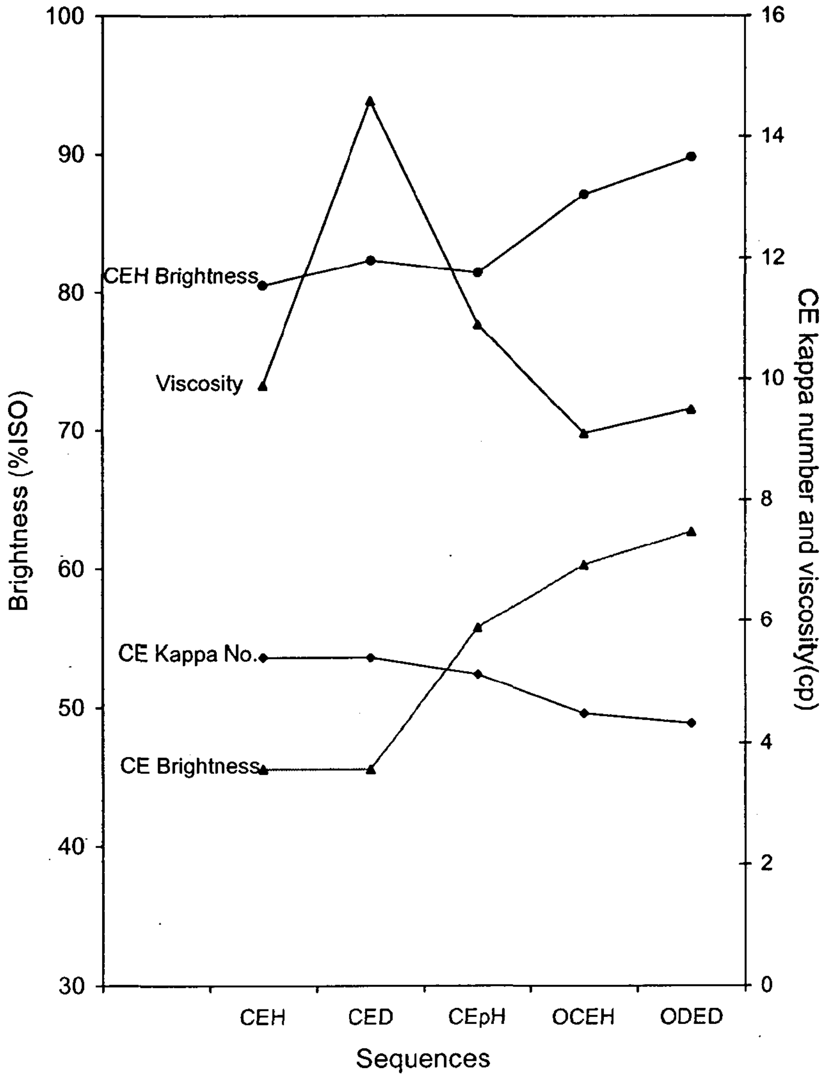


Fig 3.37 Effect of changed sequences on brightness, viscosity and CE kappa number.

Table 3.30 Estimation of chlorophenolic compounds in various effluents obtained by bleaching pulp when 80% target brightness achieved by different sequences

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at different sequences														
	Normal CEH			$D_{50}C_{50}EH$			$C_{splitting}EH$			ODED			Modified CEH		
	C	E	H	$D_{50}C_{50}$	E	H	$C_{splitting}$	E	H	D	E	D	C	E	H
2,4 Dichlorophenol	0.80	0.39	0.14	0.99	0.21	0.04	0.20	0.15	0.07	0.01	0.03	-	1.01	0.34	0.10
2,5 Dichlorophenol	1.43	2.89	0.21	1.02	1.35	0.07	0.29	1.06	0.10	0.28	0.13	0.02	1.11	1.43	0.16
2,3 2,4 Dichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3-Chloroguaiacol	-	0.25	-	-	0.14	-	-	0.10	-	-	0.04	-	-	0.21	-
2,6 2,4 Dichlorophenol	0.11	2.56	-	0.24	1.46	-	0.02	1.43	-	-	0.65	-	0.25	1.76	-
4-Chlorophenol	0.23	-	-	0.35	-	-	0.19	-	-	0.07	-	-	0.21	-	-
3-Chlorophenol	0.49	1.94	-	0.67	1.18	-	0.30	0.62	-	0.01	0.36	-	0.37	1.68	-
4-Chloroguaiacol	0.02	-	-	0.03	-	-	0.01	-	-	-	-	-	0.01	-	-
5-Chloroguaiacol	-	1.46	0.06	-	1.03	0.01	-	0.48	0.03	-	0.27	-	-	1.25	0.05
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.11	-	-	0.23	-	-	0.08	-	-	0.02	-	-	0.10	-	-
2,3,5-Trichlorophenol	0.16	3.12	0.33	0.25	1.27	0.12	0.08	1.27	0.16	-	0.36	0.02	0.13	2.62	0.28
2,4,6-Trichlorophenol	0.22	2.01	-	0.76	1.15	-	0.02	1.06	-	0.03	0.29	-	0.18	1.54	-
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.80	5.88	0.34	0.84	2.62	0.13	0.53	2.19	-	0.06	0.98	0.05	0.64	4.93	0.31
3,6 Dichloroguaiacol	0.10	-	-	-	-	-	0.03	-	-	-	-	-	0.10	-	-
3,4 Dichloroguaiacol	0.18	4.93	-	0.07	1.94	-	0.11	1.97	-	-	0.57	-	0.13	4.02	-
3,4-Dichlorocatechol	3.78	1.06	-	1.63	0.59	-	1.98	0.52	-	0.43	0.16	-	2.96	0.78	-
3,4-Dicholorophenol	0.65	-	0.65	0.75	-	0.46	0.29	-	0.27	0.11	-	0.08	0.38	-	0.46
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.06	-	-	0.02	-	-	0.02	-	-	-	-	-	0.05	-

5-Chlorovanillin	1.95	2.69	0.15	1.08	0.82	-	1.01	1.18	0.10	0.10	0.52	-	1.81	2.20	0.13
5,6 Dichloroguaiacol	-	2.39	-	-	1.07	-	-	1.59	-	-	0.78	-	-	2.06	-
4-Chlorocatechol	2.65	-	-	1.32	-	-	1.19	-	-	0.22	-	-	2.12	-	-
3,5-Dichlorocatechol	5.85	-	-	2.89	-	-	2.13	-	-	0.43	-	-	4.34	-	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.28	0.51	-	0.36	0.11	-	0.12	0.21	-	0.03	-	-	0.25	0.43	-
3,5,6-Trichloroguaiacol	-	0.21	-	-	0.08	-	-	0.09	-	-	0.02	-	-	0.16	-
3,4,6-Trichloroguaiacol	-	2.11	-	-	1.43	0.02	-	1.62	-	-	0.85	-	-	1.34	-
3,5-Dichlorosyringol	-	1.32	0.11	-	0.82	0.03	-	0.43	0.02	-	0.63	0.02	-	1.08	0.10
3,4,5-Trichloroguaiacol	0.01	-	-	-	-	-	-	-	-	-	-	-	0.01	-	-
3-Chlorocatechol	4.54	-	-	1.64	-	-	2.79	-	-	0.16	-	-	4.18	-	-
6-Chlorovanillin	0.02	1.75	-	0.01	1.02	-	0.02	0.94	-	-	0.31	-	0.02	1.21	-
3,6-Dichlorocatechol	0.79	0.38	-	0.32	0.19	-	0.52	0.20	-	0.08	0.07	-	0.71	0.32	-
4,5,6-Trichloroguaiacol	0.35	0.40	-	0.56	0.20	-	0.19	0.31	-	0.02	0.09	-	0.32	0.26	-
2-Chlorosyringaldehyde	0.26	-	-	0.08	-	-	0.15	-	-	-	-	-	0.25	-	-
4,5-Dichlorocatechol	0.65	-	-	0.27	-	-	0.38	-	-	0.06	-	-	0.54	-	-
Pentachlorophenol	1.00	8.26	0.34	0.34	1.03	-	0.10	2.41	-	-	-	-	0.93	6.23	0.25
3,4,5-Trichlorocatechol	6.78	5.92	-	2.91	2.65	-	2.15	3.26	-	0.19	-	-	6.17	3.18	-
Tetrachloroguaiacol	0.01	0.11	-	-	0.01	-	-	0.07	-	-	-	-	0.01	0.08	-
Trichlorosyringol	0.47	7.44	0.67	0.35	3.46	0.19	0.20	3.13	0.27	0.05	0.63	0.06	0.32	5.94	0.54
3,4,6-Trichlorocatechol	0.55	-	-	0.29	-	-	0.34	-	-	0.01	-	-	0.46	-	-
2,6-Dichlorosyringaldehyde	0.17	6.72	-	0.07	3.25	-	0.01	2.64	-	-	0.76	-	0.13	6.05	-
5,6-Dichlorovanillin	-	3.16	-	-	1.31	-	-	1.11	-	-	0.32	-	-	2.74	-
Tetrachlorocatechol	3.00	1.57	0.32	0.93	0.84	0.09	1.01	0.42	0.10	0.02	0.21	0.02	2.16	1.12	0.21
Total	**38.41**	**71.49**	**3.32**	**21.25**	**31.25**	**1.16**	**16.44**	**30.48**	**1.12**	**2.39**	**9.03**	**0.27**	**32.31**	**55.01**	**2.59**

C stage bleaching conditions: $C_{end\ pH} \geq 2 - 4$, Temperature 30 - 70°C and Consistency 3 - 10%.

Table 3.31 Effect on effluent COD generated during bleaching of pulp to 80% target brightness by different sequences

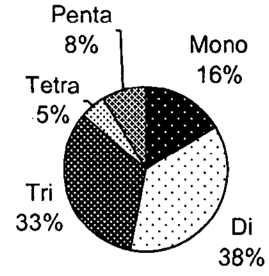
Stage/sequences	COD(kg/t) at different sequences				
	Normal CEH	Modified CEH	$C_{splitting}EH$	$D_{50}C_{50}EH$	ODED
C	29.6	22.4	19.4	13.2	5.3
E	59.7	54.8	46.9	33.5	28.6
H	19.2	14.1	12.1	10.1	3.1
Total	**108.5**	**91.3**	**78.4**	**56.8**	**37.0**

Table 3.32 Effect on effluent color generated during bleaching of pulp to 80% target brightness by different sequences

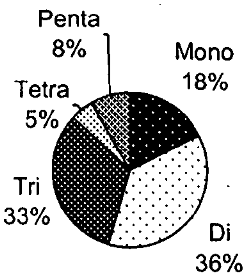
Stage/sequences	Color (kg/t) at different sequences				
	Normal CEH	Modified CEH	$C_{splitting}EH$	$D_{50}C_{50}EH$	ODED
C	32.7	21.9	18.5	12.7	12.3
E	71.5	62.7	50.0	21.3	19.3
H	1.2	1.0	0.1	0.5	0.1
Total	**105.4**	**85.6**	**68.6**	**34.5**	**31.7**

Table 3.33 Effect on CE kappa no, brightness and CED viscosity of pulp bleached to 80% target brightness by different sequences

Parameter/sequences	Different parameters at different sequences				
	Normal CEH	Modified CEH	$C_{splitting}EH$	$D_{50}C_{50}EH$	ODED
CE Kappa no	5.4	5.1	5.3	5.4	5.4
CE Brightness (%ISO)	45.6	45.6	45.3	50.7	51.2
CEH Brightness(%ISO)	80.5	80.0	80.1	80.6	80.8
Viscosity (cp)	9.9	8.4	12.5	13.0	9.6



CEH



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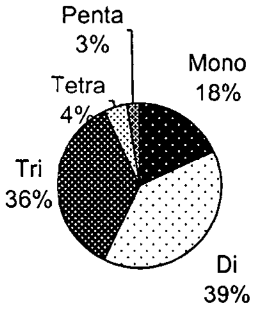
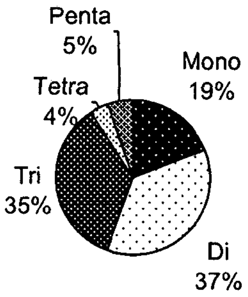
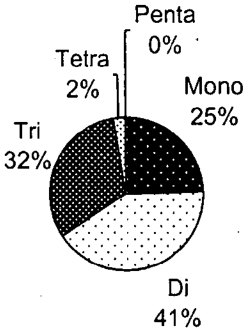


$D_{50}C_{50}EH$

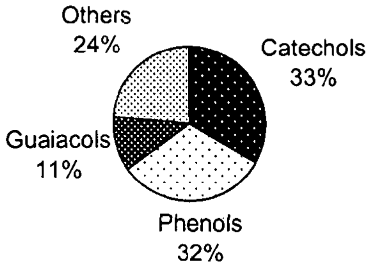


$C_{splitting}EH$

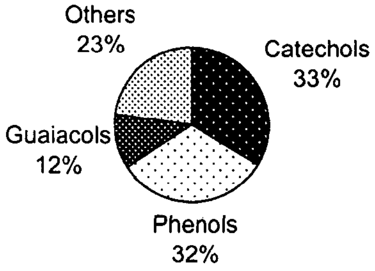


ODED

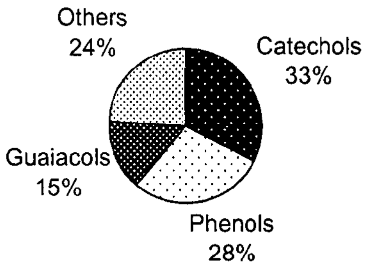
Fig 3.38 The contribution of different chlorophenolic compounds in different sequences, when target brightness achieved.



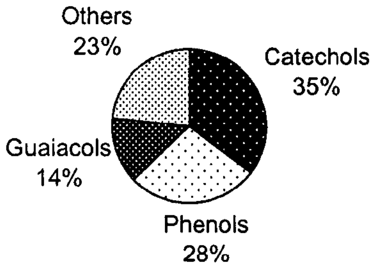
CEH



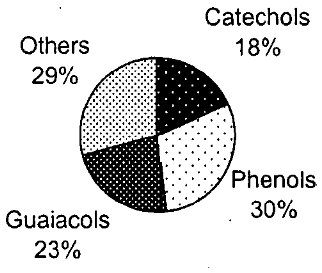
Modified CEH



$D_{50}C_{50}EH$



$C_{splitting}EH$



ODED

Fig 3.39 The contribution of different chlorophenolic compounds at different sequences, when target brightness achieved.

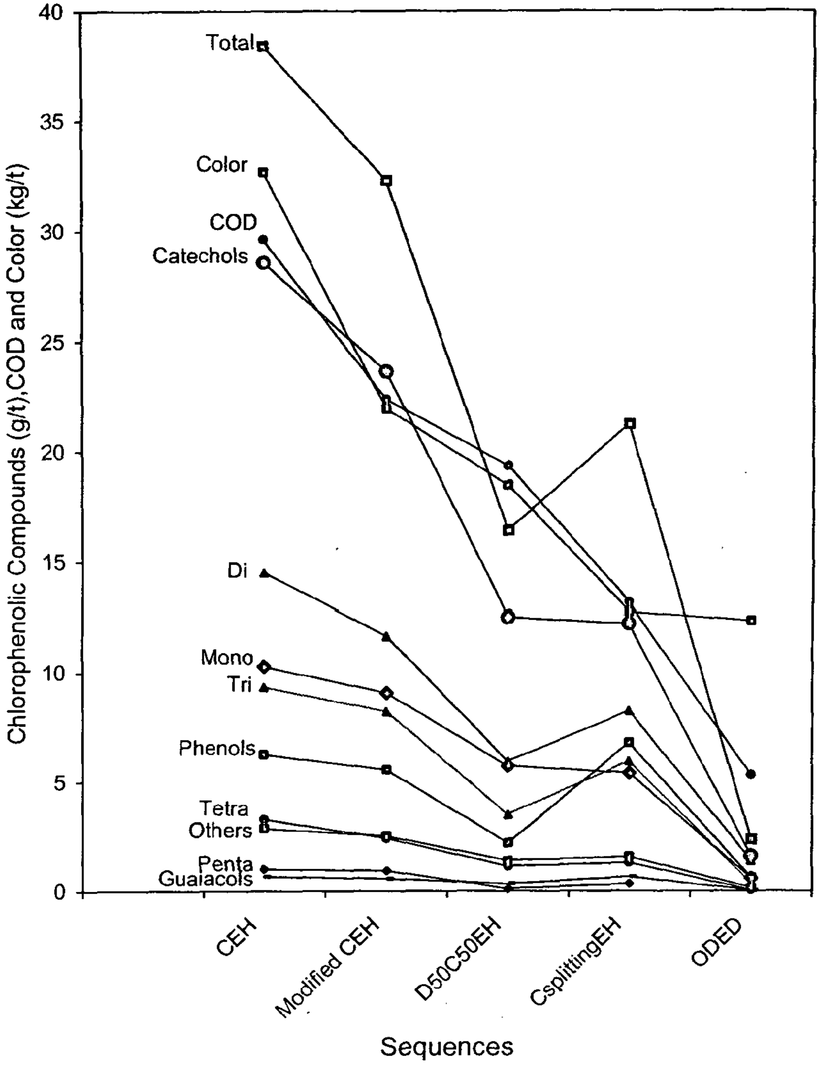


Fig 3.40 **Effect of changed sequences on the generation of chlorophenolics, COD and color in C stage effluent, when target brightness achieved.**

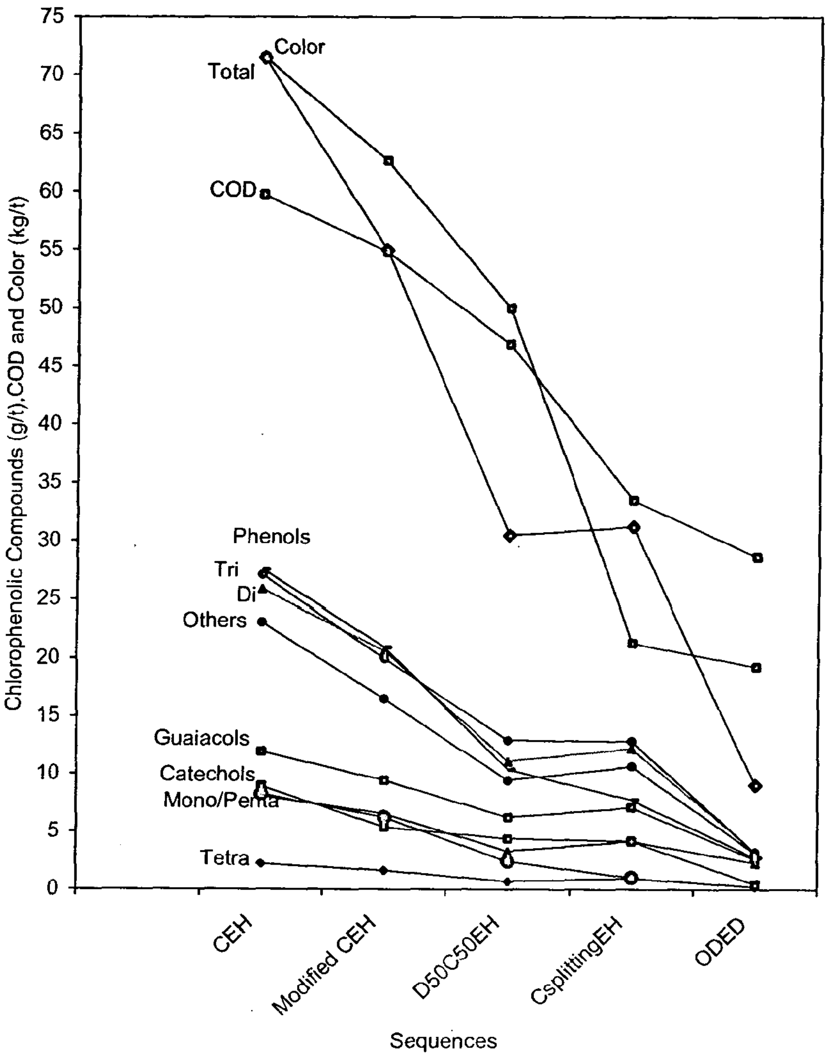


Fig 3.41 **Effect of changed sequences on the generation of chlorophenolics, COD and color in E stage effluent, when target brightness achieved.**

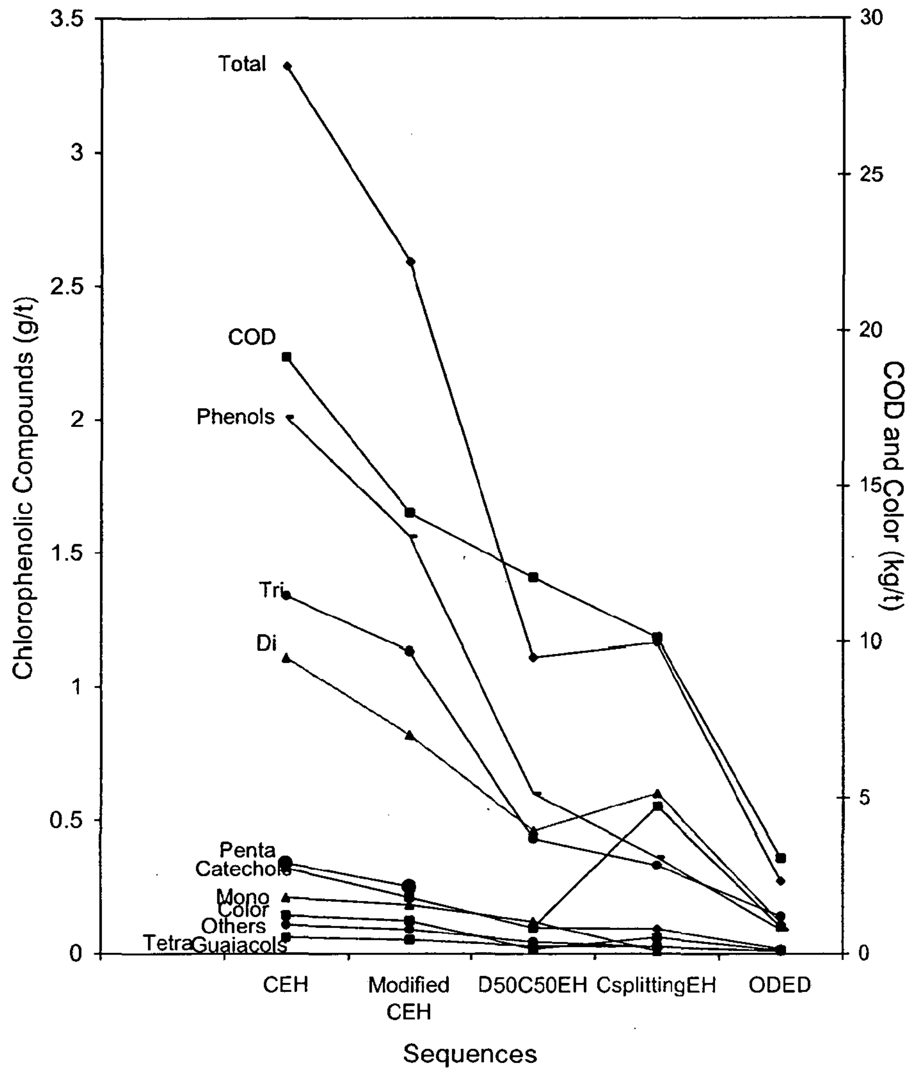


Fig 3.42 **Effect of changed sequences on the generation of chlorophenolics, COD and color in H stage effluent, when target brightness achieved.**

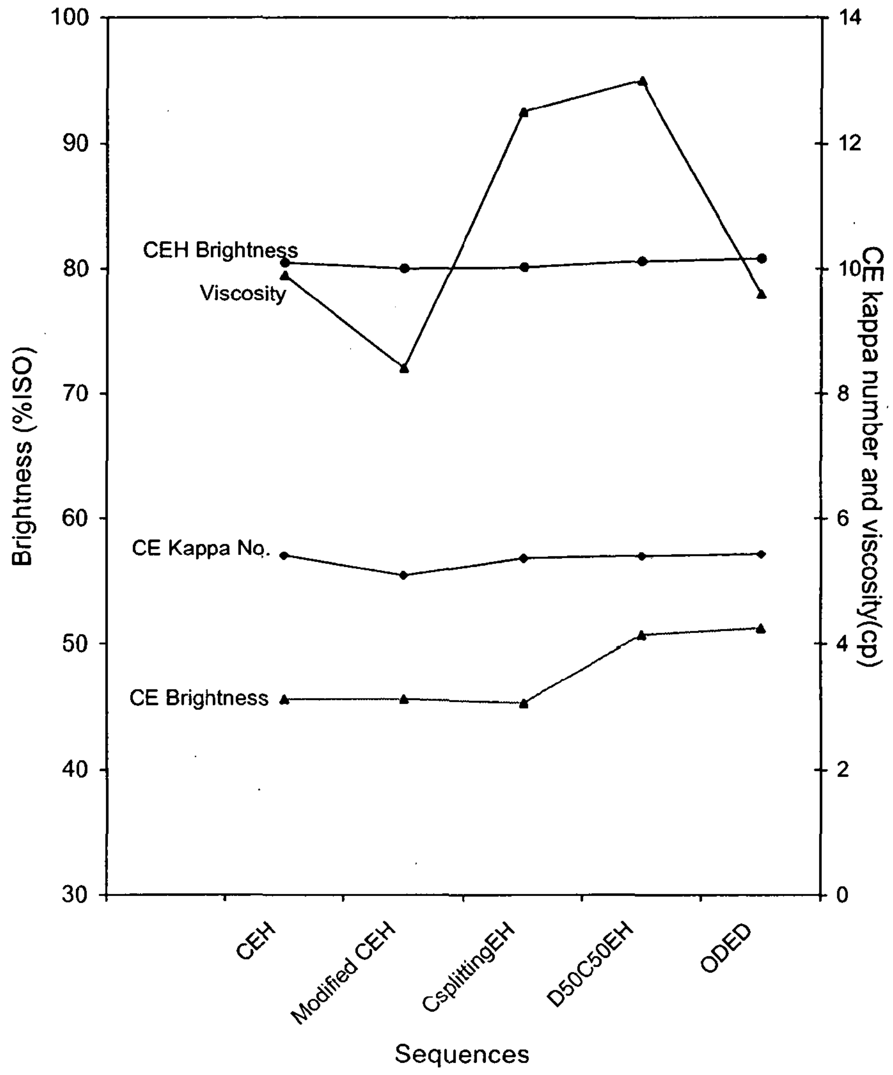


Fig 3.43 **Effect of changed sequences on brightness, viscosity and CE kappa number, when target brightness achieved.**

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Chapter - 4

ESTIMATION OF CHLOROPHENOLS IN EFFLUENT OF JUTE CADY

4.1 INTRODUCTION

Fast depletion of the natural forest in the country has resulted acute shortage of forest based raw materials for the paper and news print industry. Because of the short supply of wood and bamboo, the agricultural residues and nonwoods have gained importance. Jute is one of the promising non-wood raw materials for making international quality pulp and can compete and replace the imported soft-wood pulp [2,21].

Jute is an annual plant widely cultivated in eastern and central part of India. Jute is seasonal agricultural produce of tropical countries. India, Bangladesh, Malaysia, Thailand etc are the principle jute producer countries. India is the world's largest producer of jute and it contributes about 2/5 of the total world jute production. Main jute producing states in India are Assam, Bihar, Orrisa and West Bengal. West Bengal contributes the maximum. At present 8.5 Lac hectares of land is under jute cultivation in India.

Jute plants are classified into two broad groups i.e. Corchorus capsularis and C.Oliterious. Mesta (*Mesta is the trade name of the fibre extracted from plants also referred to as Kenaf*) yielding fibres of commerce similar to jute, constitute the third group. All the three varieties can be considered as one, although it is known that mesta sticks have slightly different pulping characteristics. Jute as a raw material for paper making has a high holocellulose, low lignin and low ash content. Solubility in different solvents is also low, indicating good yield from this material. It's long fibre characteristics with thick walled cells enabled it to manufacture high strength papers. In spite of its long fibre strand, it can be blown from the digestor and the black liquor has all the characteristics for running a chemical recovery system. It would be desirable to have as little of the lower portion as possible, because the lower portion of jute strands contain high ash and high lignin.

The average length of the jute fibre is similar to bamboo, but shorter than soft-wood. Average diameter of jute fibre is less than soft-wood fibre. The individual fibre of jute ranges from < 1mm to > 5mm in length with an average of 2.8mm. Jute has a sizable portion of fibre with length range between 2 to 3mm. Thus it contains higher percentage of fibre with uniform and longer length than bamboo. Jute plant has an advantage that it does not require any pretreatment step. It contains higher holocellulose compared to bamboo. Lignin content in jute is lower than bamboo. Like wood the whole jute contains less silica which is a positive indication for efficient working of chemical recovery unit. The jute fibre is thick walled with narrow lumen. Narrow fibre widths with thick cell wall make the jute fibre stiff compared to soft-wood fibre.

The main user of the jute plant in the country are gunny bag industries, using only the bast portion (25% of the whole plant) for the gunny bags, leaving behind the jute sticks as the waste. Due to then growing demands of the synthetic bags, the gunny bag industry is facing hard time. Lot of efforts are going on for the alternate uses of jute fibres mainly in textile and handicrafts. Jute bast fibre is already used by paper industry for the specially grade paper but in very little quantity. The efforts have been made to utilize whole jute for paper and news print. Pulps showed good bleaching response and could easily be bleached to around 83% ISO brightness by CEH bleaching. A comparison of the pulp with other non woody raw materials i.e. bagasse and bamboo showed much more superior strength properties except higher tear strength in bamboo pulp. A partial replacement of chlorine (20%) with chlorine dioxide, the pulp could be bleached to 88% ISO level. This high brightness can be used as a reinforcing pulp for certain grade of papers to replace bamboo and soft-wood pulp to some extent [2,8,14,15,21,22]. It is observed that agriculture residue has a draw back of strength. But jute cady has long fibres, so it can be used for its higher strength property and it can be mixed with other agriculture residue pulps [14,15,22].

Jute cady is being used as a raw material by small and medium sized paper mills in India, where conventional CEH or CEHH bleaching sequences are still being followed. Since most of these mills are not having chemical recovery, they produce pulp of higher kappa number and subsequently use higher chlorine dosage in bleaching stage to achieve desired brightness levels. Moreover, due to inherent poor drainage properties coupled with poor washing efficiency of the washers, a large amount of dissolved organics are also carried over along with pulp to bleaching process. The low bleaching response of the pulp gives higher consumption of chlorine. This results in generation of high level of color and COD [43].

The chlorination and first extraction stage account for the largest amount of the toxic chlorinated organic compounds in pulp mill bleachery effluent [6,23,32,34, 50,53,56]. Approximately 75 to 80% of the organically bound chlorine in bleach plant effluent is in high molecular weight material, which is not easily identified or even characterized [30,34,38,42]. These high molecular weight chlorinated organic compounds constitute the major contributor to the color and TOCl of the effluent. They accumulate in the receiving streams and over a period of time break down into low molecular mass compounds with detrimental biological effects. Low molecular weight chlorinated organic compounds formed during bleaching of pulp using elemental chlorine is reported to cause acute toxicity and mutagenicity due to their ability to penetrate living cell membrane [7,58]. The use of hypochlorite in bleaching has been reported to the major source of carcinogenic compounds like chloroform and carbon tetrachloride [5,20]. Therefore the chlorinated organic compounds generated in bleach plant effluent are of great environmental concern. Studies on the formation of chlorinated organics/phenols have been reported for softwood and hardwood [7,9], but very little on nonwoods and agro residue pulps which have a different lignin structure [17,28,40,55,56,59]. This work is planned to study the formation of different chlorophenolic compounds formed as a function of C stage bleaching condition and to identify and estimate the different chlorophenolic compounds formed and present in different bleaching effluents viz. C, E, H, D etc.

4.2 RESULT AND DISCUSSION

The Jute Caddy pulp has been bleached to 80% ISO brightness by CEH sequence under normal bleaching conditions (Table 2.2) and the effluent have been analyzed for different chlorophenolic compounds. The results on different chlorophenolic compounds present in C, E and H stage effluents formed under different condition of C stage bleaching and other bleaching modifications in CEH bleaching are given in Tables 4.1, 4.5, 4.9, 4.13, 4.17, 4.21, 4.25 and 4.29. The results on the impact of the modification in CEH sequence on pulp properties viz CE kappa number, CED viscosity and pulp brightness are shown in Tables 4.4, 4.8, 4.12, 4.16, 4.20, 4.24, 4.28 and 4.32 and on the effluent characteristics viz COD and color are given in Tables 4.2, 4.3, 4.6, 4.7, 4.10, 4.11, 4.14, 4.15, 4.18, 4.19, 4.22, 4.23, 4.26, 4.27, 4.31 and 4.32. Results on CEH bleaching also show the presence of these six categories of chlorophenolics in C, E and H stage effluents. Results further show that chlorocatechols, generated in C stage effluent (33.62 g / ton) are about 3 times more than present in E stage effluent (13.86 g / ton), and very little in H stage effluent (2.04 g/ton); chloroguaiacol in E stage effluent (20.44 g / ton) are about 4 times more than in C stage effluent (5.28 g / ton) and little in H stage effluent (2.72 g / ton); chlorophenols (35.28 g / ton) in E stage effluent are more than 3 times in C stage effluent (12.73 g/ton); other compounds, present in E stage effluent (29.98 g /ton) are 6 times more than in C stage effluent (5.51 g / ton) and very little in H stage effluent (1.20 g/ton).

It has also been reported by various authors that in general chlorocatechols are predominantly present in C stage effluent and chloroguaiacol in E stage effluent [9]. Similar results have been observed with bamboo pulp (Chapter - 3) Among the various chlorophenolic compounds 2,4 dichlorophenol, 2,5 dichlorophenol, 3,4 dichlorocatechol, 2,4,6 trichlorophenol, 3,4,5 trichlorocatechol, tetrachlorocatechol, 3 chlorocatechol, 3,4,5 trichloroguaiacol are higher in C stage effluent and 2,4/2,5 dichlorophenol, 2,6 dichlorophenol 2,3,5 trichlorophenol, 2,4,6 / 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 5,6 dichloroguaiacol, pentachlorophenol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin, 5 chlorovanillin, tetrachlorocatechol in E stage effluent.

Microgram levels of pentachlorophenol have also been detected by Guerre et. al for both C and E stage effluent. The quantity of pentachlorophenol decrease significantly with increase in pH of C stage suggesting that pentachlorophenol is also formed during bleaching. The quantity of different chlorophenolic compounds are much less in H stage effluent as compared to C stage effluent. This is due to the fact that 75 – 80% of the lignin gets removed during C and E stages of pulp bleaching. The quantity of chlorophenolic compounds present in E stage effluent is much higher than in C stage effluent which also holds true in the present case also [12,17,18,43,47 60].

The proportion of different categories of chlorophenolics in C, E and H stage effluents are shown in pie graphs. The results show that chlorocatechols and chlorophenols are predominant phenols contributing about 30% each. Similarly di and tri chlorophenolics also contribute about 35% share each, mono, tetra, pentachlorophenolic compounds are ~17%, 9% and 5% respectively of the total chlorophenolic compounds.

The different chlorophenolic compounds are formed during the chlorination step of pulp bleaching i.e. C stage and hence on the condition of C stage so the impact of bleaching conditions particularly C stage has been studied on the formation of chlorinated phenolics. The effect has been studied by changing one operating parameter and maintaining other parameter constant. The different C stage parameters studied are

- pH
- Temperature
- Pulp consistency
- Distribution of chlorine dosage between C and H stages
- Substitution of chlorine in C stage by chlorine dioxide.
- Splitting of chlorine dose in C stage
  - (i) with pulp washing
  - (ii) without pulp washing

The different modifications in CEH bleaching sequence studied are

- Replacement of hypochlorite by chlorine dioxide
- Addition of peroxide in E stage (E_P)
- Oxygen delignification stage prior to CEH sequences
- Oxygen delignification stage prior to DED sequences

The modifications in C stage bleaching conditions or amendments in CEH bleaching gives a pulp of different pulp brightness. Efforts have been made to make bleached pulp of 80% brightness through different bleaching routes with a view to reduce the generation of chlorophenolics.

The different routes investigated are

- D_{50} C_{50} EH
- Splitting of chlorine dose in C stage
- ODED
- By changing the bleaching parameter

The environmental parameters of the bleaching process (COD and Color) and the characteristics of bleached pulp (Brightness and CED viscosity) have also been determined.

Part – A : Effect of C stage bleaching conditions

(1) pH

The results shown in Table 4.1 and Figs. 4.2–4.4 indicate that the quantity of total chlorophenolic compounds formed in CEH sequences decrease with increase in C stage pH from 1.5 – 4. Likewise the quantity of $\sum Cl$, $\sum Cl_2$, $\sum Cl_3$, $\sum Cl_4$, $\sum Cl_5$, $\sum P$, $\sum C$, $\sum G$ and $\sum O$ decrease in C, E and H stage effluent with increase in C stage pH from 1.5 to 4 (Table 4.1, Figs. 4.2–4.4).

The impact of pH on the formation of few chlorophenolic compounds which are formed in higher amount or those who have high toxicity are shown in Table 4.1. The amount of all these compounds decreases with increase in C stage pH. The amount of different categories of chlorophenolics compounds follows the order

Category of compounds	**Order**
$\sum Cl_2$, $\sum Cl_3$, $\sum Cl_5$, $\sum P$, $\sum G$, $\sum O$	E > C > H
$\sum Cl$, $\sum Cl_4$, $\sum C$	C > E > H

The principal chlorinated phenolics observed in E stage effluent are chlorophenols, chloroguaiacols and chlorovanillins.

The amount of 2,4 / 2,5 dichlorophenol, 2,6 dichlorophenol, 2,3,5 / 2,4,6 / 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,5 / 3,4 dichlorocatechol, pentachlorophenol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin, 3 chlorocatechol , 4 chlorocatechol, 3,4,5 trichloroguaiacol tetrachlorocatechol decreases with increase in pH from 1.5 – 4, except 5,6 dichlorovanillin and 3,4,6 trichlorocatechol in H stage effluent. The contribution by different categories of chlorophenolic compounds i.e. mono, di, tri, tetra, pentachlorophenolic compounds and catechols, phenols, guaiacols and other chlorophenolic compounds to total chlorophenolic compounds at pH 1.5 have been given in Fig. 4.1.

There is a decrease in total quantity of chlorophenolic compounds by about 53% as pH increases 1.5 to 4 (Table 4.1, Figs. 4.2-4.4). C, E, H stage effluent contribute about 37%, 58% and 5% respectively at pH 1.5 to the total chlorophenolic compounds and by increasing pH from 1.5 to 4, there is a reduction of 47% in C stage, 58% in E stage, 5% in H stage effluent is observed (Table 4.1, Figs. 4.2–4.4). The amount of mono, di, tri, tetra and penta chlorophenolic compounds is reduced by 46%, 54%, 51%, 61% and 64% respectively (Table 4.1, Figs. 4.2-4.4) and the amount of catechols, phenols, guaiacols, and others chlorophenolic compounds decreases approximately by 50 - 56% (Table 4.1, Figs. 4.2–4.4) as pH increases from 1.5– 4.

The toxicity of effluent depends upon concentration of individual compounds. The $^{96}LC_{50}$ value given in Table 3.1 indicates that the toxicity of pentachlorophenol, catechols, tri, tetrachloroguaiacol and 2,4,6 trichlorophenol are relatively much higher than 2,4 dichlorophenol and dichloroguaiacol. An appreciable reduction in the quantity of di and trichlorophenolic compounds is observed as pH increases from 1.5 to 4 (Table 4.1, Figs. 4.2- 4.4) and consequent reduction in effluent toxicity.

The presence of different categories of chlorophenolic compounds in bleaching effluents have been reported by Folke, Chhaya, Xie and Lu Zi – Jian, the order being C > E >> H [47,60]. A similar behavior has been reported by Voss et al in the CEH bleaching of hard wood and soft wood pulps, showing that the quantity of total chlorophenolic compounds decrease with increase in end pH in C stage ranging from 1 - 2.5, when bleaching is performed at 25°C and 80% of chlorine demand is charged in C stage [54,55].

Chlorinated compounds are formed in chlorination stage of pulp bleaching. Catechols have higher solubility even at lower pH where as guaiacols, phenols and other chlorinated phenolics have low solubility under acidic conditions. These are solublized by alkali treatment performed under E stage. This accounts for higher amount of catechols in C stage and remaining chlorinated phenolics in E stage.

The results further indicate that with the increase in C stage pH from 1.5 to 4, the COD value is reduced by 24% in C stage effluent, 57% in E stage effluent and 19% in H stage effluent (Table 4.2, Figs. 4.2-4.4) and CEH effluent color by 21%. (Table 4.3, Figs. 4.2-4.4).

A small but constant change in CE kappa number and brightness is noticed suggesting that there is a minor change in these values but all these variations are with the experimental variations thus suggesting that there is not much changes in CE kappa number, CE brightness, and CEH brightness as C stage pH is raised from 1.5 to 4. However a significant drop (~13%) in CED viscosity is observed indicating a drop in pulp strength (Table 4.4, Fig. 4.5), which is in agreement with the reported facts that proportion of HOCl, responsible for pulp degradation increases as the chlorination pH is raised. Molecular chlorine forms more chlorinated compounds in comparison to HOCl / OCl$^-$ and chlorine dioxide. As the proportion of molecular chlorine decreases with increase in C stage pH, the formation of chlorinated phenolics is expected to decrease. The results reveal that all categories of chlorinated phenolics are reduced by 53% when pH is raised from 1.5 to 4.

HOCl, OCl$^-$ are stronger oxidizing and bleaching agents than molecular chlorine. With the increased formation of HOCl at higher chlorination pH, lignin is more decolorized and oxidized forming an effluent of lower COD and color. Thus the total chlorophenolic compounds and effluent load is lowest at pH 4, but at this pH the pulp strength is reduced.

(2) Temperature

C stage temperature in the range of 35° – 15°C has been chosen for the study of impact of temperature. The results obtained are shown in Table 4.5.

The result indicates that the total chlorophenolic compounds generated in C, E and H stages effluents decrease with decrease in C stage temperature in the range of 35° - 15° C (Table 4.5, Figs. 4.7-4.9). At a temperature of 35°C, C stage effluent contributes 35%, E stage effluent 59% and H stage effluent 6% to total chlorophenolic compounds. As temperature decreases from 35° to 15°C, the total chlorophenolic compounds decreases by 59% in C stage effluent, 57 % in E stage effluent and 46% in H stage effluent (Table 4.5, Figs. 4.7-4.9).

At temperature of 35°C, the di and trichlorophenolic compounds contribute the largest share to total chlorophenolic compounds. The contribution of different categories of chlorophenolic compounds at temperature 35°C is given in Fig. 4.6. As the temperature decreases from 35° to 15°C, the quantity of mono, di and penta chlorophenolic compound decreases by 55% (Table 4.5, Figs. 4.7- 4.9), tri chlorophenolic compounds by 57% (Figs. 4.7-4.9) and tetrachlorophenolic compounds decrease by 67% (Table 4.5, Figs. 4.7-4.9). Likewise the quantity of catechols, phenols, guaiacols and others chlorophenolic compounds also decreases by ~ 55-58 % (Table 4.5, Figs. 4.7-4.9).

The amount of 2,4 / 2,5 dichlorophenol, 2,4,6 trichlorophenol, 2,3,6 trichlorophenol, 3,6/3,4 dichloroguaiacol, 2,6 dichlorosyringaldehyde, 3–5 dichlorocatechol, pentachlorophenol, 3,4,5 trichlorocatechol, trichlorosyringol, 5,6 dichlorovanillin, tetrachlorocatechol in C, E, H stage effluents also decrease as the temperature decreases from 35° to 15° C.

The quantity of all categories of chlorinated compounds present in C, E, H and combined CEH effluent decreases by 50% or more when chlorination temperature is reduced from 35° to 15° C. Voss et. al also observed that quantity of total chlorophenolic compounds formed during CEH bleaching of softwood and hard wood pulps was much higher at chlorination temperature of 60°C than at 25°C when 50% or 80% chlorine demand was applied in C stage [54,55].

A steady decrease of 24% in COD value is observed when the temperature decrease from 35° to 15° C (Table 4.6, Figs. 4.7-4.9). A similar trend is also observed in the case of color, giving 29% reduction (Table 4.7, Figs. 4.7-4.9). There is also marginal decrease in the pulp brightness nearly by 2.6 points after E stage and nearly 1.8 point after H stage. But the CED pulp viscosity is increased by 13% indicating a decrease in pulp degradation with decrease in C stage bleaching temperature, CE kappa number is found to increase by 4 % showing that the residual lignin increases, as temperature decreases (Table 4.8 and Fig. 4.10).

At higher temperature the proportion of chlorine and hypochlorous acid responsible for pulp degradation is also enhanced. The reactivity of bleaching agent towards both lignin and carbohydrate is enhanced, leading to the increased formation of chlorinated phenolics which results in the increased pulp degradation as shown by the drop in CED pulp viscosity. It is concluded from the results on bleaching at different temperatures that a temperature of 15°C is best suited as it gives stronger bleached pulp with lower environmental loads and lower chlorophenolic compounds, but it is difficult to maintain a temperature of 15°C in Indian mill conditions.

(3) Consistency

Study has been performed at C stage pulp consistency between 2-4% and the results of the study are given in Table 4.9.

The total chlorophenolic compounds present in C, E, H stage effluent increase with increase in C stage consistency (Table 4.9, Figs. 4.12-4.14). At 2% consistency, C stage contributes 33%, E stage 63% and H stage 4% share to total chlorophenolic compound. As consistency increases from 2 – 4%, the quantity of total chlorophenolic compounds increase by 124% in C and E stages and 268% in H stage (Table 4.9, Figs. 4.12-4.14).

At 2% consistency, the contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 4.11. As consistency increases from 2 to 4%, the amount of mono and trichlorophenolic compounds increases by 134% and 131% (Table 4.9, Figs. 4.12-4.14), di, tetra and pentachlorophenolic compounds increases by 135%, 90%, and 145% respectively (Table 4.9, Figs. 4.12-4.14). Similarly the quantities of catechols, phenols, guaiacols and others chlorinated compounds also increase with increase in C stage pulp consistency, the increase being 113%, 137%, 146%, and 126% respectively (Table 4.9, Figs. 4.12-4.14).

The results are in agreement with that of Earl and Douglas Reeve where the chlorophenolic compounds reported were higher at 10% Cy than 4% Cy. The quantity of di and trichlorophenolic compounds increase where as tetrachlorophenolic compounds decrease when the pulp consistency is raised from 4 - 10% [54,55].

The amount of 2,4 dichlorophenol, 2,6 dichlorophenol, 2,3,5 trichlorophenol, 2,3,6 trichlorophenol, 2,4,6 trichlorophenol, 3,4 dichloroguaiacol, 3–5 dichlorocatechol, 3 chlorocatechol,5 chlorovanillin, pentachlorophenol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin, tetrachlorocatechol in C, E, H stage effluents also increases as the consistency is increased.

Increase in C stage pulp consistency increases the total COD by 20% (Table 4.10 and Figs. 4.12-4.14) and total color by 41% (Table 4.11 and Figs. 4.12-4.14).There is about 1 point increase in brightness after E and H stages (Table 4.12 and Fig. 4.15). A CED drop of about 11% and increase of about 5% in CE kappa number is also noticed (Table 4.12 and Fig. 4.15).

The increase in pulp consistency at the same bleach chemical charge gives increased concentration of bleach chemicals and increased reaction rates. This is responsible for increased formation of chlorinated phenolic compounds, increased resolution of lignin and carbohydrate giving effluent of higher COD and color with a small increase in pulp brightness.

(4) Distribution of bleaching chemical between C and H stage

The effect of change in the distribution of chlorine dose between C and H stages has been studied at constant total chlorine dose. The results obtained are given in Table 4.13. The results show that the quantity of total chlorinated phenolic compounds increase by 120% in C stage effluent, 75% in E stage effluent and 46% decrease in H stage effluent as distribution of bleach chemical between C and H stages is varied from 50:50 to 70:30 (Table 4.13, Figs. 4.17-4.19) [54.55].

At ratio of 50:50, C stage effluent contributes 30%, E stage effluent contributes 61% and H stage effluent 9% to total chlorophenolic compounds. At this ratio the contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 4.16.

The results in Figs. 4.17-4.19 show that there is consistent increase in the quantity of mono, di tri tetra and penta chlorophenolic compounds in C and E stage effluent and decrease in H stage effluent as the quantity of chlorine in C stage is increased from 50% to 70%. By varying the proportion of bleach chemical between C and H stages, the quantity of mono, di, tri, tetra and pentachlorophenolic compounds increase by 69%, 44%, 79%, 93%, 68% respectively (Table 4.13, Figs. 4.17-4.19). Similar trend is observed with different categories of chlorophenolic compounds as catechols, phenols, guaiacols, and other chlorophenolic compounds increase by 90%, 84%, 100% and 40% respectively (Table 4.13, Figs. 4.17–4.19).

The results in Figs. 4.17-4.19 show that the amount of different categories of phenolic compounds increases consistently with increase in proportion of chlorine in C stage. The amount of 2,4/2,6 dichlorophenol, 2,6 dichlorosyringaldehyde, 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,5 dichlorosyringol, tetrachlorocatechol, 3,4,5 trichloroguaiacol in C, E and H stage effluents also increase as C:H ratio increases, but 2,4 / 2,5 dichlorophenol, 3 chlorophenol and other chlorophenolic compounds decrease but amount of 4,6 dichloroguaiacol and 3,5 dichlorosyringol increases in the H stage effluent.

The results show that COD of the combined CEH effluent increase by 39% with the increase in proportion of chlorine in C stage (Table 4.14 and Figs. 4.17-4.19). Individually in C stage effluent COD increases by 116%, in E stage effluent increases by 33%, but in H stage effluent decreases by 8% (Table 4.14 and Figs. 4.17-4.19). A similar trend is followed by color values. The total color value of CEH effluent increases by 52% (Table 4.15 and Fig. 4.54). An increase of 47% in C stage, 54 % in E stage and 51% in H stage is observed. There is a small decrease in brightness 1.9 point after E stage and 2.2 point after H stage and viscosity is increased by 8%, CE kappa number is decreased by 6% (Table 4.16 and Fig. 4.20).

The change in proportion from 50:50 to 70:30 means charging more chlorine in C stage and less hypochlorite in H stage. The action of chlorine on lignin in C stage results in the formation of chlorophenolic compounds. The increased proportion of chlorine will form more chlorinated phenolic compounds in C and E stage effluents. Alkali extraction stage involves the dissolution of undissolved portion of chlorinated phenolic compounds formed during C stage pulp bleaching, thus this stage becomes the major contributor to pollution in terms of COD, color and TOCl. Increased quantity of chlorine in C stage gives more hydrophilic lignin, which is fragmented by hypochlorite and results in increased dissolution of lignin and giving effluent of higher COD and color values. The lower quantity of hypochlorite charged in H stage will give lower amount of chlorinated phenolics in H stage effluent.

(5) Substitution of chlorine by chlorine dioxide in C stage

The study has been performed by substituting 25 to 100% of chlorine by chlorine dioxide in C stage. The results obtained are given in Table 4.17 .The results show that the formation of total chlorophenolic compounds decrease substantially (82%) at 100% replacement of chlorine by chlorine dioxide in C stage [2,4,19,31,35,37,39,41,45,48,53]. But some reports indicate that the amount of total chlorinated phenolics formed increases with increase in chlorine dioxide substitution, pass through maxima at 50% substitution and then decreases rapidly to low levels at 100% chlorine dioxide substitution [3,49].

The results in Figs. 4.22-4.24 show that quantity of the total chlorophenolic compounds formed decreases up to 77%. A decrease of 83% in C stage effluent, 74% in E stage effluent and 87% in H stage effluent is observed when chlorine in C stage is completely replaced by ClO_2 (Figs. 4.22-4.24). At $C_{75}D_{25}EH$ sequence, the contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 4.21. The results in Figs. 4.22 – 4.44 show that quantity of all categories of chlorophenolics, COD and color decrease as the substitution of chlorine by chlorine dioxide in C stage is increase from 0 to 100%. The formation of mono, di, tri, tetra, and penta chlorophenolic compounds decrease up to 81%, 73%, 76%, 82%, and 100% at 100% chlorine substitution by chlorine dioxide (Table 4.17, Figs. 4.22-4.24). Likewise the formation of catechols, phenols, guaiacols and other chlorophenolic compounds decrease up to 83%, 76%, 76% and 75% respectively at 100% substitution of chlorine by ClO_2 in C stage (Table 4.17, Figs. 4.22-4.24). The quantity of some mono, di and trichlorophenolic compounds in C stage effluent increases up to 50% replacement and then decrease gradually up to 100% substitution (Table 4.17, Figs. 4.22-4.24).

The amount of 3,4 dichlorocatechol, 3,5 dichlorocatechol, 3 chlorocatechol, 6 chlorovanillin, pentachlorophenol, 3,4,5 trichlorocatechol, tetrachlorocatechol, 2,6 dichlorosyringaldehyde in C and E stage effluent decrease with increase in chlorine dioxide substitution. But the amount of 2,4/ 2,5 dichlorophenol, 2,6 dichlorophenol, 3 chlorophenol, 4 chloroguaiacol, 2 chlorophenol, 2,3,6 trichlorophenol, and 4 chloroguaiacol in C and E stage effluent increase up to 50% substitution and fall rapidly to zero at 100% chlorine dioxide substitution. The amount of tetrachlorocatechol, 5,6 dichlorovanillin, 2,6 dichlorosyringaldehyde, tetrachloroguaiacol, 3,4,5 trichlorocatechol, 3,6 dichlorocatechol, 4,5 dichlorocatechol in C and E stage effluent also decrease with increase in chlorine dioxide substitution.

A 38% reduction in effluent COD (Table 4.18 and Figs. 4.22-4.24) and 62% reduction in color value of CEH effluent (Table 4.19 and Figs. 4.22-4.24) indicate a significant drop in pollution load. Under same conditions the viscosity of pulp is improved by 24% and brightness of pulp is improved by 14.4 point after E stage and 8.7 point after H stage and CE kappa number is reduced by 6% (Table 4.20 and Fig. 4.25) [31,44,53].

Chlorine dioxide is a highly selective bleaching agent as it attacks only lignin. It is also a strong decolorization agent. Increased substitution of chlorine by chlorine dioxide reduces the attack on cellulose that reduces the drop in pulp viscosity very significantly i.e. higher pulp viscosity and lower dissolution of cellulose fragments giving much lower effluent COD and color. The chlorine dioxide can give a pulp of higher brightness and cleanliness without impairing its strength.

High level of ClO_2 has been substituted for chlorine in the traditional first bleaching stage. 40 – 60% substitution has been practiced because this is the normal optimum condition for full delignification. The change to 100% substitution with chlorine dioxide is a response of market pressure. The greatest economic consideration in the use of chlorine dioxide in delignification is the chemical cost. The relatively high cost of bleaching chemicals is basically a function of present of chlorine dioxide and the price ratio of chlorine dioxide and chlorine. This is typical of many studies in which the lowest cost is obtained in the range of 30 – 50% substitution with the cost being relatively insensitive over this range. As 100% substitution is approached, the chemical cost increases sharply.

(6) Splitting of chlorine dose in C stage

(a) Without pulp washing

The chlorine dose in C stage has been divided into two equal parts. Firstly chlorination has been performed with half the dose and then chlorination with the next half dose is performed. No washing of pulp has been done between two chlorine stages. The extraction and hypochlorite stages are performed under same conditions as performed with out chlorine splitting. The results are given in Table 4.21.

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 4.26.The results shown in Figs. 4.27–4.29 indicate that quantity of mono, di, tri, tetra, penta chlorophenolic compounds, phenols, catechols, guaiacols and other chlorinated compound in C, E, H stage effluents, all decrease with the use of split chlorine dose in C stage. Lieber Gott has also reported a decrease in the formation of chlorinated compounds when chlorine dose was split into two portions [24,25].

The results shown in Figs. 4.27–4.29 indicate that splitting of chlorine dose gives 46% lower formation of chlorinated phenolic compounds in CEH stage effluent, 49% reduction in chlorinated phenolic compounds in C stage effluent, 43% reduction in E stage effluent and 62% reduction in H stage effluent [32 - 35].The reduction of 47%, 45%, 45%, 49% and 52% of mono, di, tri, tetra and pentachlorophenolic compounds respectively is observed (Table 4.21, Figs. 4.27–4.29). Similarly the formation of phenol, catechol, guaiacol and other chlorinated compounds is reduced by 45%, 49%, 44% and 46% respectively (Table 4.21, Figs. 4.27–4.29).

A very large decrease in tetrachlorocatechol, 5,6 dichlorovanillin, 2,6 dichlorosyringaldehyde, 3,4,5 trichlorocatechol, 3,4,5 trichloroguaiacol, pentachlorophenol, 5,6 dichloroguaiacol is observed when chlorine dose in C stage is splitted into two equal doses and no washing between chlorination stage has been done. A reduction of 11% in effluent COD (Table 4.22 and Figs. 4.27–4.29) and 19% in effluent color was also observed (Table 4.23 and Figs. 4.27–4.29). The pulp brightness is improved by 0.4 point after E stage and 0.8 point after H stage and appreciable increase in pulp viscosity (12%) is observed (Table 4.24 and Fig. 4.30). So splitting of chlorine dose reduces the pollution load and gives a stronger and brighter pulp. So, pulp can be bleached at lower chlorine doses (lower chlorine multiple) to bleach to the same brightness.

The splitting of chlorine dose means applying lower concentration of chlorine over longer period. The attack on cellulose and hemicellulose is mild giving lower dissolution of carbohydrate fraction and effluent lower COD and color. Mild attack on cellulose gives lower pulp degradation and will yield stronger pulp of higher viscosity.

(b) With pulp washing

As the chlorine dose in C stage has been divided into two equal parts, pulp washing has been done after applying first chlorine dose. The rest half dose is applied on the pulp after first chlorination stage and after completion of second chlorination stage, again washing has been done. Both C_1 and C_2 effluents are collected, mixed and used for further analysis. The results are given in Table 4.21. The results show that the amount of chlorophenolic compounds decrease more when pulp is washed after the first split chlorination stage [24,25].

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Fig. 4.26.The total chlorophenolic compounds decreases by 51%, which is 5% more in comparison to chlorination stage (*Dosage being splitted into two equal parts and no in between washing has taken place*). A reduction of 55% in C stage, 47% in E stage and 67% in H stage effluent in total chlorophenolic compounds is observed (Table 4.21, Figs. 4.27–4.29). The reduction of 52%, 48%, 49%, 57% and 56% in mono, di, tri, tetra, and penta chlorophenolic compounds respectively is also observed (Table 4.21, Figs. 4.27–4.29). A similar trend has also been shown by phenol, catechol, guaiacol and other chlorophenolic compounds, the respective reductions being 48%, 55%, 48% and 50% (Table 4.21, Figs. 4.27–4.29).

The effluent COD is reduced by 15% and color is reduced by 23% (Table 4.22-4.23 and Figs. 4.27–4.29). There is an increase in brightness of 0.8 point after E stage and 1.1 point after H stage, viscosity is improved by 21% and CE kappa Number is reduced by 5% (Table 3.25 and Fig. 4.30).

Washing of pulp after first chlorination stage removes the water soluble fraction of the lignin and other color constituents which consumes a portion of chlorine when fresh chlorine is charged in second split chlorination stage. The lignin and other colored constituents are attacked better, forming a lower CE kappa number and gives some improvement in pulp brightness after E and H stages.

Part – B : The impact of the modifications in CEH bleaching sequences

(1) Replacement of hypochlorite by ClO_2 in H stage

The complete replacement of hypochlorite by chlorine dioxide will change the bleaching sequence from CEH to CED. The results of this replacement are given in Table 4.25.

The results show that there is practically no change in the quantity of various chlorophenolic compounds in combined CEH effluent because main contribution in total chlorophenolic compounds is from C and E stage effluents which remain unchanged (Table 4.25, Figs. 4.33-4.34). The contribution from H stage is minor.

There is a reduction of 4% in total chlorophenolic compound (Table 4.25, Figs. 4.34-36) as there is decrease in the quantity of 2,4 dichlorophenol, 3 chlorophenol, 4 chloroguaiacol, 2,4,6 trichlorophenol, 4,6 dichloroguaiacol, 5,6 dichloroguaiacol, 3,4,5 trichloroguaiacol, tetrachloroguaiacol, and tetrachlorocatechol in H stage effluent. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 4.31-4.32.

Nearly 4% reduction in mono, di, trichlorophenolic compounds, 6-10% in tetra, penta chlorophenolic compounds, phenol, guaiacol and other chlorophenolic compounds and negligible reduction in catechol is observed (Table 4.25, Figs. 4.34-36). In C and E stage effluents the bleaching results and environmental loads remain nearly unchanged. The contribution of H stage effluent to the bleaching sequence in terms of chlorinated phenolic compounds and effluent COD is very small i.e. 4%. The color is reduced by 2%. The replacement of H by D reduces the formation of chlorophenolic compounds, effluent COD and color in D stage but the overall impact remains small because the improvement is small 2-10% (Tables 4.26 – 4.27 and Figs. 4.34-36). The impact of replacement of H by D stage on pulp properties is shown in Fig. 4.36.

Pulp viscosity and brightness is the biggest gain in this replacement. The improvement in pulp viscosity is 37% and in brightness by 2.3 point after H stage (Table 4.28 and Fig. 4.37). Hypochlorite is strongly pulp degrading where as ClO_2 is inert to pulp. So replacement of H by D stage is expected to give a stronger pulp. Chlorine dioxide is also known to give lower PC Number – pulp with lower color reversion tendency.

(2) Addition of peroxide in E stage (E_p)

Reinforced extraction stage with peroxide has been performed i.e. E_p. The results are given in the Table 4.25. The total chlorophenolic compounds decrease appreciably when E stage changes to E_p stage; there is no change in the conditions of chlorination and hypochlorite stage [10].

There is a reduction of 52% in total chlorophenolic compound in the CEH effluent when E stage is changed to E_p. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 4.32-4.33. A reduction of 78% in E stage effluent and 86% in H stage effluent in the amount of chlorophenolic compounds is obtained (Table 4.25, Figs. 4.34-36). Mono, di, tri, tetra chlorophenolic compound also decrease by 34%, 50%, 61%, 31% respectively, pentachlorophenolic compound was not detected in E and H stage effluents (Table 4.25, Figs. 4.34-36). A similar trend is shown by phenols, catechols, guaiacols and other chlorophenolic compounds as they are reduced by 60%, 25%, 63% and 67% respectively (Table 4.25, Figs. 4.34-36).

There is a appreciable reduction in the amount of 2,4 / 2,5 dichlorophenol, 5 chloroguaiacol, 2,3,5-trichlorophenol, 2,3,6 trichlorophenol, 2,4,6 trichlorophenol, 3,4 dichloroguaiacol, 5 chlorovanillin, 5,6 dichloroguaiacol, 3,5 dichlorosyringol, 3,4,5 trichlorocatechol, trichlorosyringol, 2,6 dichlorosyringaldehyde, 5,6 dichlorovanillin, tetrachlorocatechol.

The COD and color values are reduced by 30% and 33% respectively as E stage is changed to E_p stage (Table 4.28 and Figs. 4.34-36). The pulp brightness is improved by 7.8 point after E stage and 1.2 point after H stage, the pulp viscosity is increased by 5% and the CE kappa number is decreased by 13% (Table 4.28 and Fig. 4.37).

Peroxide is an oxidizing and decolouring agent. The chlorophenolic compounds are oxidized and thus reducing the quantity of chlorophenolics in E_p stage effluent. The oxidation reaction results in increased dissolution of lignin fragments giving a lower effluent COD and small reduction in CE kappa number of pulp. The bleaching action of peroxide also slightly improves the brightness of the pulp.

(3) Oxygen delignification stage followed by sequential CEH – (OCEH)

Oxygen delignified pulp was bleached by CEH sequence; the results obtained are given in Table 4.25. Oxygen delignification stage (prebleaching stage) reduced the formation of chlorophenolic compounds by 73% [11,13,16,26,27,29,36,51,52]. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 4.32-4.33. A reduction of total chlorophenolic compounds by 75%in C stage, 72% in E stage effluent and 72% in H stage effluent by oxygen delignification (Table 4.25, Figs. 4.34-36). In case of mono, di, tri, tetra and penta chlorophenolic compounds, a reduction of 71 - 77% is being observed (Figs. 4.34-36). The similar trend is shown by phenols, catechols, guaiacols and others chlorophenolic compounds. These are also reduced by 70 - 74% (Table 4.25, Figs. 4.34-36).

On using Oxygen delignification stage, there is a large reduction in the quantities of 2,4 dichlorophenol, 2,5 dichlorophenol, 2,3,5 / 2,4,6 / 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,4 dichlorocatechol, pentachlorophenol, 3,4,5 trichloroguaiacol, 2,3,5 trichlorophenol, 3,5 dichloroguaiacol, 3,4,6 trichloroguaiacol, trichloroguaiacol, 2,6 dichlorosyringaldehyde and 5,6 dichlorovanillin.

The effluent COD is reduced by 45% and the color value is reduced by 28% (Tables 4.26 and 4.27, Figs. 4.34-36). There is major improvement in brightness by 7.2 points after H stage but viscosity drop by 5% and the CE kappa number is reduced by 20% (Table 4.28, Fig. 4.37).

The process of oxygen delignification is another way to reduce the amount of chlorophenolic compounds. This procedure is used to reduce the pulp kappa number by 40 – 50% which in turn reduces the bleach chemical demand in the following C, E, and H stages to nearly the same extent which reduces the environmental loads – chlorophenolic compounds, COD and color very significantly.

(4) Oxygen delignification stage followed by DED i.e. (ODED)

After oxygen delignification stage, the bleach liquor is replaced by chlorine dioxide in chlorination and hypochlorite stage i.e. ODED. The results are given in Table 4.25.

The result indicates that the total chlorophenolic compounds are reduced by 83% as the sequence changes from CEH to ODED and corresponding reduction in C stage effluent by 92%, in E stage effluent by 72% and in H stage effluent by 78% (Table 4.25, Figs. 4.34-36) [21].

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 4.32-4.33. Mono and tetra chlorophenolic compounds are reduced by 85%. The di and tri chlorophenolic compounds reduced by 81% each (Table 4.25, Figs. 4.34-36) and no pentachlorophenolic compound has been found (Figs. 4.34-36). In case of phenols and catechols, there is a reduction of 84% and 87% respectively; the amount of guaiacols and other chlorophenolic compounds are reduced by 80% in each case (Table 4.25, Figs. 4.34-36).

The quantity of 2,4/2,6 dichlorophenol, 2,3,5 trichlorophenol, 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,4,6 trichloroguaiacol, 5 chlorovanillin, 5,6 dichloroguaiacol, pentachlorophenol, 2,3,4,6 tetrachlorophenol, tetrachlorocatechol, 5,6 dichlorovanillin, trichlorosyringol, 2,6 dichlorosyringaldehyde decrease as CEH changes to ODED.

The COD values and color values are reduced by 51% and 55% (Tables 4.26 and 4.27, Figs. 4.34-36). The CEH brightness is improved by 9.8 points. The viscosity drops by 4% and CE kappa number is reduced by 25% (Table 4.28, Fig. 4.37).

Part – C : 80% brightness pulp by different routes

The results on the studies shown in Part A and Part B indicate that the changes in various C stage bleaching conditions and changes in bleaching sequence can give effluent of lower chlorophenolic compounds but the final brightness is different. In order to make comparative study, a target pulp brightness of 80% ISO was chosen. A few modified bleaching sequences as given below have been tried.

(1) $D_{50}C_{50}EH$

To get the target brightness i.e. 80% the bleach chemical demand has been changed. In sequential bleaching (i.e. CEH), the bleach chemical demand is 13.5%, but when the sequence changed to $D_{50}C_{50}EH$, the bleach chemical demand drops to 10.25%. All the other parameters remain same. The results are given in Table 4.29.

The results show that there is a substantial decrease in the amount of total chlorophenolic compounds i.e. by 44%. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 4.38-4.39. In C, E and H stage effluent there is reduction of total chlorophenolic compounds by 35%, 48% and 62% respectively (Table 4.29, Figs. 4.40-4.42). In mono, di, tri, tetra and penta chlorophenolic compounds, there is a reduction of 44%, 35%, 44%, 64%, 65% respectively (Table 4.29, Figs. 4.40-4.42). A similar trend of reduction has shown by catechols (49%), phenols (32%), guaiacols (46%) and others chlorophenolic compounds (51%) whose concentration are decreased, as bleach chemical demand decrease from 13.5 to 10.25% (Table 4.29, Figs. 4.40-4.42) except some chlorophenolic compounds in C stage effluent.

The results indicate that all individual chlorophenolic compounds decreases, and there is large reduction in the quantity of 2,5 dichlorophenol, 4 chlorophenol, 3,4 dichloroguaiacol, 3,5 dichlorocatechol, 3,4,6 trichloroguaiacol, pentachlorophenol, tetrachlorocatechol, 5,6 dichlorovanillin.

The effluent COD and color reduce by 42% and 54% respectively (Tables 4.30 and 4.31 and Figs. 4.40-4.42). The brightness is increased to 80.6%. There is also a gain of 28% in viscosity. The CE kappa number remains nearly unchanged (Table 4.32, Fig. 4.43).

(2) Splitting of chlorine dose in C stage (without washing)

The other sequence to get the 80% brightness is the splitting of chlorine dose. The bleach chemical demand decreases from 13.5 to 11.35 kg/t. However, there was no change in the conditions in the extraction and hypochlorite stages. The results are shown in Table 4.29.

The results show that there is a reduction of 52% in the amount of total chlorophenolic compounds. The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 4.38-4.39. There is a reduction of 56% in total chlorophenolic compounds in C stage effluent, 48% reduction in E stage effluent and 70% reduction in H stage effluent (Table 4.29, Figs. 4.40-4.42). Amount of all categories of chlorophenolic compounds in C, E and H stage effluent has decreased (Table 4.29, Figs. 4.40 – 4.42). Mono, di, tri, tetra and pentachlorophenolic compounds are reduced by 51 - 57% (Table 4.29, Figs. 4.40-4.42). A similar trend has shown by catechols, phenols, guaiacols and others chlorophenolic compounds the reductions being 49 – 56% (Table 4.29, Figs. 4.40-4.42).

The results shows a large reduction in the quantity of 2,5 dichlorophenol, 4 chloroguaiacol, 3,4 dichlorocatechol, 3,5 dichlorocatechol, 5,6 dichloroguaiacol, tetrachlorocatechol, pentachlorophenol and trichlorosyringol.

The splitting of chlorine dose reduces the pollution load in terms of effluent COD and color values by 23% and 34% respectively (Tables 4.30 and 4.31 and Figs. 4.40-4.42). Along this, a gain of 20% in viscosity is also observed at the target brightness (80%) (Table 4.32, Fig. 4.43).

(3) Oxygen delignification followed by DED (ODED)

In this bleaching, the bleach chemical demand is reduced very sharply from 13.5 – 7.45 kg/t. The results are shown in Table 4.29.

The result shows a very large reduction in the concentration of total chlorophenolic compounds i.e. 87%. In C stage effluent there is a reduction of 93%, 84% in E stage effluent and 88% reduction in H stage effluent of total chlorophenolic compounds (Table 4.29, Figs. 4.40-4.42). The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 4.38-4.39. The quantity of all categories of chlorophenolic compounds in C, E and H stage effluents decrease as sequence DED is changed to ODED. In case of mono, di, tri, and tetrachlorophenolic compounds there is a reduction of 89%, 85%, 85%, 91% respectively (Figs. 4.40-4.42). The concentration of penta chloro phenolic compounds is nil (Table 4.29, Figs. 4.40-4.42). The amount of catechol, phenol, guaiacol, and other chlorophenolic compounds is reduced by 90%, 87%, 84% and 84% respectively (Table 4.29, Figs. 4.40-4.42). This sequence gives a very high reduction in concentration of chlorophenolic compound but the viscosity drops down by 12% (Table 4.32 and Figs. 4.40-4.43).

The result shows a large reduction in the quantity of 2,4 dichlorophenol, 2,5 dichlorophenol, 4 chloroguaiacol, 2,3,6 trichlorophenol, 3,4 dichloroguaiacol, 3,5 dichlorocatechol, 3,4 dichlorocatechol, 5,6 dichloroguaiacol, tetrachlorocatechol, 2,3,4,6 tetrachlorophenol, trichlorosyringol and 5,6 dichlorovanillin. The concentration of pentachlorophenol is observed nil.

The effluent COD and color values are also reduced by 59% and 66% respectively (Tables 4.30 and 4.31, Figs. 4.40-4.42). There is no change in CE kappa number and the brightness remains the target brightness (80%) (Table 4.32, Fig. 4.43).

(4) Modified CEH bleaching

By changing all the C stage bleaching conditions, the target brightness of 80% has also been achieved, the new bleaching condition used are: temperature 30°C, pH 2.5, consistency 2.5 and the bleach chemical demand remain unchanged. The results are shown in the Table 4.29.

The contribution of mono, di, tri, tetra, penta chlorophenolic compounds and catechols, phenols, guaiacols and others chlorinated compounds have been given in Figs. 4.38-4.39. The result shows a reduction of 21% in total chlorophenolic compounds. The similar trend was observed in C, E, and H stage effluent i.e. 25%, 20%, 18% respectively (Table 4.29, Figs. 4.40-4.42). In the case of mono, di, tri, tetra and penta chlorophenolic compound, the result shows a reduction of 22%, 19%, 23%, 22% and 58% respectively (Table 4.29, Figs. 4.40-4.42).

The amount of catechols, phenols, guaiacols, and other chlorophenolic compounds are reduced by 19%, 22%, 22%, and 20% respectively (Table 4.29, Figs. 4.40-4.42). The effluent COD and color value is reduced by 9% and 17% respectively (Tables 4.30 and 4.31, Figs. 4.40-4.42). But the main draw back of this sequence is pulp strength. The viscosity drops down by 21% and the brightness remains the target brightness (80%) (Table 4.32, Fig. 4.43).

Summary of Results

Part – A : (Changes in C stage bleaching conditions)

(a) pH

(1) Increasing pH from 1.5 – 4, gives about 23% drop in effluent COD and 21% drop in effluent color.

(2) The total amount of total chlorophenolic compounds reduce by 53% and the di and tri chlorophenolic compounds decrease by 54% and 51% respectively.

(3) There is not much change in the pulp brightness and CE kappa number, but a drop of 13% is observed in CED viscosity.

(b) Temperature

(1) As the temperature decreases from 35 – 15°C, the total chlorophenolic compounds reduce by 57% and di, tri and tetra chlorophenolic compounds decrease by 55%, 57%, and 67% respectively.

(2) The effluent COD and color reduce by 24% and 29% respectively.

(3) The CEH brightness decrease by 1.8 point, but the pulp viscosity is improved by 13%.

(c) Consistency

(1) Increasing pulp consistency from 2 to 4%, the COD and effluent color value increase by 20% and 41% respectively.

(2) Only 1 point increment in brightness is observed after H stage.

(3) CE kappa number increase by 5%.

(4) 11% drop in pulp viscosity is an indication of increased pulp degradation.

(5) Chlorophenolic compounds increase by 172%.

(d) Distribution of bleaching chemical between C and H stage

(1) On changing the proportion of chlorine from 50:50 to 70:30, the total

chlorophenolic compounds increase by 77%. And an increase of 120% in C stage and 75% in E stage, but 46% reduction in H stage effluent.

(2) COD and color of combined CEH effluent increase by 39% and 52%.
(3) Brightness decrease by 2.2 point.
(4) CE kappa number decrease by 6%.
(5) Pulp viscosity improves by 8%.

(e) Chlorine dioxide substitution

(1) Total chlorophenolic compounds reduce by 77% when chlorine is substituted by chlorine dioxide from 0 to 100%.
(2) COD and color reduced by 38% and 62%.
(3) Gain of 24% in viscosity is an indication of protective action of chlorine dioxide.
(4) Brightness improves by 8.7 points.

(f) Splitting of chlorine dose

- ***Without pulp washing***
  (1) 46% reduction in the chlorophenolic compounds.
  (2) 11% and 19% reduction in effluent COD and color.
  (3) 12% improvement in CED pulp viscosity.
  (4) A minor improvement of 0.8 point in brightness.
- ***With pulp washing***
  (1) 51% reduction in the chlorophenolic compounds.
  (2) 15% and 23% reduction in effluent COD and color.
  (3) 21% improvement in CED pulp viscosity.
  (4) A minor improvement of 1.1 point in brightness.

Part – B : (Change in the bleaching sequences)

(a) Replacement of hypochlorite by chlorine dioxide

(1) Small reduction (4%) in chlorophenolic compounds.
(2) Small reduction (2 – 4%) in effluent color and COD.
(3) A very significant improvement in pulp viscosity (37%).
(4) A minor improvement (2.3 point) in pulp brightness.

(b) Addition of peroxide in E stage

1. 52% reduction in chlorophenolic compounds.
2. Effluent COD and color reduce by 30% and 33% respectively.
3. Pulp viscosity improves by 5%.
4. Pulp brightness increases by 1.2 point.

(c) Oxygen delignification followed by CEH (OCEH)

1. 73% reduction in chlorophenolic compounds.
2. 45% reduction in COD and 28% reduction in color.
3. Viscosity drops by 5%.
4. 7.2 point improvement in brightness.

(d) Oxygen delignification followed by DED (ODED)

1. Chlorophenolic compounds reduce by 83%.
2. Effluent COD and color reduce by 51% and 55%.
3. Pulp brightness improves by 9.8 point.
4. Viscosity drops by 4%.

Part – C : (80% target brightness by different routes)

(a) $D_{50}C_{50}EH$

1. 44% reduction in chlorophenolic compounds.
2. Effluent COD and color reduce by 42% and 54%.
3. Gain of 28% in pulp viscosity.
4. 80.6% brightness achieved

(b) Splitting of chlorine dose in C stage (Without pulp washing)

1. Chlorophenolic compounds reduce by 52%.
2. 23% and 34% reduction in effluent COD and color.
3. 20% improvement in pulp viscosity

(c) Oxygen delignification followed by DED (ODED)

1. Reduction of 87% in chlorophenolic compounds.
2. Effluent COD and color reduce by 59% and 66%.
3. Viscosity drops by 12%.

(d) Modified CEH bleaching

1. 21% reduction in chlorophenolic compounds.
2. 9 – 17% reduction in effluent COD and color values.
3. Pulp viscosity drop by 21%.

Table 4.1 Effect of C stage pH on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at pH values of														
	1.5			2.0			2.5			3.0			4.0		
	C	E	H	C	E	H	C	E	H	C	E	H	C	E	H
2,4-Dichlorophenol	3.15	5.03	1.61	2.94	4.24	1.53	2.78	3.04	1.23	2.34	2.83	1.06	2.01	2.04	1.01
2,5-Dichlorophenol	1.23	1.78	-	1.04	1.19	-	0.92	1.02	-	0.89	0.95	-	0.63	0.86	-
2,3-Dichlorophenol	0.38	-	-	0.22	-	-	0.10	-	-	0.09	-	-	-	-	-
3-Chloroguaiacol	-	0.46	-	-	0.37	-	-	0.32	-	-	0.21	-	-	0.19	-
2,6-Dichlorophenol	0.36	4.17	-	0.32	3.92	-	0.29	2.15	-	0.25	1.76	-	0.17	1.32	-
4-Chlorophenol	0.72	-	-	0.64	-	-	0.51	-	-	0.49	-	-	0.32	-	-
3-Chlorophenol	0.93	2.19	0.32	0.78	2.16	0.28	0.59	1.98	0.26	0.57	1.64	0.21	0.53	1.58	0.13
4-Chloroguaiacol	0.09	-	0.38	0.06	-	0.34	0.03	-	0.28	0.03	-	0.25	0.01	-	0.25
5-Chloroguaiacol	-	1.84	0.21	-	1.78	0.18	-	1.24	0.10	-	1.03	0.09	-	0.86	0.08
6-Chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Chlorophenol	0.35	-	-	0.26	-	-	0.20	-	-	0.18	-	-	0.15	-	-
2,3,5-Trichlorophenol	0.21	3.92	-	0.18	3.73	-	0.14	3.06	-	0.12	2.32	-	0.10	1.96	-
2,4,6-Trichlorophenol	2.94	5.28	0.83	2.79	4.94	0.76	2.68	3.32	0.64	2.34	2.46	0.53	1.95	2.08	0.43
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5-Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6-Trichlorophenol	1.09	7.18	-	0.96	6.91	-	0.94	4.32	-	0.86	4.15	-	0.85	3.73	-
3,6-Dichloroguaiacol	0.23	-	-	0.11	-	-	0.08	-	-	0.06	-	-	0.05	-	-
3,4-Dichloroguaiacol	0.51	5.94	-	0.33	5.37	-	0.29	4.78	-	0.25	3.27	-	0.23	2.14	-
3,4-Dichlorocatechol	4.86	2.78	-	4.65	2.34	-	3.45	2.23	-	3.17	1.86	-	2.99	1.53	-
3,4-Dicholorophenol	1.12	-	-	0.99	-	-	0.83	-	-	0.79	-	-	0.68	-	-
4,5-Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6-Dichloroguaiacol	-	-	-	-	0.45	0.14	-	0.44	0.08	-	0.41	0.01	-	0.38	0.11
5-Chlorovanillin	2.35	3..89	-	2.14	3.66	-	1.95	3.53	-	1.80	2.29	-	1.67	2.20	-
5,6-Dichloroguaiacol	-	3.34	0.32	-	3.18	0.27	-	3.02	0.20	-	2.15	0.13	-	-	-

4-Chlorocatechol	3.93	-	-	3.72	-	-	2.94	-	-	2.86	-	-	2.24	-	-
3,5-Dichlorocatechol	6.56	2.38	-	6.15	2.10	-	5.73	1.97	-	5.18	1.34	-	4.32	1.03	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	1.21	0.88	-	0.92	0.68	-	0.80	0.65	-	0.63	0.48	-	0.51	0.40	-
3,5,6-Trichloroguaiacol	-	0.52	-	-	0.50	-	-	0.43	-	-	0.41	-	-	0.32	-
3,4,6-Trichloroguaiacol	-	2.47	-	-	2.27	-	-	2.16	-	-	2.05	-	-	1.96	-
3,5-Dichlorosyringol	-	1.65	0.40	-	1.60	0.35	-	1.42	0.29	-	1.13	0.16	-	1.09	0.13
3,4,5-Trichloroguaiacol	3.64	3.78	1.01	2.41	3.34	0.96	2.18	3.21	0.66	2.20	2.78	0.42	2.25	1.54	0.40
3-Chlorocatechol	5.92	-	-	4.78	-	-	4.31	-	-	4.15	-	-	3.93	-	-
6-Chlorovanillin	0.98	2.18	-	0.68	2.01	-	0.63	1.85	-	0.58	1.34	-	0.47	1.01	-
3,6-Dichlorocatechol	1.03	0.71	-	0.94	0.62	-	0.62	0.51	-	0.61	0.50	-	0.59	0.38	-
4,5,6-Trichloroguaiacol	0.86	0.52	-	0.62	0.48	-	0.46	0.45	-	0.45	0.40	-	0.48	0.25	-
2-Chlorosyringaldehyde	2.27	2.76	0.67	1.19	2.18	0.48	0.97	2.03	0.21	0.86	1.93	0.19	0.60	1.12	0.16
4,5-Dichlorocatechol	0.89	-	-	0.85	-	-	0.55	-	-	0.54	-	-	0.32	-	-
Pentachlorophenol	0.71	8.03	0.84	0.69	7.51	0.66	0.44	6.18	0.54	0.23	4.86	0.40	0.19	3.02	0.26
3,4,5-Trichlorocatechol	8.25	6.94	-	7.18	6.10	-	6.98	5.27	-	5.19	3.78	-	3.03	2.77	-
Tetrachloroguaiacol	1.94	2.85	0.91	1.75	2.70	0.83	1.56	2.34	0.63	1.42	1.23	0.56	1.21	0.88	0.43
Trichlorosyringol	0.58	8.90	-	0.50	8.89	-	0.48	7.25	-	0.43	5.56	-	0.32	4.14	-
3,4,6-Trichlorocatechol	1.65	-	0.90	1.03	-	0.92	0.93	-	0.94	0.90	-	0.95	0.85	-	0.96
2,6-Dichlorosyringaldehyde	0.39	7.32	-	0.29	7.18	-	0.26	6.93	-	0.24	4.84	-	0.21	3.56	-
5,6-Dichlorovanillin	0.98	4.81	0.33	0.71	4.46	0.37	0.69	3.16	0.38	0.60	2.01	0.39	0.44	1.11	0.38
Tetrachlorocatechol	5.56	2.77	1.24	4.32	2.70	1.12	3.91	2.54	0.76	3.13	1.13	0.53	1.93	0.93	0.40
Total	**67.87**	**103.38**	**9.97**	**57.14**	**99.56**	**9.19**	**50.22**	**82.8**	**7.20**	**44.43**	**63.1**	**5.88**	**36.23**	**46.38**	**5.13**

C stage bleaching conditions: Temperature 30°C, Consistency 3%.

Table 4.2 Effect of C stage pH on COD generation

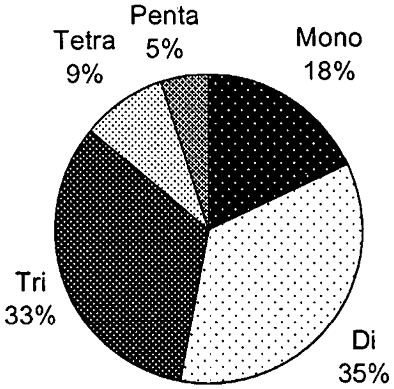
Stage/pH	COD (kg/t) at different pH values of				
	1.5	2.0	2.5	3.0	4.0
C	33.9	31.3	29.5	27.6	26.1
E	81.0	76.5	72.8	68.4	63.9
H	26.7	24.6	22.1	21.9	19.3
Total	**141.6**	**132.4**	**124.4**	**117.9**	**109.3**

Table4.3 Effect of C stage pH on color generation

Stage/pH	Color (kg/t) at different pH values of				
	1.5	2.0	2.5	3.0	4.0
C	44.7	43.8	40.6	38.9	36.4
E	87.6	83.9	77.7	73.7	68.5
H	2.8	2.4	1.9	1.4	1.2
Total	**135.1**	**130.1**	**120.2**	**114.0**	**106.1**

Table 4.4 Effect of C stage pH on CE kappa no, brightness and CED viscosity

Parameter/pH	Different parameter at different pH values of				
	1.5	2.0	2.5	3.0	4.0
CE Kappa no.	5.9	6.1	6.0	6.1	6.2
CE Brightness(%ISO)	48.5	48.1	47.6	47.2	46.8
CEH Brightness(%ISO)	80.6	79.8	79.3	79.0	78.6
Viscosity(cp)	15.9	15.6	15.0	14.5	13.9



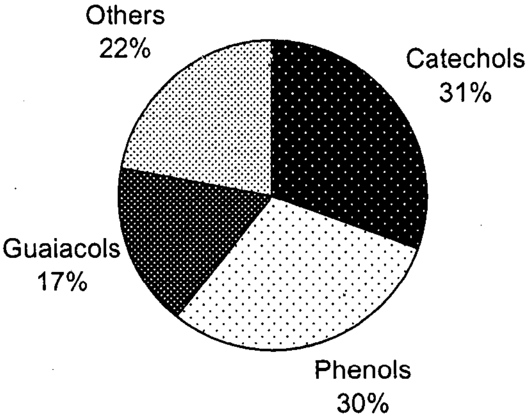


Fig. 4.1 The contribution of different chlorophenolic compounds at pH 1.5

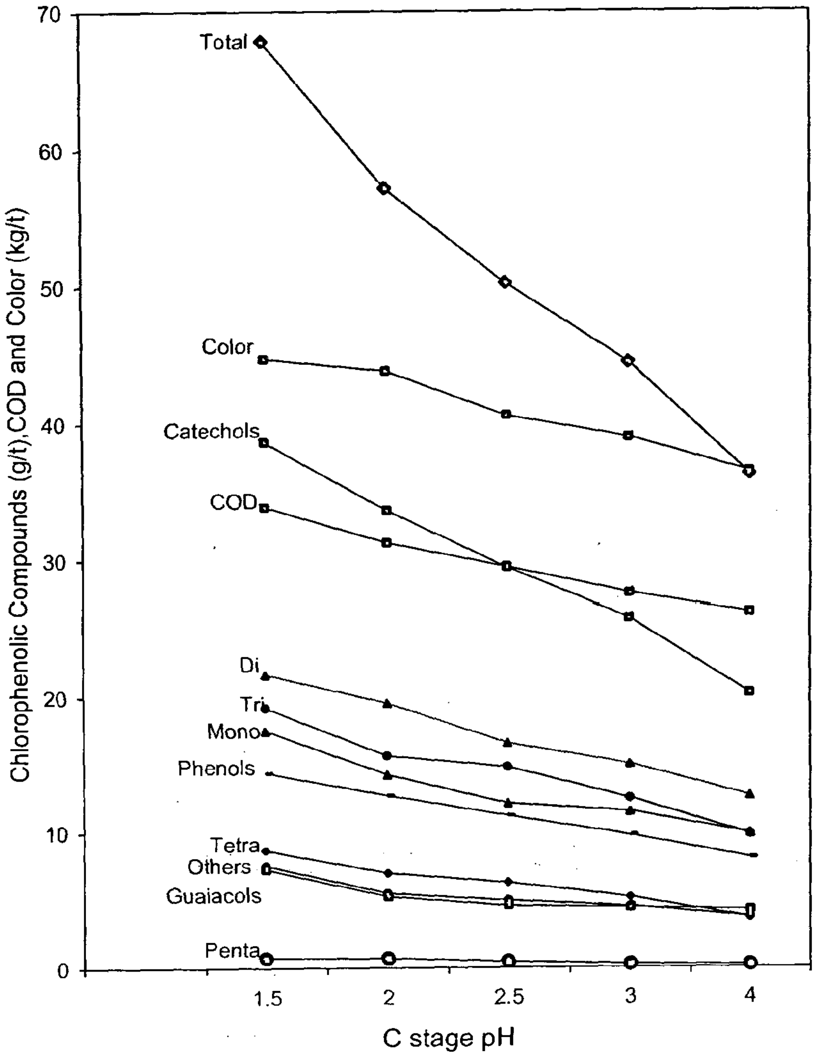


Fig 4.2 **Effect of C stage pH on the generation of chlorophenolics, COD and color in C stage effluent.**

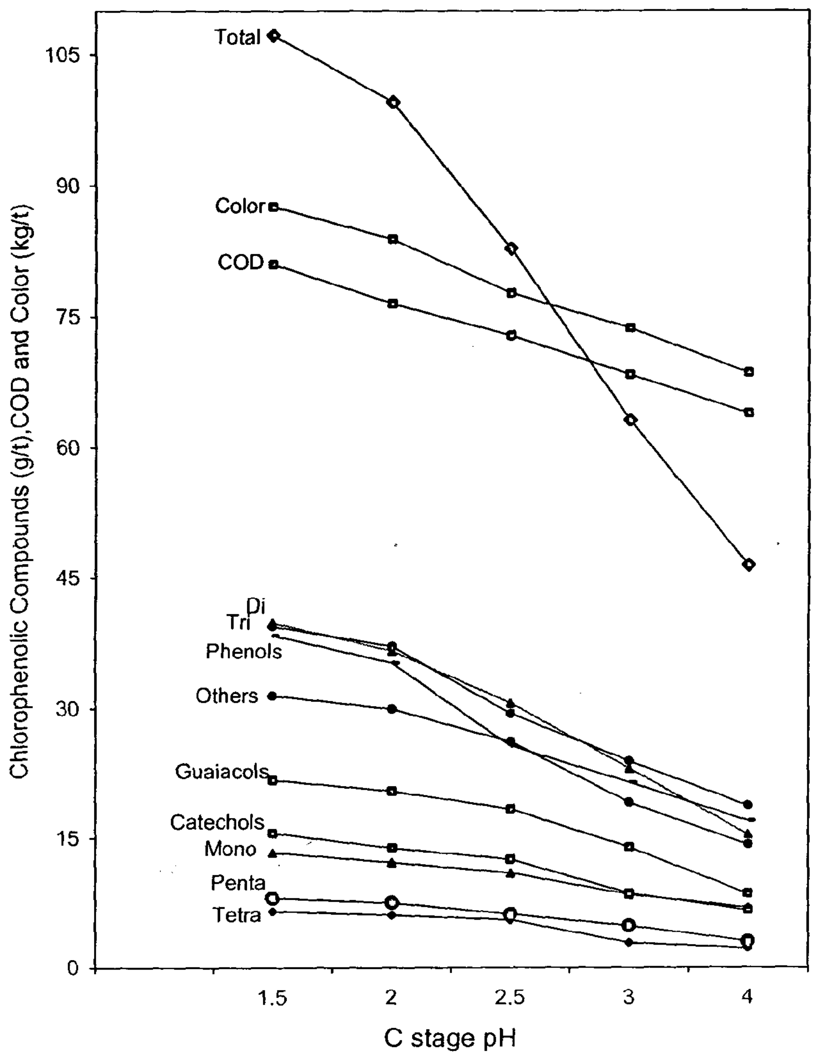


Fig 4.3 **Effect of C stage pH on the generation of chlorophenolics, COD and color in E stage effluent.**

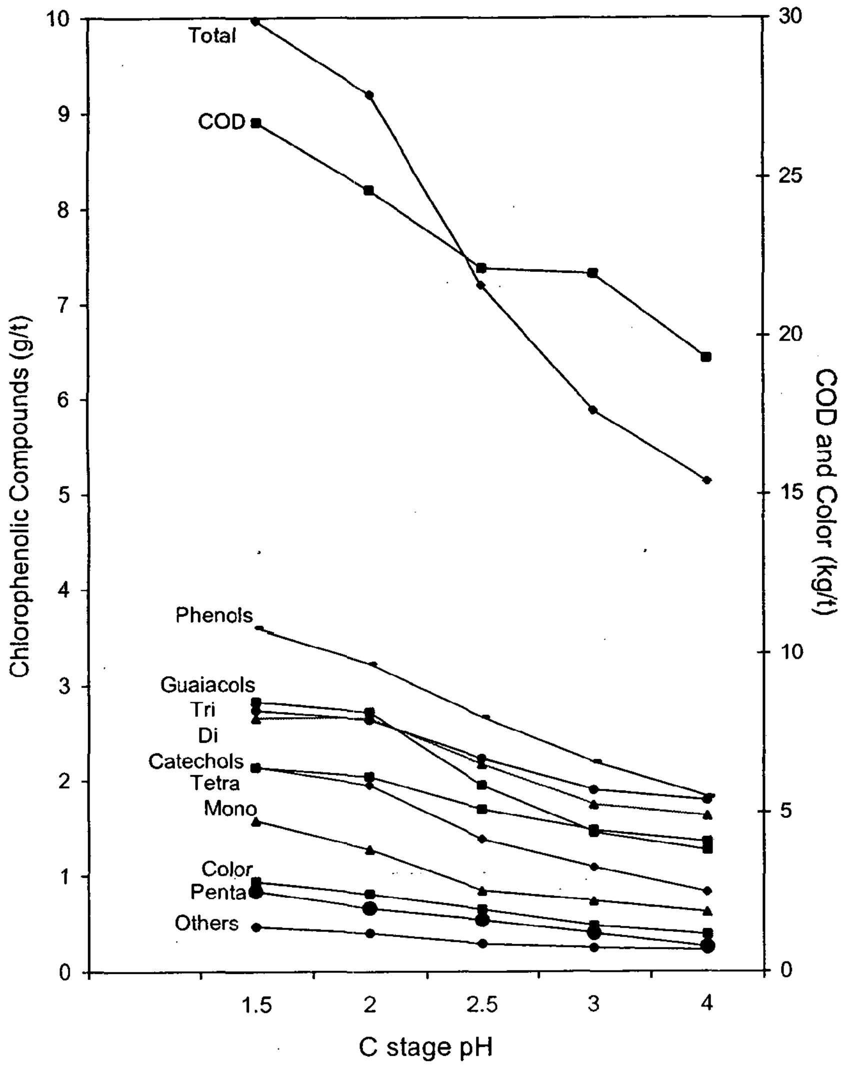


Fig 4.4 Effect of C stage pH on the generation of chlorophenolics, COD and color in H stage effluent.

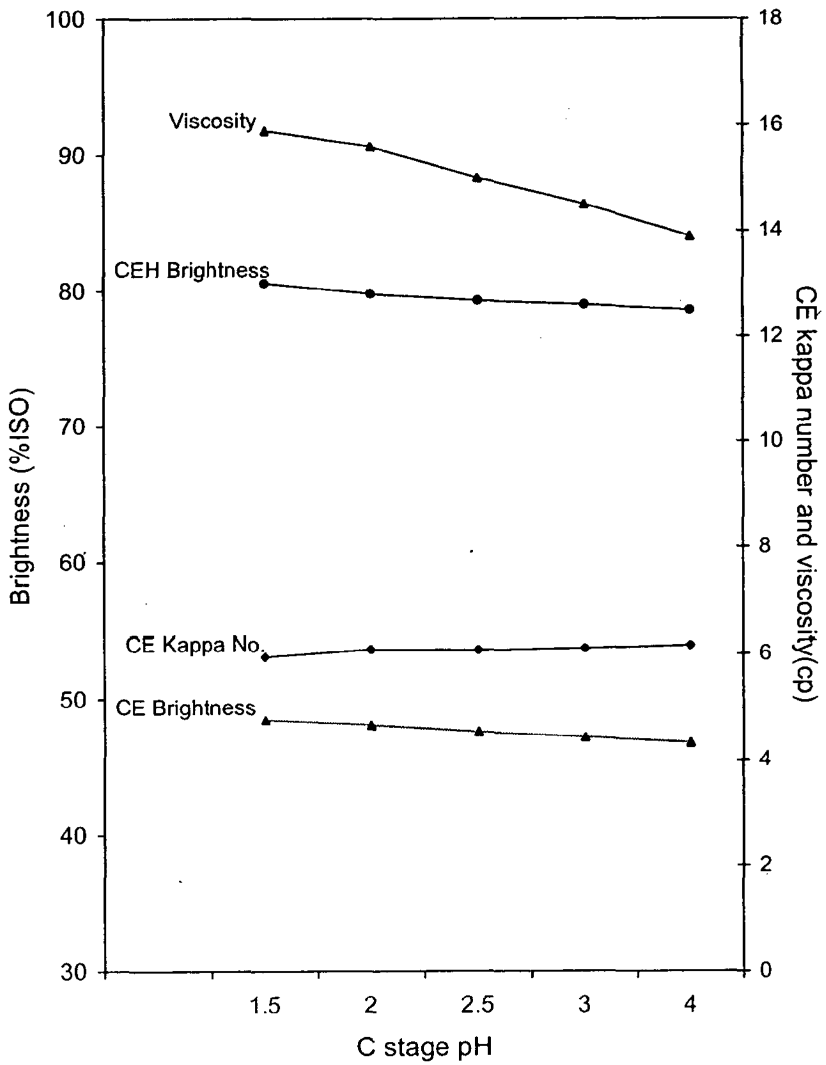


Fig 4.5 Effect of C stage pH on brightness, viscosity and CE kappa number.

Table 4.5 Effect of temperature in C stage on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at temperature														
	35° C			30° C			25° C			20° C			15° C		
	C	E	H	C	E	H	C	E	H	C	E	H	C	E	H
2,4 Dichlorophenol	3.09	4.36	1.64	2.94	4.24	1.53	2.32	3.86	1.50	1.74	3.34	1.31	1.06	2.21	1.29
2,5 Dichlorophenol	1.21	1.38	-	1.04	1.19	-	0.95	1.04	-	0.21	0.99	-	0.19	0.92	-
2,3- Dichlorophenol	0.37	-	-	0.22	-	-	0.16	-	-	-	-	-	-	-	-
3-chloroguaiacol	-	0.46	-	-	0.37	-	-	0.35	-	-	0.34	-	-	0.30	-
2,6 Dichlorophenol	0.41	4.15	-	0.32	3.92	-	0.27	2.96	-	0.19	2.69	-	0.17	1.58	-
4-chlorophenol	0.73	-	-	0.64	-	-	0.60	-	-	0.45	-	-	0.41	-	-
3-chlorophenol	0.84	2.94	0.27	0.78	2.16	0.28	0.72	1.97	0.25	0.64	1.88	0.18	0.63	0.76	0.15
4-chloroguaiacol	0.11	-	0.45	0.06	-	0.34	0.06	-	0.32	0.05	-	0.28	-	-	-
5-chloroguaiacol	-	2.07	0.22	-	1.78	0.18	-	1.39	0.16	-	1.28	0.10	-	0.95	0.08
6-chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-chlorophenol	0.32	-	-	0.26	-	-	0.19	-	-	0.15	-	-	0.14	-	-
2,3,5-Trichlorophenol	0.25	3.92	-	0.18	3.73	-	0.15	3.01	-	0.11	2.97	-	0.10	1.66	-
2,4,6-Trichlorophenol	2.88	5.41	0.86	2.79	4.94	0.76	2.34	4.15	0.73	2.01	4.11	0.56	0.36	2.94	0.52
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	--	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	1.01	7.16	-	0.96	6.91	-	0.85	5.92	-	0.78	5.66	-	0.63	2.98	-
3,6 Dichloroguaiacol	0.15	-	-	0.11	-	-	0.08	-	-	0.08	0.02	-	0.06	-	-
3,4 Dichloroguaiacol	0.46	5.99	-	0.33	5.37	-	0.27	4.86	-	0.23	4.35	-	0.21	2.29	-
3,4-Dichlorocatechol	4.87	3.04	-	4.65	2.34	-	3.96	2.11	-	3.02	2.02	-	1.95	1.95	-
3,4-Dicholorophenol	1.02	-	-	0.99	-	-	0.92	-	-	0.85	-	-	0.80	-	-
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.40	0.19	-	0.45	0.14	-	0.46	0.14	-	0.44	0.11	-	0.41	0.10
5-Chlorovanillin	2.34	3.68	-	2.14	3.66	-	1.73	2.99	-	1.66	2.73	-	1.01	1.67	-
5,6 Dichloroguaiacol	0.21	3.35	0.33	-	3.18	0.27	-	3.02	0.22	-	2.95	0.19	-	1.83	0.17

4-Chlorocatechol	3.93	-	-	3.72	-	-	3.29	-	-	2.98	-	-	1.84	-	-
3,5-Dichlorocatechol	6.61	2.42	-	6.15	2.10	-	5.58	1.87	-	4.79	1.67	-	2.36	0.64	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	1.01	0.92	-	0.92	0.68	-	0.86	0.64	-	0.67	0.61	-	0.32	0.58	-
3,5,6-Trichloroguaiacol	-	0.64	-	-	0.50	-	-	0.43	-	-	0.40	-	-	0.36	-
3,4,6-Trichloroguaiacol	-	2.36	-	-	2.27	-	-	2.15	-	-	2.05	-	-	1.97	-
3,5-Dichlorosyringol	-	1.83	0.48	-	1.60	0.35	-	1.37	0.30	-	1.28	0.28	-	1.25	0.25
3,4,5-Trichloroguaiacol	2.78	3.95	1.01	2.41	3.34	0.96	1.82	3.30	0.89	1.15	3.01	0.64	1.10	1.82	0.62
3-Chlorocatechol	5.26	-	-	4.78	-	-	3.47	-	-	3.06	-	-	2.89	-	-
6-Chlorovanillin	0.93	2.68	-	0.68	2.01	-	0.58	1.65	-	0.55	1.58	-	0.53	0.96	-
3,6-Dichlorocatechol	1.16	0.77	-	0.94	0.62	-	0.62	0.58	-	0.46	0.56	-	0.42	0.53	-
4,5,6-Trichloroguaiacol	1.00	0.93	-	0.62	0.48	-	0.49	0.46	-	0.39	0.43	-	0.36	0.41	-
2-Chlorosyringaldehyde	1.35	2.45	0.49	1.19	2.18	0.48	0.96	1.82	0.23	0.83	1.16	0.19	0.79	1.07	0.11
4,5-Dichlorocatechol	0.99	-	-	0.85	-	-	0.83	-	-	0.78	-	-	0.76	-	-
Pentachlorophenol	0.70	7.55	0.69	0.69	7.51	0.66	0.54	6.57	0.31	0.21	6.35	0.25	0.10	3.76	0.20
3,4,5-Trichlorocatechol	7.78	6.74	-	7.18	6.10	-	6.17	5.86	-	5.94	5.06	-	3.32	2.24	-
Tetrachloroguaiacol	2.11	2.86	0.92	1.75	2.70	0.83	0.78	2.14	0.78	0.65	1.97	0.69	0.31	0.89	0.65
Trichlorosyringol	0.95	9.52	-	0.50	8.89	-	0.45	7.93	-	0.43	6.79	-	0.40	3.45	-
3,4,6-Trichlorocatechol	1.60	-	0.98	1.03	-	0.92	0.89	-	0.85	0.88	-	0.77	0.83	-	0.63
2,6-Dichlorosyringaldehyde	0.34	7.83	-	0.29	7.18	-	0.23	6.56	-	0.19	6.05	-	0.17	2.97	-
5,6-Dichlorovanillin	0.93	5.13	0.42	0.71	4.46	0.37	0.66	3.82	0.29	0.58	3.03	0.13	0.54	1.98	0.11
Tetrachlorocatechol	4.92	2.81		4.32	2.70	1.12	3.13	1.77	1.01	2.99	1.06	0.86	1.87	0.25	0.60
Total	**64.62**	**109.7**	**8.95**	**57.14**	**99.56**	**9.19**	**46.92**	**87.01**	**7.98**	**39.7**	**78.83**	**6.54**	**26.63**	**47.58**	**5.80**

C Stage bleaching conditions: $C_{end\ pH} \geq 2$ and Consistency 3%.

Table 4.6 Effect of C stage temperature on COD generation

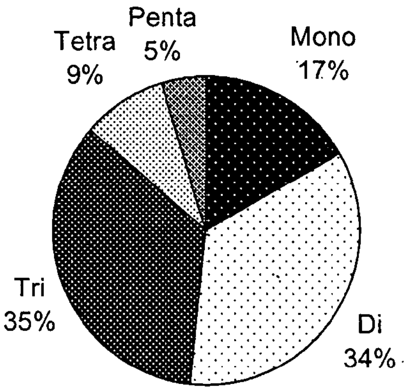
Stage/temperature	COD (kg/t) at different temperature				
	35°C	30°C	25°C	20°C	15°C
C	32.4	31.3	30.5	29.1	22.5
E	78.6	76.5	67.9	65.5	61.4
H	25.1	24.6	23.4	22.0	20.2
Total	**136.1**	**132.4**	**121.8**	**116.6**	**104.1**

Table 4.7 Effect of C stage temperature on color generation

Stage/temperature	Color (kg/t) at different temperature				
	35°C	30°C	25°C	20°C	15°C
C	47.1	43.8	35.3	32.6	27.5
E	86.8	83.9	79.8	73.6	68.3
H	2.9	2.4	2.1	1.9	1.4
Total	**136.8**	**130.1**	**117.2**	**108.1**	**97.2**

Table 4.8 Effect of C stage temperature on CE kappa no, brightness and CED viscosity

Parameter/temperature	Different parameter at different temperature				
	35°C	30°C	25°C	20°C	15°C
CE Kappa No	5.9	6.0	6.1	6.0	6.2
CE Brightness(%ISO)	48.6	48.1	47.7	47.2	46.8
CEH Brightness(%ISO)	80.7	79.8	79.2	78.9	78.1
Viscosity(cp)	**14.8**	**15.6**	**15.9**	**16.4**	**19.9**



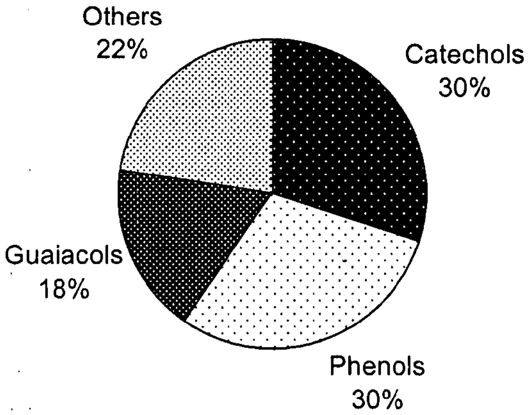


Fig. 4.6 **The contribution of different chlorophenolic compounds at 35°C temperature**

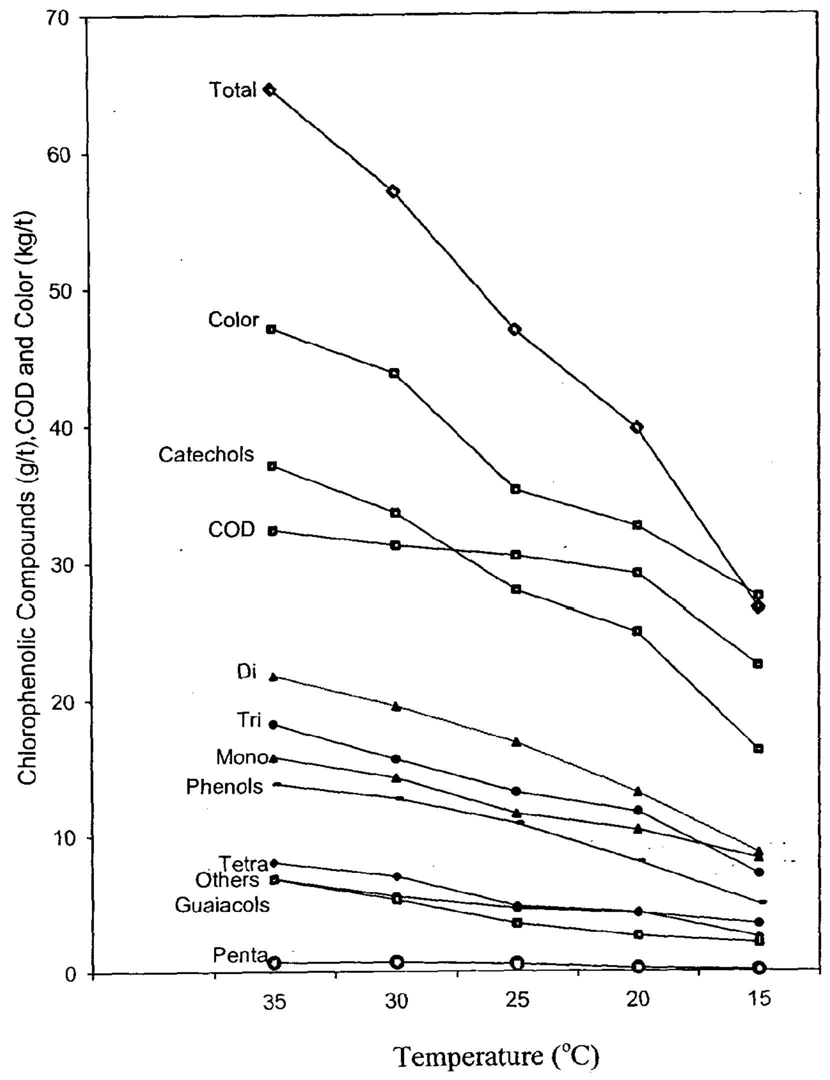


Fig 4.7 **Effect of C stage temperature on the generation of chlorophenolics, COD and color in C stage effluent.**

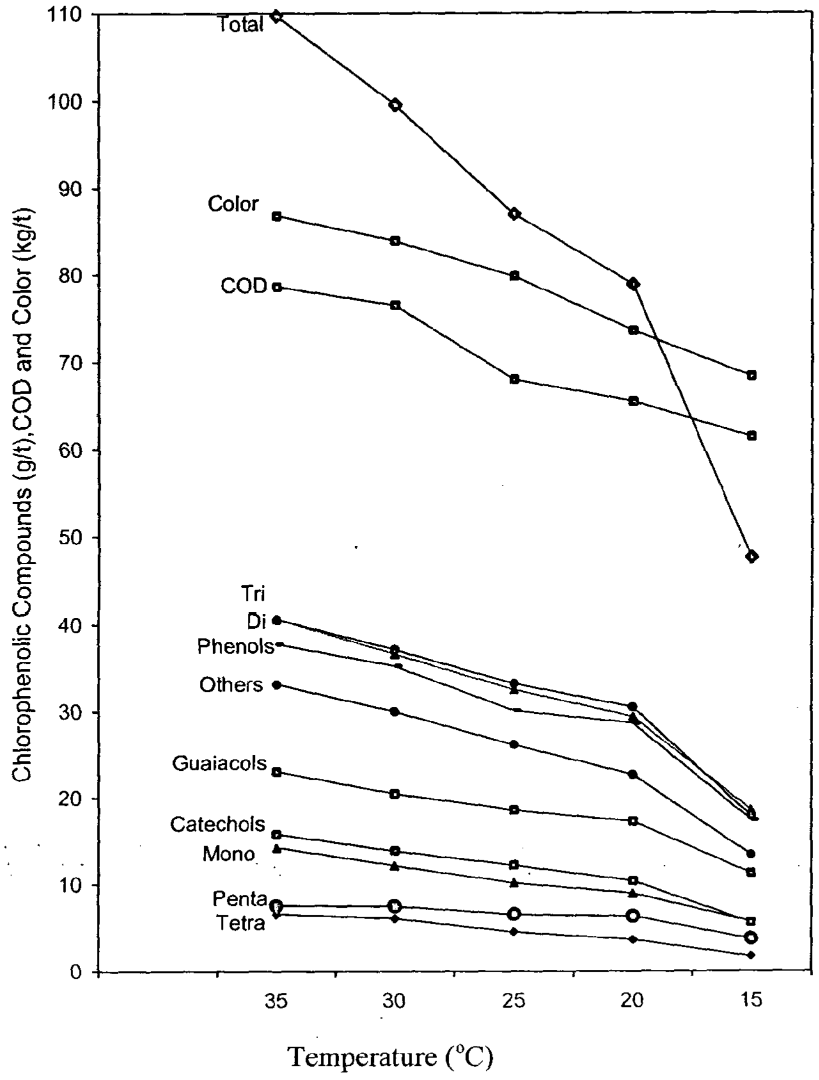


Fig 4.8 **Effect of C stage temperature on the generation of chlorophenolics, COD and color in E stage effluent.**

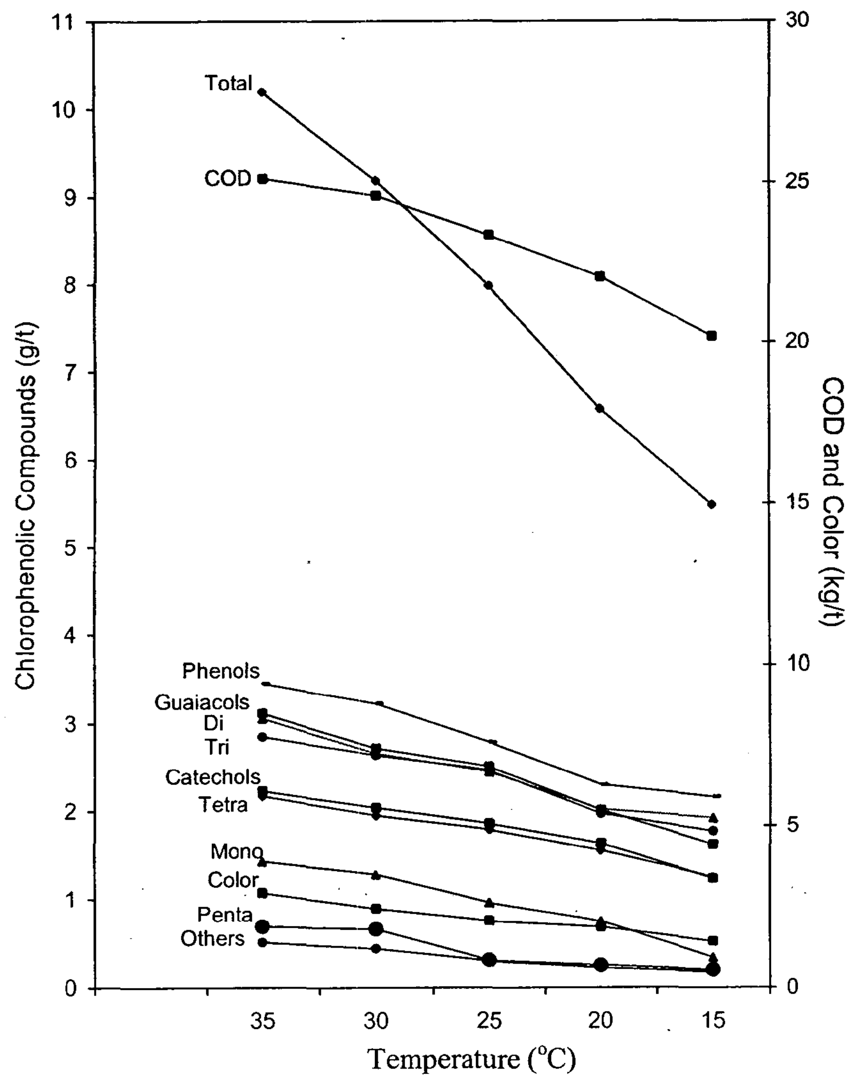


Fig 4.9 **Effect of C stage temperature on the generation of chlorophenolics, COD and color in H stage effluent.**

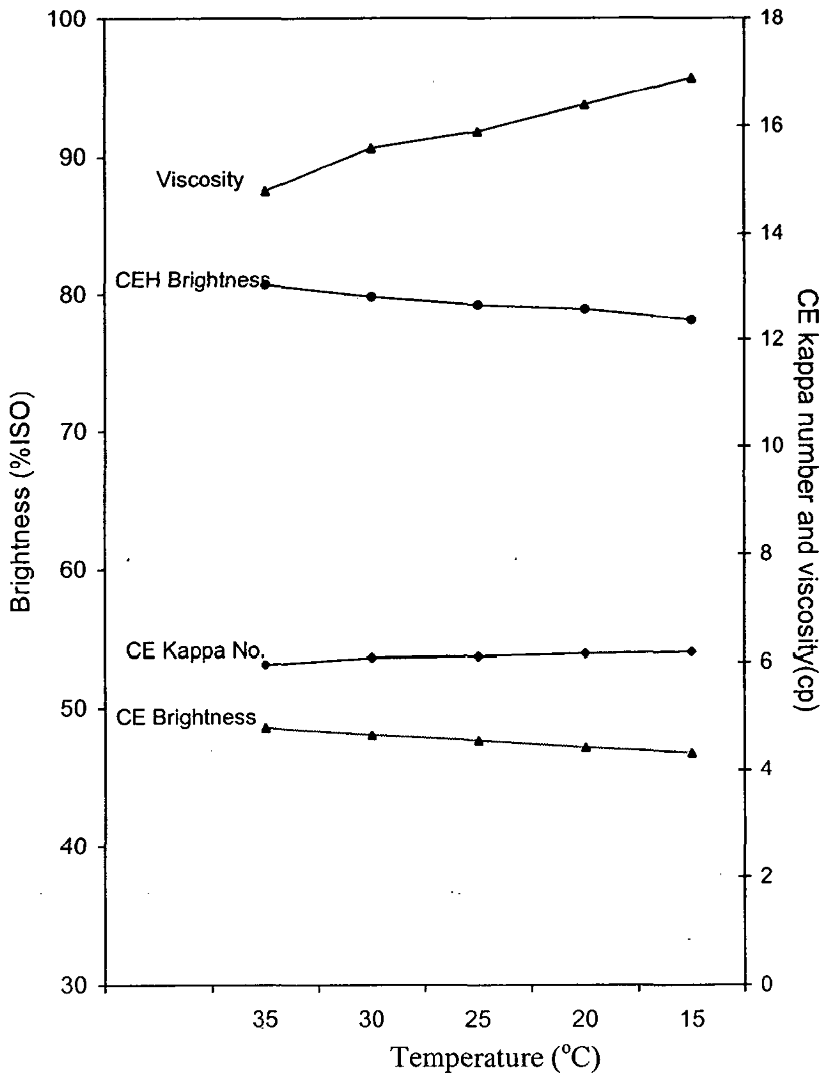


Fig 4.10 **Effect of C stage temperature on brightness, viscosity and CE kappa number.**

Table 4.9 Effect of consistency in C stage on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at consistency														
	2%			2.5%			3%			3.5%			4%		
	C	E	H	C	E	H	C	E	H	C	E	H	C	E	H
2,4 Dichlorophenol	1.35	2.73	0.96	2.10	3.15	1.52	2.94	4.24	1.53	3.26	4.56	1.84	3.98	4.92	1.96
2,5 Dichlorophenol	0.40	0.84	-	0.79	1.02	-	1.04	1.19	-	1.25	1.21	-	1.36	1.56	-
2,3- Dichlorophenol	0.18	-	-	-	-	-	0.22	-	-	0.31	0.10	-	0.47	0.25	-
3-chloroguaiacol	-	-	-	-	0.30	-	-	0.37	-	-	0.39	-	-	0.43	-
2,6 Dichlorophenol	0.21	2.25	-	0.28	2.96	-	0.32	3.92	-	0.43	4.08	-	0.58	4.99	-
4-chlorophenol	0.33	-	-	0.57	-	-	0.64	-	-	0.72	-	-	0.89	-	-
3-chlorophenol	0.57	1.15	0.06	0.63	1.98	0.15	0.78	2.16	0.28	0.86	2.47	0.32	1.01	3.14	0.58
4-chloroguaiacol	-	-	0.18	0.04	-	0.29	0.06	-	0.34	0.06	-	0.46	0.08	-	0.63
5-chloroguaiacol	-	1.36	0.05	-	1.53	0.10	-	1.78	0.18	-	1.96	0.25	-	2.27	0.47
6-chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-chlorophenol	0.15	-	-	0.20	-	-	0.26	-	-	0.37	-	-	0.41	-	-
2,3,5-Trichlorophenol	0.01	1.97	-	0.11	2.68	-	0.18	3.73	-	0.25	4.12	-	0.36	4.36	-
2,4,6-Trichlorophenol	1.02	2.38	0.23	1.36	3.77	0.61	2.79	4.94	0.76	2.86	5.23	0.75	3.03	5.78	0.82
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.76	3.24	-	0.85	5.68	-	0.96	6.91	-	1.10	7.13	-	1.25	8.25	-
3,6 Dichloroguaiacol	0.05	-	-	0.09	-	-	0.11	-	-	0.28	-	-	0.30	-	-
3,4 Dichloroguaiacol	0.18	3.01	-	0.27	4.09	-	0.33	5.37	-	0.46	6.24	-	0.52	6.90	-
3,4-Dichlorocatechol	2.56	1.46	-	2.43	2.13	-	4.65	2.34	-	3.48	3.55	-	2.56	3.71	-
3,4-Dicholorophenol	0.63	-	-	0.86	-	-	0.99	-	-	1.15	-	-	1.31	-	-
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.30	-	-	0.42	0.05	-	0.45	0.14	-	0.58	0.19	-	0.96	0.25
5-Chlorovanillin	0.89	1.96	-	1.08	2.56	-	2.14	3.66	-	2.57	3.93	-	2.76	4.14	-
5,6 Dichloroguaiacol	-	1.43	0.11	-	2.84	0.18	-	3.18	0.27	-	3.87	0.36	-	4.08	0.44

4-Chlorocatechol	1.76	-	-	2.19	-	-	3.72	-	-	3.89	-	-	3.94	-	-
3,5-Dichlorocatechol	2.13	1.24	-	3.34	1.87	-	6.15	2.10	-	6.86	2.76	-	6.90	2.99	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.89	0.46	-	0.90	0.58	-	0.92	0.68	-	0.96	0.93	-	1.01	1.25	-
3,5,6-Trichloroguaiacol	-	0.32	-	-	0.46	-	-	0.50	-	-	0.88	-	-	1.04	-
3,4,6-Trichloroguaiacol	-	1.28	-	-	2.01	-	-	2.27	-	-	2.79	-	-	3.16	-
3,5-Dichlorosyringol	-	1.05	0.20	-	1.49	0.32	-	1.60	0.35	-	1.90	0.41	-	2.08	0.62
3,4,5-Trichloroguaiacol	1.21	2.07	0.33	1.88	2.95	0.48	2.41	3.34	0.96	2.93	3.84	1.06	3.18	4.17	1.38
3-Chlorocatechol	2.64	-	-	3.74	-	-	4.78	-	-	5.16	-	-	5.32	-	-
6-Chlorovanillin	0.42	1.18	-	0.53	1.88	-	0.68	2.01	-	0.92	2.65	-	0.99	2.79	-
3,6-Dichlorocatechol	0.33	0.58	-	0.59	0.60	-	0.94	0.62	-	1.03	1.01	-	1.14	1.32	-
4,5,6-Trichloroguaiacol	0.27	0.29	-	0.41	0.36	-	0.62	0.48	-	0.98	0.76	-	1.03	0.94	-
2-Chlorosyringaldehyde	0.58	1.34	0.16	0.96	1.79	0.29	1.19	2.18	0.48	1.55	2.43	0.59	1.67	2.93	0.61
4,5-Dichlorocatechol	0.29	-	-	0.68	-	-	0.85	-	-	0.96	-	-	1.05	-	-
Pentachlorophenol	-	4.10	-	0.32	5.32	0.31	0.69	7.51	0.66	0.82	7.97	0.88	0.91	8.15	0.97
3,4,5-Trichlorocatechol	2.81	4.23	-	5.15	5.14	-	7.18	6.10	-	7.21	6.48	-	7.34	7.26	-
Tetrachloroguaiacol	1.80	1.35	0.38	1.76	1.96	0.47	1.75	2.70	0.83	1.78	3.14	0.93	2.01	3.98	1.00
Trichlorosyringol	0.34	5.07	-	0.49	6.13	-	0.50	8.89	-	0.55	9.10	-	0.68	10.01	-
3,4,6-Trichlorocatechol	0.45	-	0.49	0.72	-	0.80	1.03	-	0.92	1.19	-	1.01	1.24	-	1.28
2,6-Dichlorosyringaldehyde	0.07	5.28	-	0.10	6.32	-	0.29	7.18	-	0.84	8.23	-	0.99	8.94	-
5,6-Dichlorovanillin	0.32	2.06	-	0.68	3.45	0.18	0.71	4.46	0.37	1.03	5.60	0.68	1.23	6.13	0.73
Tetrachlorocatechol	4.10	1.09	0.54	4.15	1.68	0.93	4.32	2.70	1.12	4.38	3.24	1.64	4.92	4.17	1.85
Total	**29.7**	**57.07**	**3.69**	**40.25**	**79.1**	**6.68**	**57.14**	**99.56**	**9.19**	**62.45**	**113.13**	**11.37**	**66.42**	**127.05**	**13.59**

C stage bleaching conditions: $C_{end\ pH} \geq 2$ and Temperature 30°C.

Table 4.10 Effect of C stage consistency on COD generation

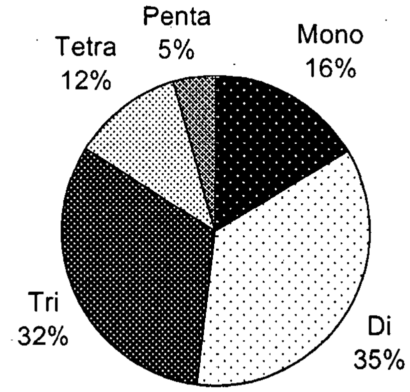
Stage/consistency	COD (kg/t) at different consistency				
	2.0%	**2.5%**	**3.0%**	**3.5%**	**4.0%**
C	28.7	31.0	31.3	32.7	35.0
E	70.1	73.5	76.5	78.4	80.1
H	18.9	21.8	24.6	25.3	26.2
Total	**117.7**	**126.3**	**132.4**	**136.4**	**141.3**

Table 4.11 Effect of C stage consistency on color generation

Stage/consistency	Color (kg/t) at different consistency				
	2.0%	**2.5%**	**3.0%**	**3.5%**	**4.0%**
C	36.5	40.2	43.8	45.3	48.4
E	61.3	70.7	83.9	86.8	89.3
H	1.8	2.2	2.4	2.7	2.8
Total	**99.6**	**113.1**	**130.1**	**134.8**	**140.5**

Table 4.12 Effect of C stage consistency on CE kappa no, brightness and CED viscosity

Parameter/consistency	Different parameter at different consistency				
	2.0%	**2.5%**	**3.0%**	**3.5%**	**4.0%**
CE Kappa No	6.1	6.1	6.0	5.9	5.8
CE Brightness(%ISO)	47.3	47.8	48.1	48.4	48.9
CEH Brightness(%ISO)	78.6	79.1	79.8	80.2	80.6
Viscosity(cp)	16.1	15.8	15.6	14.9	14.4



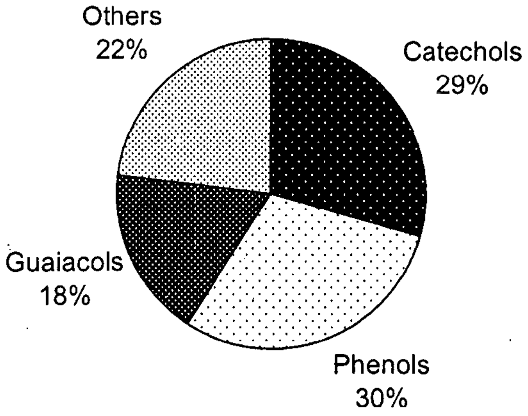


Fig. 4.11 The contribution of different chlorophenolic compounds at 2% consistency

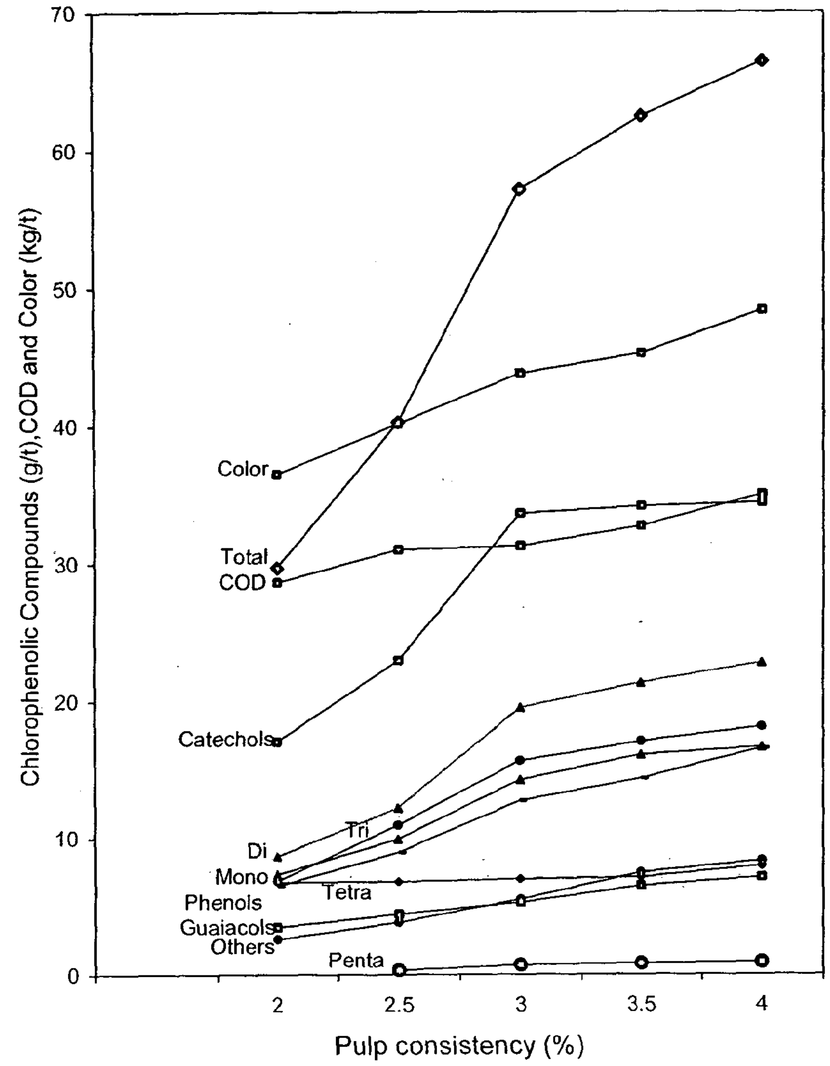


Fig 4.12 **Effect of C stage consistency on the generation of chlorophenolics, COD and color in C stage effluent.**

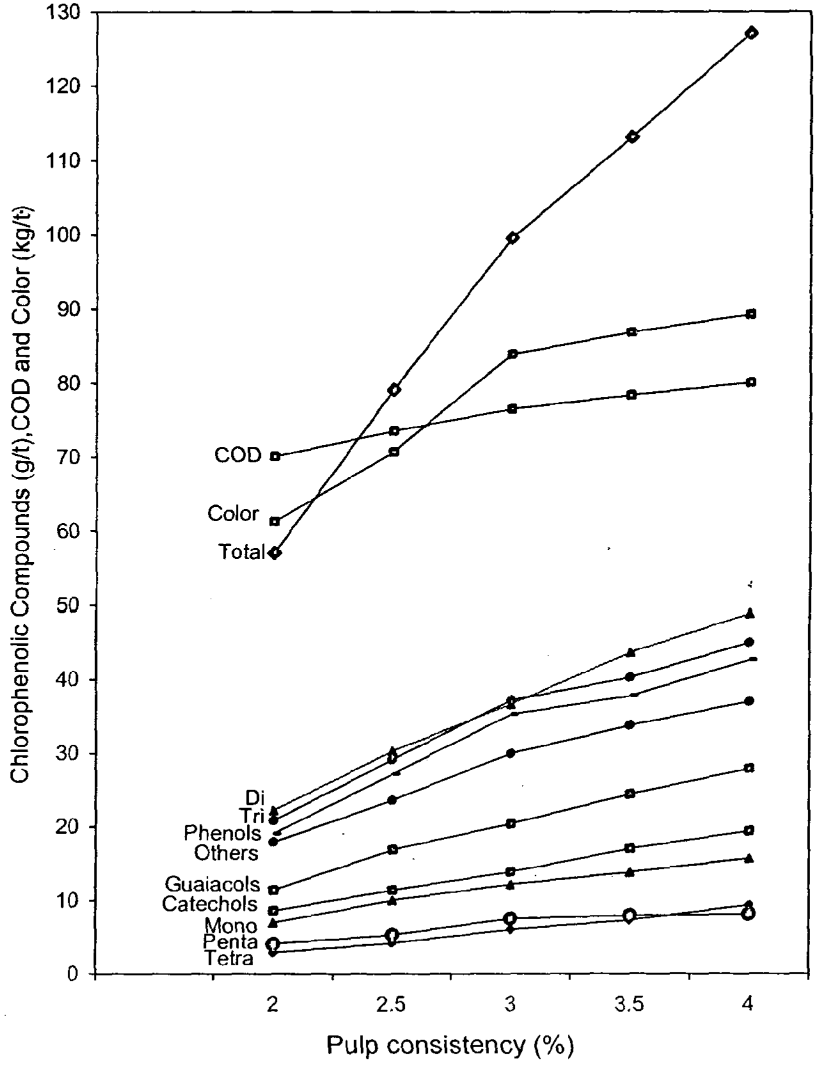


Fig 4.13 **Effect of C stage consistency on the generation of chlorophenolics, COD and color in E stage effluent.**

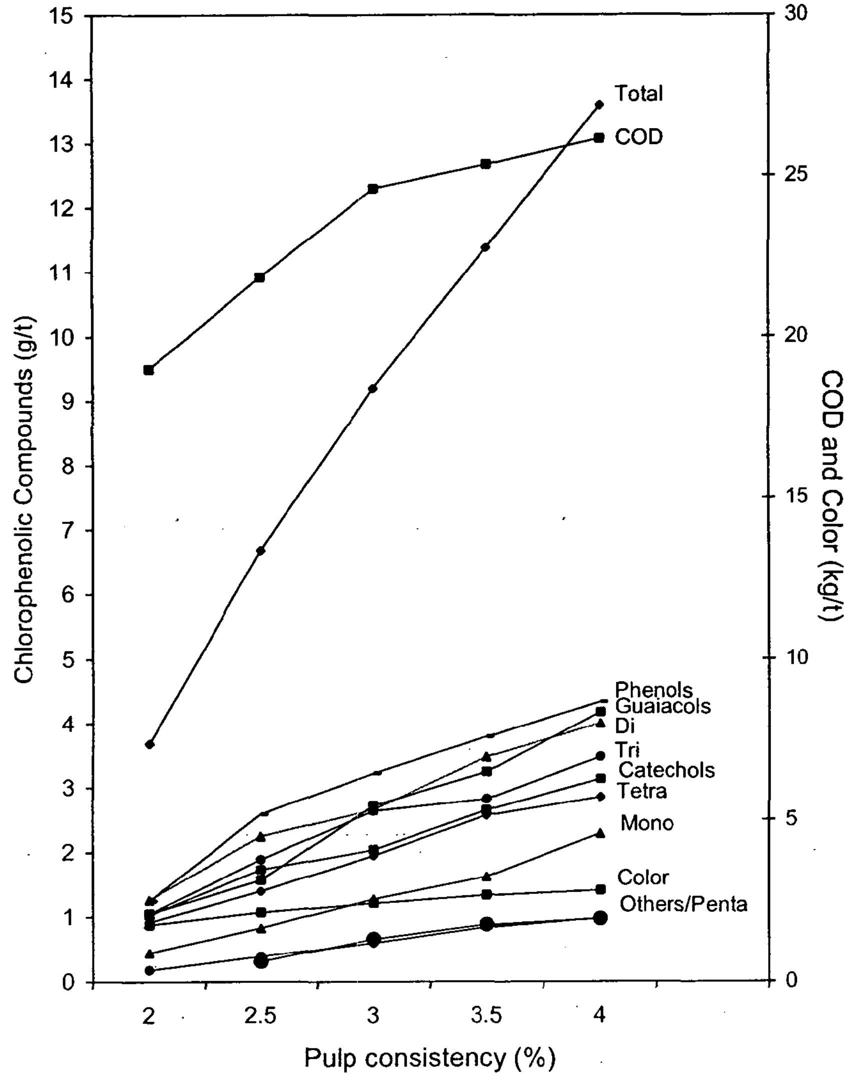


Fig 4.14 **Effect of C stage consistency on the generation of chlorophenolics, COD and color in H stage effluent.**

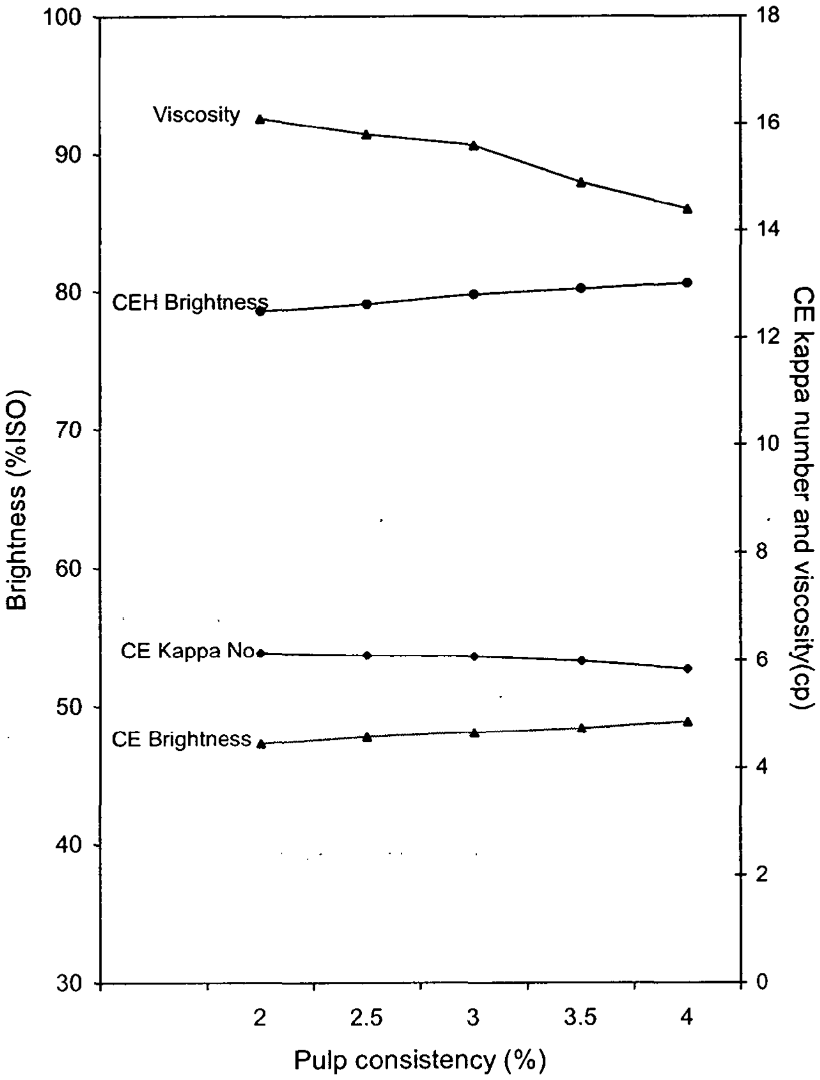


Fig 4.15 **Effect of C stage consistency on brightness, viscosity and CE kappa number.**

Table 4.13 Effect of distribution of bleach chemical between C and H stage on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at different distribution between C:H stages														
	50:50			55:45			60:40			65:35			70:30		
	C	E	H	C	E	H	C	E	H	C	E	H	C	E	H
2,4 Dichlorophenol	1.46	3.40	1.76	2.54	3.83	1.62	2.94	4.24	1.53	3.07	4.68	1.23	3.48	4.99	1.04
2,5 Dichlorophenol	0.53	0.96	0.13	0.86	1.07	-	1.04	1.19	-	1.19	1.42	-	1.26	1.67	-
2,3-Dichlorophenol	-	-	-	0.10	-	-	0.22	-	-	0.41	-	-	0.67	-	-
3-chloroguaiacol	-	0.14	-	-	0.28	-	-	0.37	-	-	0.43	-	-	0.64	-
2,6 Dichlorophenol	0.20	2.57	-	0.25	2.89	-	0.32	3.92	-	0.48	4.17	-	0.55	5.23	-
4-chlorophenol	0.29	-	-	0.47	-	-	0.64	-	-	0.72	-	-	0.96	-	-
3-chlorophenol	0.38	1.68	0.36	0.59	1.97	0.28	0.78	2.16	0.28	0.93	2.82	0.18	1.04	2.96	0.10
4-chloroguaiacol	-	-	0.44	0.01	-	0.39	0.06	-	0.34	0.08	-	0.21	0.18	-	0.17
5-chloroguaiacol	-	1.21	0.30	-	1.32	0.20	-	1.78	0.18	-	1.94	0.14	-	2.15	0.09
6-chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-chlorophenol	0.18	-	-	0.24	-	-	0.26	-	-	0.30	-	-	0.68	-	-
2,3,5-Trichlorophenol	0.14	1.89	-	0.17	2.64	-	0.18	3.73	-	0.22	3.96	-	0.43	4.31	-
2,4,6-Trichlorophenol	1.65	2.64	1.03	2.01	3.25	0.94	2.79	4.94	0.76	2.94	5.28	0.76	3.20	6.07	0.54
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.48	4.85	-	0.68	5.23	-	0.96	6.91	-	1.07	7.27	-	1.35	8.19	-
3,6 Dichloroguaiacol	0.01	-	-	0.09	-	-	0.11	-	-	0.25	-	-	0.46	-	-
3,4 Dichloroguaiacol	0.21	3.27	-	0.03	4.94	-	0.33	5.37	-	0.48	6.28	-	0.69	7.34	-
3,4-Dichlorocatechol	2.37	1.86	-	3.74	2.10	-	4.65	2.34	-	4.93	3.16	-	5.17	4.05	-
3,4-Dicholorophenol	0.55	-	-	0.76	-	-	0.99	-	-	1.06	-	-	1.38	-	-
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.28	0.02	-	0.32	0.10	-	0.45	0.14	-	0.54	0.16	-	0.72	0.19
5-Chlorovanillin	1.54	3.26	-	1.83	3.84	-	2.14	3.66	-	2.49	3.82	-	2.64	3.76	-
5,6 Dichloroguaiacol	-	1.65	0.32	-	2.08	0.29	-	3.18	0.27	-	3.47	0.25	-	3.89	-

4-Chlorocatechol	2.63	-	-	2.99	-	-	3.72	-	-	4.04	-	-	4.29	-	-
3,5-Dichlorocatechol	4.05	1.74	-	5.46	1.93	-	6.15	2.10	-	6.91	2.46	-	7.13	3.04	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.52	0.32	-	0.75	0.55	-	0.92	0.68	-	1.06	0.79	-	1.38	0.93	-
3,5,6-Trichloroguaiacol	-	0.29	-	-	0.42	-	-	0.50	-	-	0.63	-	-	0.99	-
3,4,6-Trichloroguaiacol	-	1.05	-	-	1.98	-	-	2.27	-	-	2.46	-	-	3.12	-
3,5-Dichlorosyringol	-	1.21	0.20	-	1.46	0.28	-	1.60	0.35	-	1.83	0.38	-	1.96	0.42
3,4,5-Trichloroguaiacol	1.66	2.06	1.03	1.98	2.81	1.01	2.41	3.34	0.96	3.10	3.67	0.73	3.49	3.84	0.51
3-Chlorocatechol	2.08	-	-	3.84	-	-	4.78	-	-	5.25	-	-	5.87	-	-
6-Chlorovanillin	0.29	1.54	-	0.47	1.74	-	0.68	2.01	-	0.83	2.24	-	0.99	2.20	-
3,6-Dichlorocatechol	0.57	0.38	-	0.72	0.42	-	0.94	0.62	-	1.09	0.89	-	1.36	1.06	-
4,5,6-Trichloroguaiacol	0.34	0.19	-	0.59	0.23	-	0.62	0.48	-	0.94	0.67	-	1.05	0.92	-
2-Chlorosyringaldehyde	0.72	1.83	0.61	0.96	2.05	0.50	1.19	2.18	0.48	1.29	2.35	0.32	1.44	2.45	0.28
4,5-Dichlorocatechol	0.49	-	-	0.62	-	-	0.85	-	-	0.98	-	-	1.18	-	-
Pentachlorophenol	0.16	5.11	0.73	0.48	6.01	0.69	0.69	7.51	0.66	0.86	7.89	0.54	1.03	8.72	0.33
3,4,5-Trichlorocatechol	4.35	4.25	-	6.10	5.83	-	7.18	6.10	-	7.79	6.43	-	8.12	6.64	-
Tetrachloroguaiacol	1.01	1.79	0.94	1.26	2.16	0.90	1.75	2.70	0.83	2.16	2.96	0.63	2.58	3.15	0.46
Trichlorosyringol	0.23	6.34	-	0.44	7.32	-	0.50	8.89	-	0.68	8.99	-	0.85	9.13	-
3,4,6-Trichlorocatechol	0.64	-	1.03	0.87	-	0.99	1.03	-	0.92	1.32	-	0.78	1.47	-	0.52
2,6-Dichlorosyringaldehyde	0.20	4.82	-	0.25	6.28	-	0.29	7.18	-	0.37	7.84	-	0.49	8.29	-
5,6-Dichlorovanillin	1.07	4.78	0.17	0.92	4.47	0.26	0.71	4.46	0.37	0.78	4.20	0.40	0.89	4.11	0.46
Tetrachlorocatechol	2.06	1.03	1.21	3.14	1.96	1.18	4.32	2.70	1.12	4.96	2.93	0.72	5.14	3.08	0.39
Total	**33.06**	**68.39**	**10.28**	**46.21**	**83.38**	**9.63**	**57.14**	**99.56**	**9.19**	**65.03**	**108.47**	**7.43**	**72.89**	**119.6**	**5.5**

C stage bleaching conditions: Temperature 30°C, Consistency 3%, and $C_{end\ pH} \geq 2$.

Table 4.14 Effect of distribution of bleach chemical between C and H stage on COD generation

Stage/distribution	COD (kg/t) at different distribution between C:H stages				
	50:50	55:45	60:40	65:35	70:30
C	19.9	28.5	31.3	37.7	43.1
E	62.7	70.7	76.5	80.2	83.2
H	25.1	24.9	24.6	23.0	23.1
Total	**107.7**	**124.1**	**132.4**	**140.9**	**149.4**

Table 4.15 Effect of distribution of bleach chemical between C and H stage on color generation

Stage/distribution	Color (kg/t) at different distribution between C:H stages				
	50:50	55:45	60:40	65:35	70:30
C	33.5	36.2	43.8	44.1	49.2
E	60.2	72.6	83.9	87.8	92.6
H	1.2	1.9	2.4	2.5	2.6
Total	**94.9**	**110.7**	**130.1**	**134.4**	**144.4**

Table 4.16 Effect of distribution of bleach chemical between C and H stage on CE kappa no, brightness and CED viscosity

Parameters/distributions	Different parameter at different at different distribution between C:H stages				
	50:50	55:45	60:40	65:35	70:30
CE Kappa no.	5.8	5.9	6.1	6.2	6.1
CE Brightness(%ISO)	48.9	48.6	48.1	47.3	47.0
CEH Brightness(%ISO)	80.8	80.2	79.8	79.1	78.6
Viscosity(cp)	14.7	15.1	15.6	15.7	15.9

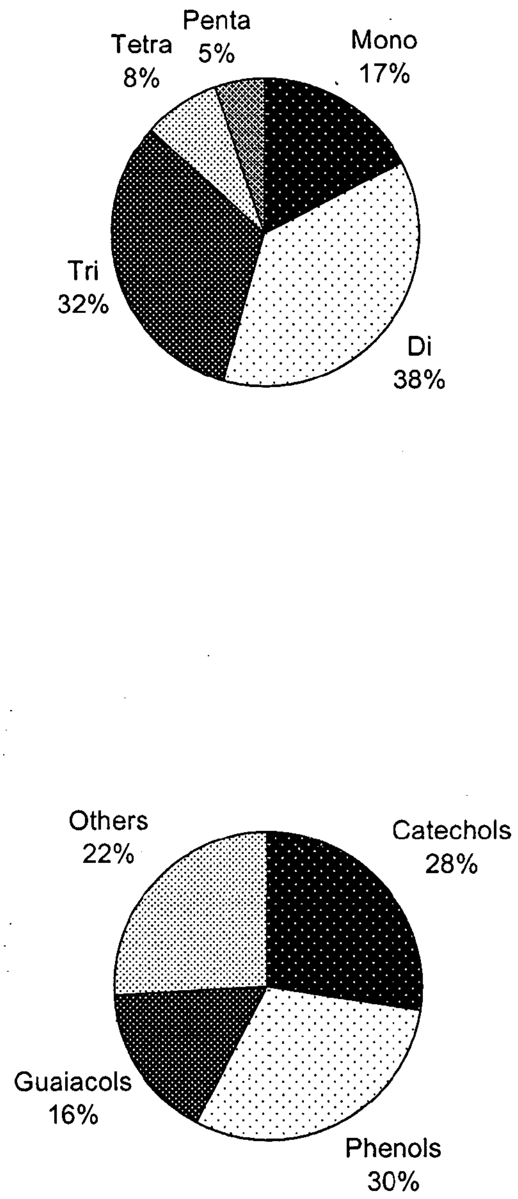


Fig. 4.16 The contribution of different chlorophenolic compounds at distribution of bleach chemical between C and H stage.

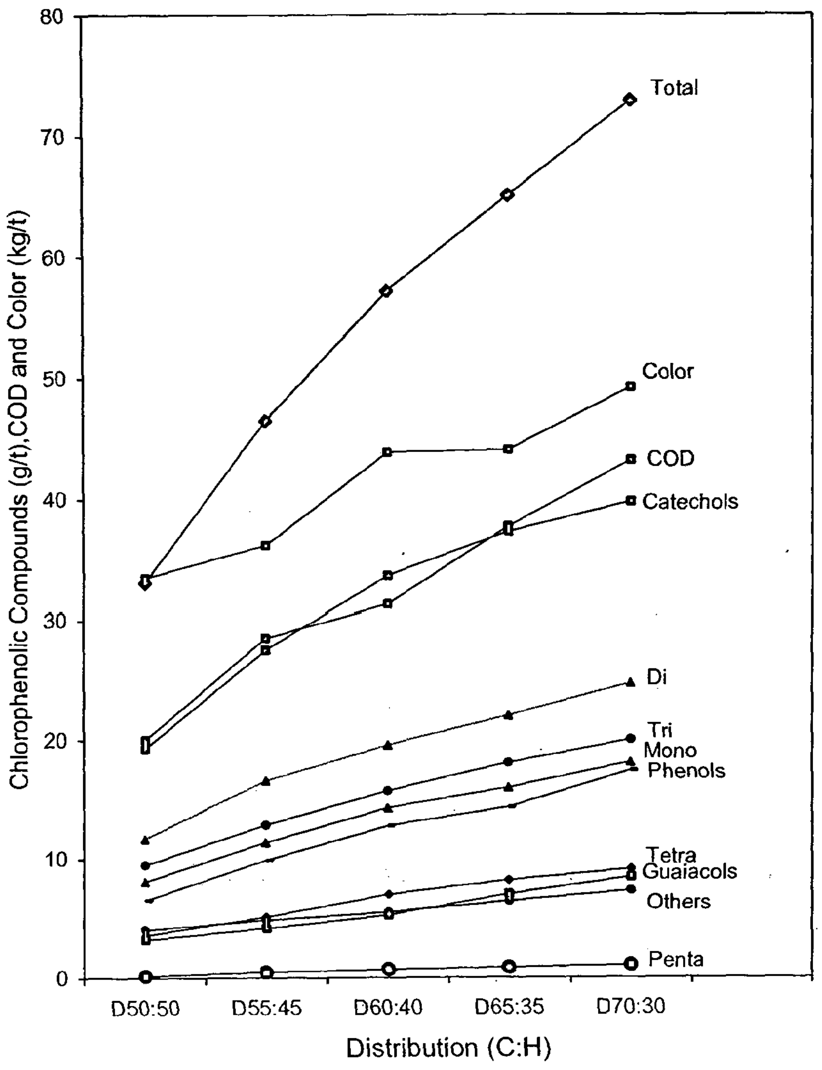


Fig 4.17 Effect of distribution of bleach chemical between C and H stage on the generation of chlorophenolics, COD and color in C stage effluent.

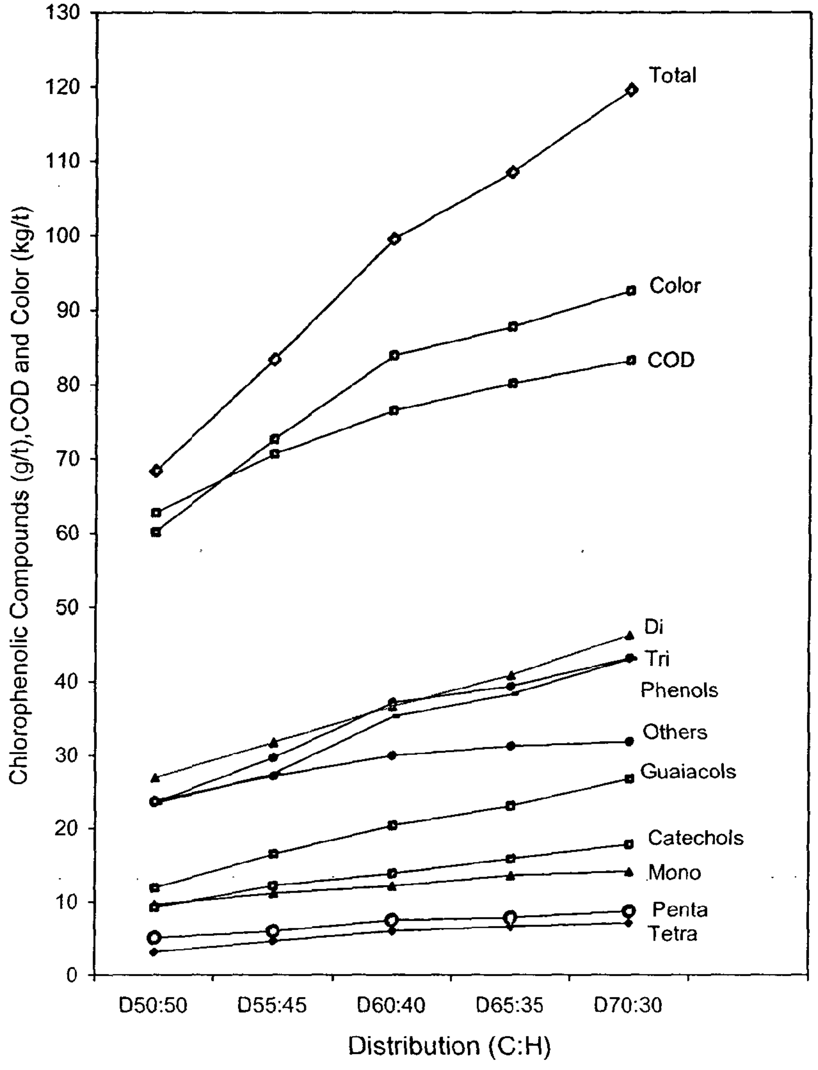


Fig 4.18 Effect of distribution of bleach chemical between C and H stage on the generation of chlorophenolics, COD and color in E stage effluent.

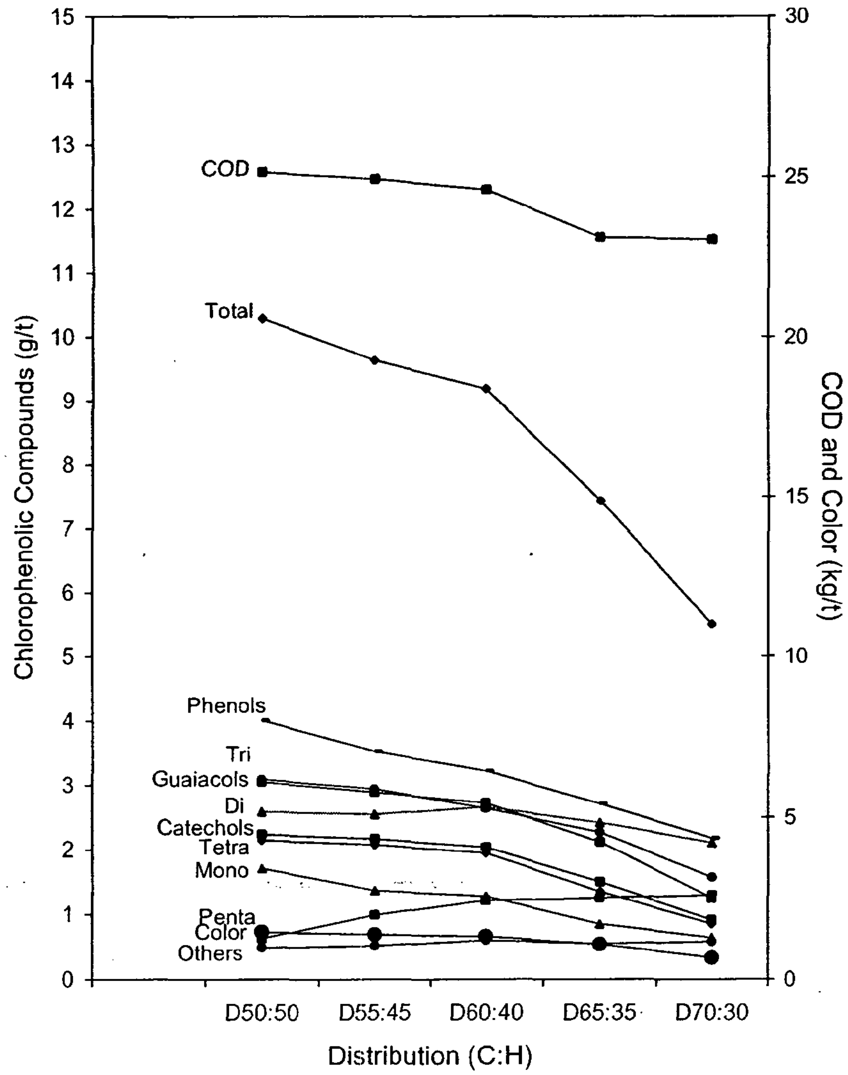


Fig 4.19 **Effect of distribution of bleach chemical between C and H stage on the generation of chlorophenolics, COD and color in H stage effluent.**

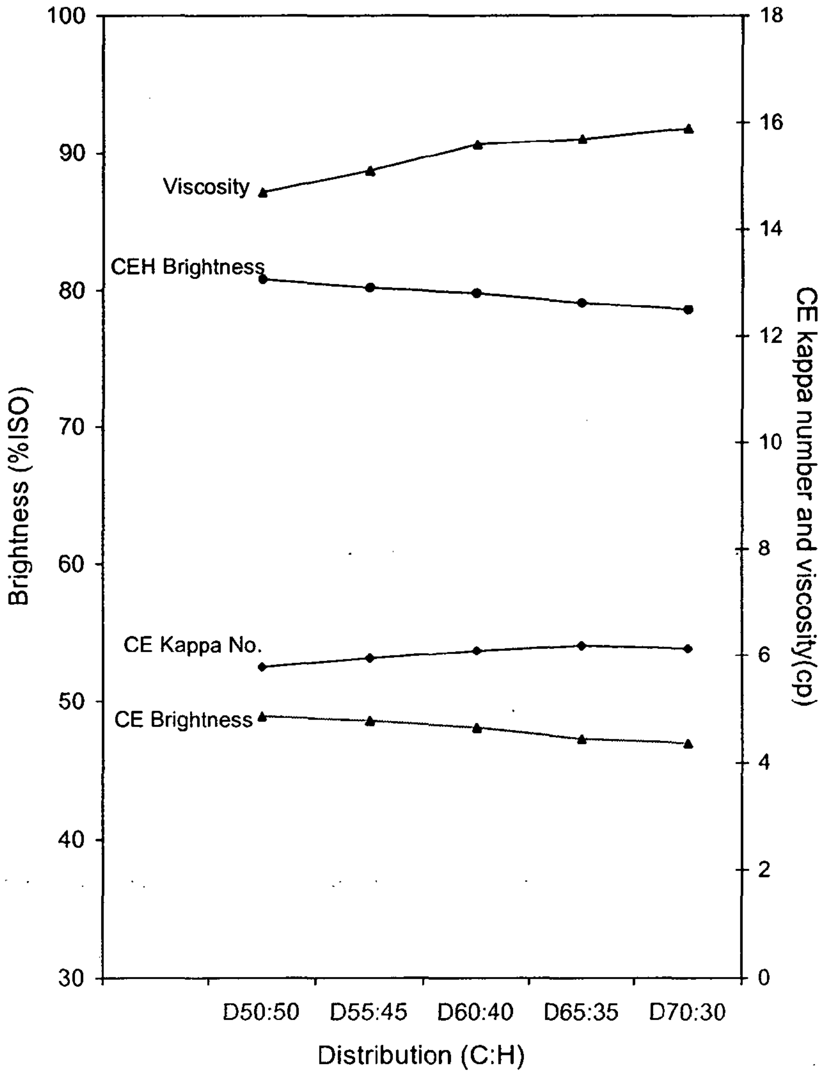


Fig 4.20 **Effect of distribution of bleach chemical between C and H stage on brightness, viscosity and CE kappa number.**

Table 4.17 Effect of replacement of chlorine by chlorine dioxide in C stage on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at chlorine dioxide substituted sequences														
	Normal CEH			$C_{75}D_{25}EH$			$C_{50}D_{50}EH$			$C_{25}D_{75}EH$			DEH		
	C	E	H	$C_{75}D_{25}$	E	H	$C_{50}D_{50}$	E	H	$C_{25}D_{75}$	E	H	D	E	H
2,4 Dichlorophenol	2.94	4.24	1.53	3.22	3.95	1.24	3.34	3.10	1.16	1.76	2.54	0.52	0.59	1.49	0.31
2,5 Dichlorophenol	1.04	1.19	-	1.48	1.13	-	1.61	1.12	-	0.95	0.98	-	0.31	0.75	-
2,3-Dichlorophenol	0.22	-	-	0.56	-	-	0.78	-	-	0.43	-	-	0.14	-	-
3-chloroguaiacol	-	0.37	-	-	0.34	-	-	0.26	-	-	0.18	-	-	0.12	-
2,6 Dichlorophenol	0.32	3.92	-	0.39	3.20	-	0.42	3.25	-	0.22	2.17	-	0.08	1.28	-
4-chlorophenol	0.64	-	-	0.94	-	-	1.01	-	-	0.67	-	-	0.25	-	-
3-chlorophenol	0.78	2.16	0.28	0.97	2.09	0.13	1.08	1.83	0.05	0.69	1.14	-	0.24	0.71	-
4-chloroguaiacol	0.06	-	0.34	0.10	-	0.10	0.25	-	0.08	0.13	-	0.05	0.04	-	0.02
5-chloroguaiacol	-	1.78	0.18	-	1.62	0.12	-	1.34	0.07	-	0.79	0.04	-	0.56	0.04
6-chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-chlorophenol	0.26	-	-	0.33	-	-	0.39	-	-	0.20	-	-	0.08	-	-
2,3,5-Trichlorophenol	0.18	3.73	-	0.21	3.51	-	0.26	2.57	-	0.14	1.71	-	0.05	1.22	-
2,4,6-Trichlorophenol	2.79	4.94	0.76	2.88	3.92	0.59	2.94	3.48	0.41	1.47	2.18	0.18	0.51	1.25	0.10
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.96	6.91	-	1.04	5.46	-	1.28	5.32	-	0.94	3.34	-	0.31	2.23	-
3,6 Dichloroguaiacol	0.11	-	-	0.10	-	-	0.07	-	-	0.05	-	-	0.02	-	-
3,4 Dichloroguaiacol	0.33	5.37	-	0.28	4.90	-	0.25	4.11	-	0.12	2.57	-	0.04	1.84	-
3,4-Dichlorocatechol	4.65	2.34	-	4.27	1.87	-	4.01	1.23	-	2.76	0.88	-	0.98	0.59	-
3,4-Dicholorophenol	0.99	-	-	1.11	-	-	1.26	-	-	0.63	-	-	0.25	-	-
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.45	0.14	-	0.40	0.10	-	0.36	0.08	-	0.21	0.01	-	0.15	0.05
5-Chlorovanillin	2.14	3.66	-	1.53	2.83	-	1.34	1.94	-	0.68	1.22	-	0.24	0.76	-
5,6 Dichloroguaiacol	-	3.18	0.27	-	2.11	0.23	-	1.78	0.26	-	1.11	0.10	-	0.80	-

4-Chlorocatechol	3.72	-	-	3.70	-	-	3.20	-	-	1.69	-	-	0.63	-	-
3,5-Dichlorocatechol	6.15	2.10	-	4.84	1.85	-	3.75	1.32	-	1.97	0.83	-	0.70	0.52	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.92	0.68	-	0.76	0.58	-	0.69	0.46	-	0.38	0.32	-	0.13	0.21	-
3,5,6-Trichloroguaiacol	-	0.50	-	-	0.46	-	-	0.32	-	-	0.28	-	-	0.18	-
3,4,6-Trichloroguaiacol	-	2.27	-	-	1.97	-	-	1.14	-	-	0.67	-	-	0.42	-
3,5-Dichlorosyringol	-	1.60	0.35	-	1.21	0.28	-	0.98	0.21	-	0.76	0.13	-	0.56	0.06
3,4,5-Trichloroguaiacol	2.41	3.34	0.96	2.49	2.29	0.64	2.66	1.75	0.64	1.82	1.15	0.32	0.49	0.77	0.11
3-Chlorocatechol	4.78	-	-	4.08	-	-	3.82	-	-	0.24	-	-	0.09	-	-
6-Chlorovanillin	0.68	2.01	-	0.52	1.83	-	0.47	1.07	-	0.32	0.66	-	0.11	0.38	-
3,6-Dichlorocatechol	0.94	0.62	-	0.79	0.54	-	0.63	0.38	-	0.39	0.25	-	0.13	0.17	-
4,5,6-Trichloroguaiacol	0.62	0.48	-	0.68	0.30	-	0.74	0.26	-	0.43	0.16	-	0.15	0.11	-
2-Chlorosyringaldehyde	1.19	2.18	0.48	0.94	1.92	0.29	0.81	1.45	0.18	0.46	0.97	0.10	0.27	0.69	0.08
4,5-Dichlorocatechol	0.85	-	-	0.73	-	-	0.70	-	-	0.38	-	-	0.19	-	-
Pentachlorophenol	0.69	7.51	0.66	0.58	6.06	0.20	0.55	3.13	-	-	1.92	-	-	-	-
3,4,5-Trichlorocatechol	7.18	6.10	-	6.10	5.21	-	5.83	4.04	-	2.89	2.38	-	1.03	1.80	-
Tetrachloroguaiacol	1.75	2.70	0.83	1.02	2.13	0.44	0.96	1.82	0.21	0.46	1.05	0.13	0.25	0.65	0.09
Trichlorosyringol	0.50	8.89	-	0.46	6.15	-	0.41	4.99	-	0.27	3.32	-	0.16	2.14	-
3,4,6-Trichlorocatechol	1.03	-	0.92	0.84	-	0.56	0.79	-	0.13	0.33	-	0.11	0.24	-	0.10
2,6-Dichlorosyringaldehyde	0.29	7.18	-	0.23	6.87	-	0.18	5.06	-	0.08	3.37	-	0.03	2.06	-
5,6-Dichlorovanillin	0.71	4.46	0.37	0.66	3.24	0.30	0.54	2.73	0.26	0.27	1.71	0.19	0.18	1.13	0.16
Tetrachlorocatechol	4.32	2.70	1.12	2.41	1.16	0.83	2.40	0.95	0.42	1.18	0.68	0.12	0.97	0.28	0.08
Total	**57.14**	**99.56**	**9.19**	**51.24**	**81.1**	**6.05**	**49.42**	**63.54**	**4.16**	**25.4**	**41.5**	**2**	**9.88**	**25.82**	**1.2**

C stage bleaching conditions: $C_{end\ pH} \geq 2 - 4.25$, Temperature 30 - 70°C and Consistency 3 - 10%.

Table 4.18 Effect of replacement of chlorine by ClO_2 in C stage on COD generation

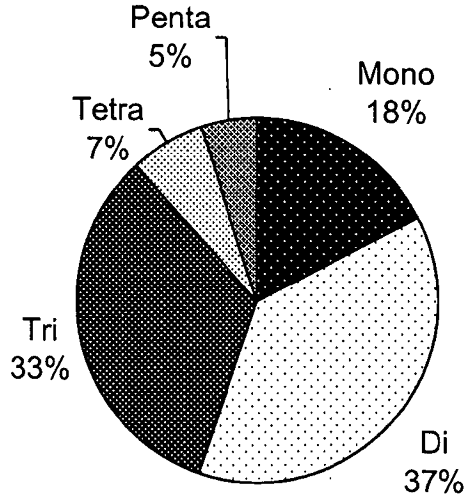
Stage/Replacement	COD (kg/t) at different chlorine dioxide substituted sequences				
	Normal CEH	$C_{75}D_{25}EH$	$C_{50}D_{50}EH$	$C_{25}D_{75}EH$	DEH
C	31.3	22.3	19.1	15.8	12.1
E	76.5	67.5	64.4	60.2	57.1
H	24.6	22.3	19.2	17.5	13.3
Total	**132.4**	**112.1**	**102.7**	**93.4**	**82.5**

Table 4.19 Effect of replacement of chlorine by ClO_2 in C stage on color generation

Stage/ Replacement	Color (kg/t) at different chlorine dioxide substituted sequences				
	Normal CEH	$C_{75}D_{25}EH$	$C_{50}D_{50}EH$	$C_{25}D_{75}EH$	DEH
C	43.8	34.5	30.6	25.5	18.5
E	83.9	79.3	61.1	40.9	29.5
H	2.4	2.1	1.8	1.4	0.9
Total	**130.1**	**115.9**	**93.5**	**67.8**	**48.9**

Table 4.20 Effect of replacement of bleach chemical by ClO_2 on CE kappa no, brightness and CED viscosity

Parameter/ Replacement	Different parameters at chlorine dioxide substituted sequences				
	Normal CEH	$C_{75}D_{25}EH$	$C_{50}D_{50}EH$	$C_{25}D_{75}EH$	DEH
CE Kappa No	6.1	5.1	5.6	5.3	5.0
CE Brightness(%ISO)	48.1	51.3	56.5	60.9	62.5
CEH Brightness(%ISO)	79.8	84.1	86.7	87.8	88.5
Viscosity(cp)	15.6	16.5	17.9	18.2	20.5



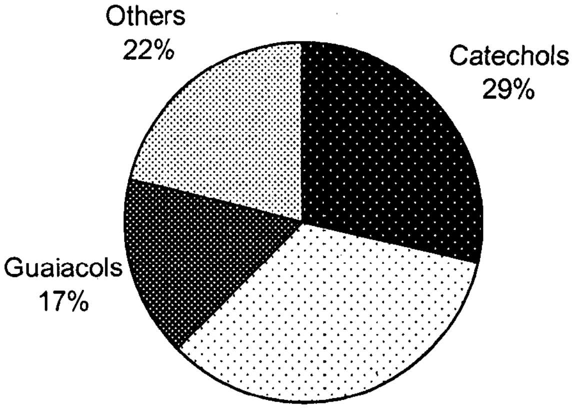


Fig. 4.21 **The contribution of different chlorophenolic compounds at 25% substitution of chlorine by chlorine dioxide in C stage.**

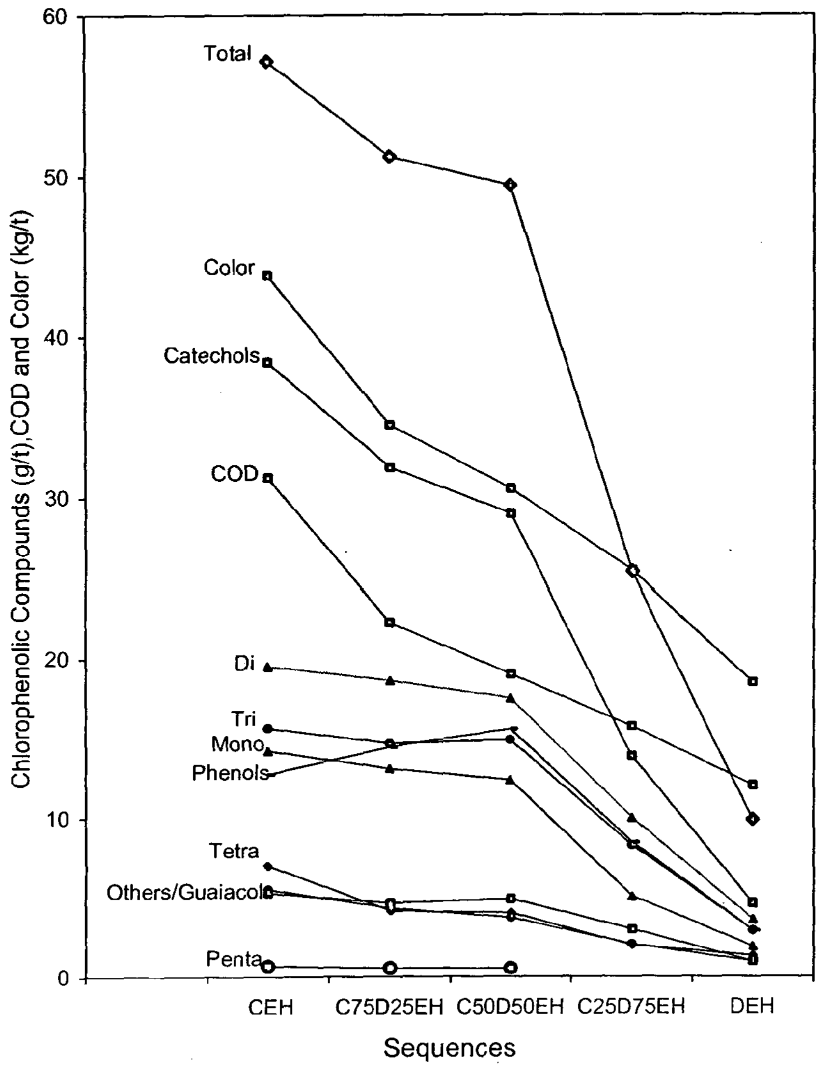


Fig 4.22 **Effect of replacement of chlorine by chlorine dioxide on the generation of chlorophenolics, COD and color in C stage effluent.**

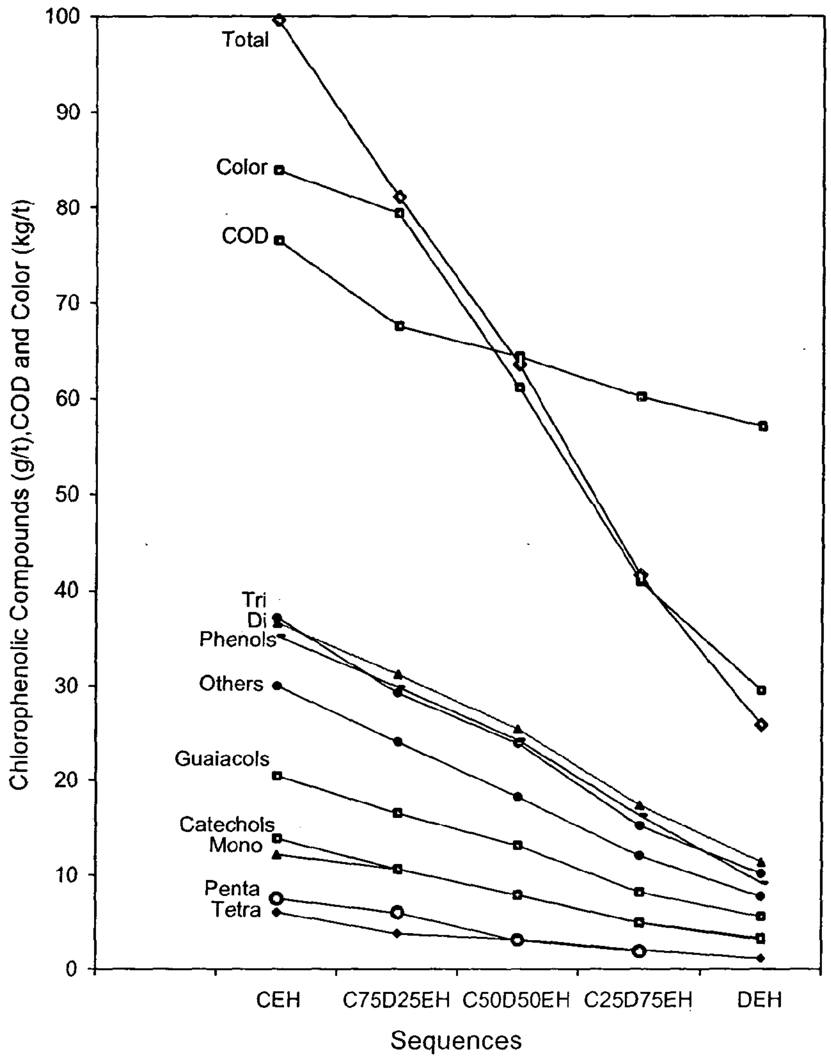


Fig 4.23 **Effect of replacement of chlorine by chlorine dioxide on the generation of chlorophenolics, COD and color in E stage effluent.**

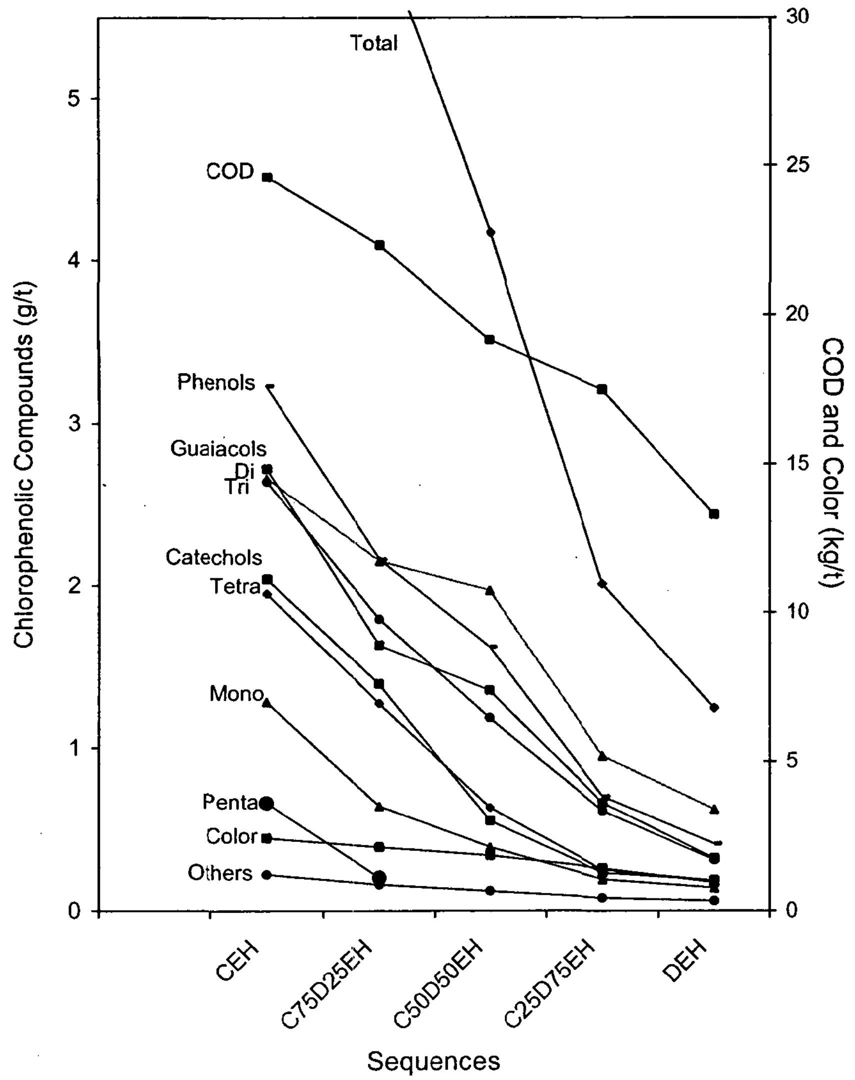


Fig 4.24 **Effect of replacement of chlorine by chlorine dioxide on the generation of chlorophenolics, COD and color in H stage effluent.**

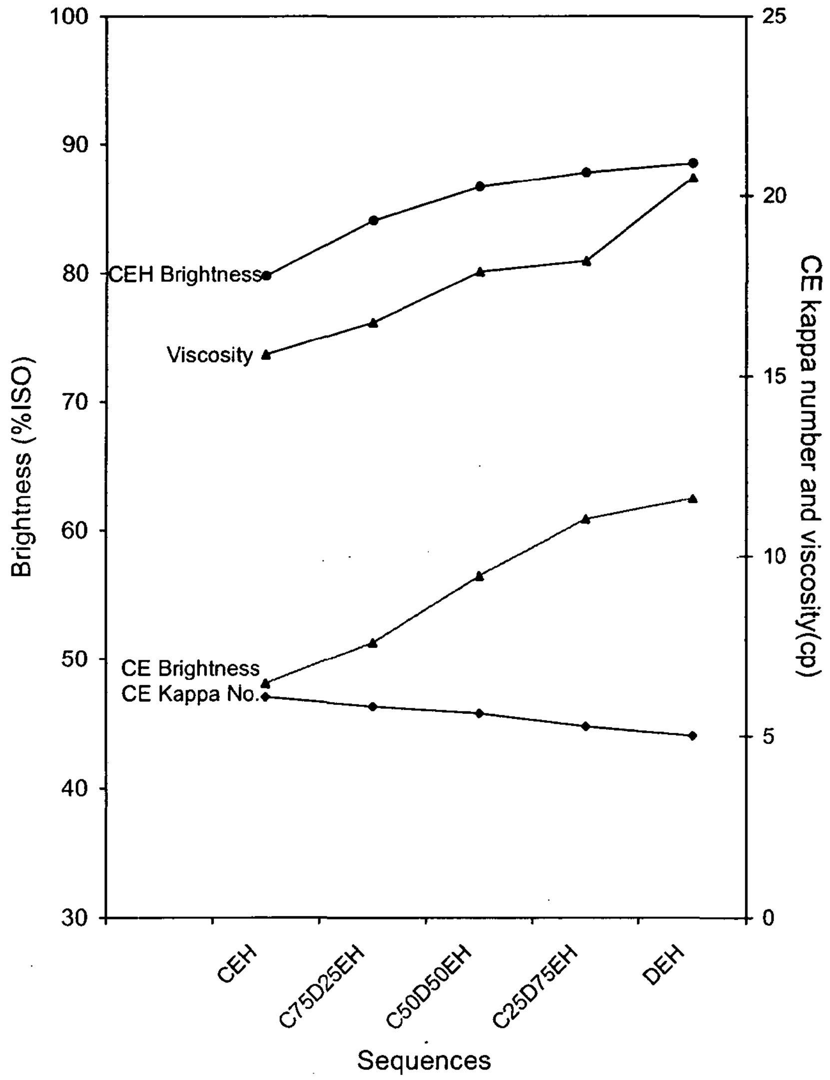


Fig 4.25 **Effect of replacement of chlorine by chlorine dioxide on brightness, viscosity and CE kappa number.**

Table 4.21 Effect of splitting of chlorine dose in C stage (with and without washing) on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Normal CEH			C (splitting) EH					
				Without pulp washing			With pulp washing		
	C	E	H	$C_{splitting}$	E	H	$C_{splitting}$	E	H
2,4 Dichlorophenol	2.94	4.24	1.53	1.54	2.36	0.57	1.50	2.24	0.56
2,5 Dichlorophenol	1.04	1.19	-	0.63	0.74	-	0.61	0.72	-
2,3-Dichlorophenol	0.22	-	-	0.12	-	-	0.10	-	-
3-chloroguaiacol	-	0.37	-	-	0.19	-	-	0.17	-
2,6 Dichlorophenol	0.32	3.92	-	0.18	2.45	-	0.15	2.32	-
4-chlorophenol	0.64	-	-	0.37	-	-	0.34	-	-
3-chlorophenol	0.78	2.16	0.28	0.41	1.27	0.10	0.39	1.25	0.09
4-chloroguaiacol	0.06	-	0.34	0.03	-	0.18	0.02	-	0.17
5-chloroguaiacol	-	1.78	0.18	-	0.98	0.06	-	0.76	0.06
6-chloroguaiacol	-	-	-	-	-	-	-	-	-
2-chlorophenol	0.26	-	-	0.12	-	-	0.11	-	-
2,3,5-Trichlorophenol	0.18	3.73	-	0.08	2.39	-	0.08	2.28	-
2,4,6-Trichlorophenol	2.79	4.94	0.76	1.84	2.61	0.27	1.81	2.53	0.20
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.96	6.91	-	0.57	3.83	-	0.52	3.64	-
3,6 Dichloroguaiacol	0.11	-	-	0.05	-	-	0.04	-	-
3,4 Dichloroguaiacol	0.33	5.37	-	0.19	3.35	-	0.16	3.21	-
3,4-Dichlorocatechol	4.65	2.34	-	2.34	1.40	-	2.02	1.27	-
3,4-Dicholorophenol	0.99	-	-	0.41	-	-	0.29	-	-
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.45	0.14	-	0.26	-	-	0.20	-

5-Chlorovanillin	2.14	3.66	-	1.07	2.03	-	0.98	1.89	-
5,6 Dichloroguaiacol	-	3.18	0.27	-	1.67	0.15	-	1.58	0.15
4-Chlorocatechol	3.72	-	-	1.85	-	-	1.64	-	-
3,5-Dichlorocatechol	6.15	2.10	-	3.07	1.16	-	2.93	1.12	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.92	0.68	-	0.48	0.42	-	0.45	0.39	-
3,5,6-Trichloroguaiacol	-	0.50	-	-	0.28	-	-	0.24	-
3,4,6-Trichloroguaiacol	-	2.27	-	-	1.26	-	-	1.17	-
3,5-Dichlorosyringol	-	1.60	0.35	-	0.94	0.12	-	0.90	0.12
3,4,5-Trichloroguaiacol	2.41	3.34	0.96	1.26	1.96	0.53	1.20	1.72	0.49
3-Chlorocatechol	4.78	-	-	2.51	-	-	2.26	-	-
6-Chlorovanillin	0.68	2.01	-	0.32	1.16	-	0.28	1.08	-
3,6-Dichlorocatechol	0.94	0.62	-	0.54	0.36	-	0.44	0.34	-
4,5,6-Trichloroguaiacol	0.62	0.48	-	0.26	0.29	-	0.25	0.26	-
2-Chlorosyringaldehyde	1.19	2.18	0.48	0.57	1.21	0.18	0.52	1.13	0.13
4,5-Dichlorocatechol	0.85	-	-	0.42	-	-	0.39	-	-
Pentachlorophenol	0.69	7.51	0.66	0.37	3.85	-	0.30	3.62	-
3,4,5-Trichlorocatechol	7.18	6.10	-	3.49	3.58	-	3.11	3.43	-
Tetrachloroguaiacol	1.75	2.70	0.83	0.88	1.68	0.37	0.82	1.66	0.32
Trichlorosyringol	0.50	8.89	-	0.31	4.76	-	0.27	4.15	-
3,4,6-Trichlorocatechol	1.03	-	0.92	0.49	-	0.32	0.45	-	0.28
2,6-Dichlorosyringaldehyde	0.29	7.18	-	0.16	3.89	-	0.12	3.64	-
5,6-Dichlorovanillin	0.71	4.46	0.37	0.36	2.73	0.14	0.34	4.58	0.12
Tetrachlorocatechol	4.32	2.70	1.12	1.78	1.50	0.48	1.05	1.47	0.33
Total	**57.14**	**99.56**	**9.19**	**29.07**	**56.56**	**3.47**	**25.94**	**54.96**	**3.02**

C Stage bleaching conditions: $C_{end\ pH} \geq 2$, Temperature 30°C and Consistency 3%.

Table 4.22 Effect of splitting of chlorine dose in C stage on COD generation

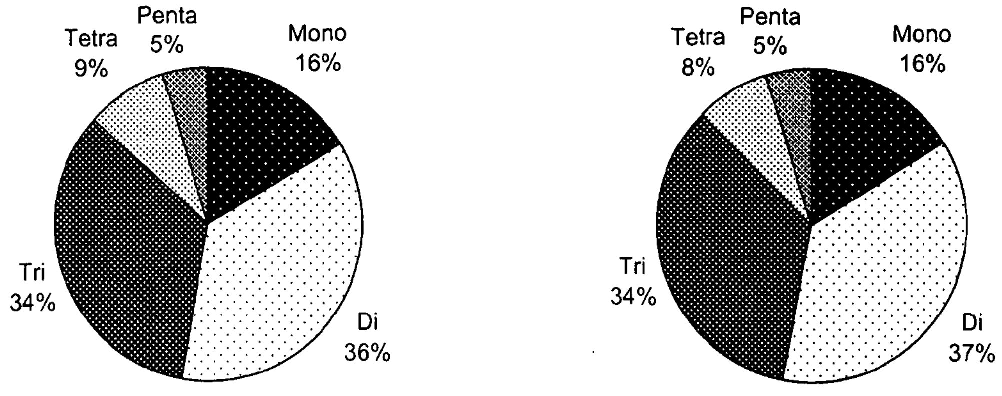
Stage/sequences	COD (kg/t) at different sequences		
	Normal CEH	C(splitting)EH	
		Without pulp washing	With pulp washing
C	31.3	23.9	22.4
E	76.5	71.8	68.7
H	24.6	21.9	21.5
Total	**132.4**	**117.6**	**112.6**

Table 4.23 Effect of splitting of chlorine dose in C stage on color generation

Stage/sequences	Color (kg/t) at different sequences		
	Normal CEH	C(splitting)EH	
		Without pulp washing	With pulp washing
C	43.8	32.7	29.7
E	83.9	71.6	70.1
H	2.4	0.9	0.9
Total	**130.1**	**105.2**	**100.7**

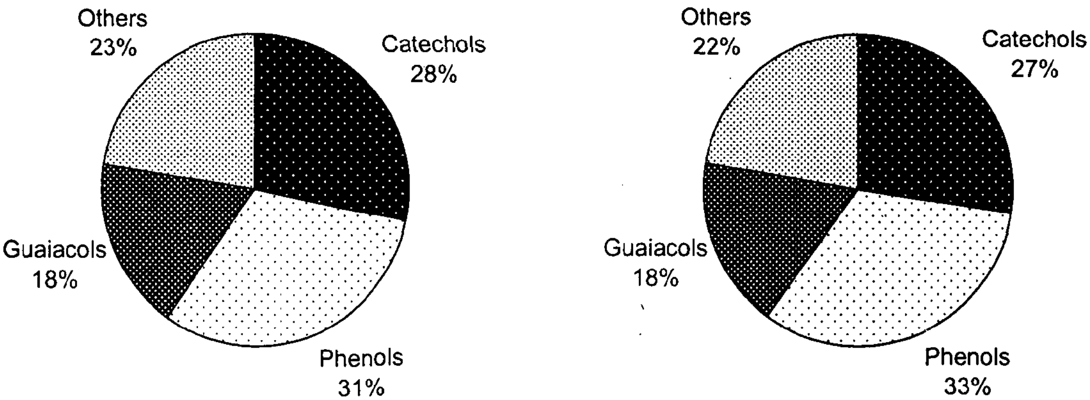
Table 4.24 Effect of splitting of chlorine dose in C stage on CE kappa no, brightness and CED viscosity

Parameter/ sequences	Different parameter at different sequences		
	Normal CEH	C(splitting)EH	
		Without pulp washing	With pulp washing
CE Kappa no	6.0	5.9	5.7
CE Brightness(%ISO)	48.1	48.9	48.6
CEH Brightness(%ISO)	79.8	80.2	80.9
Viscosity(cp)	15.6	17.5	18.9



C(splitting without washing)EH

C(splitting with washing)EH



C(splitting without washing)EH

C(splitting with washing)EH

Fig. 4.26 **The contribution of different chlorophenolic compounds at splitting of chlorine dose in C stage (with and without washing).**

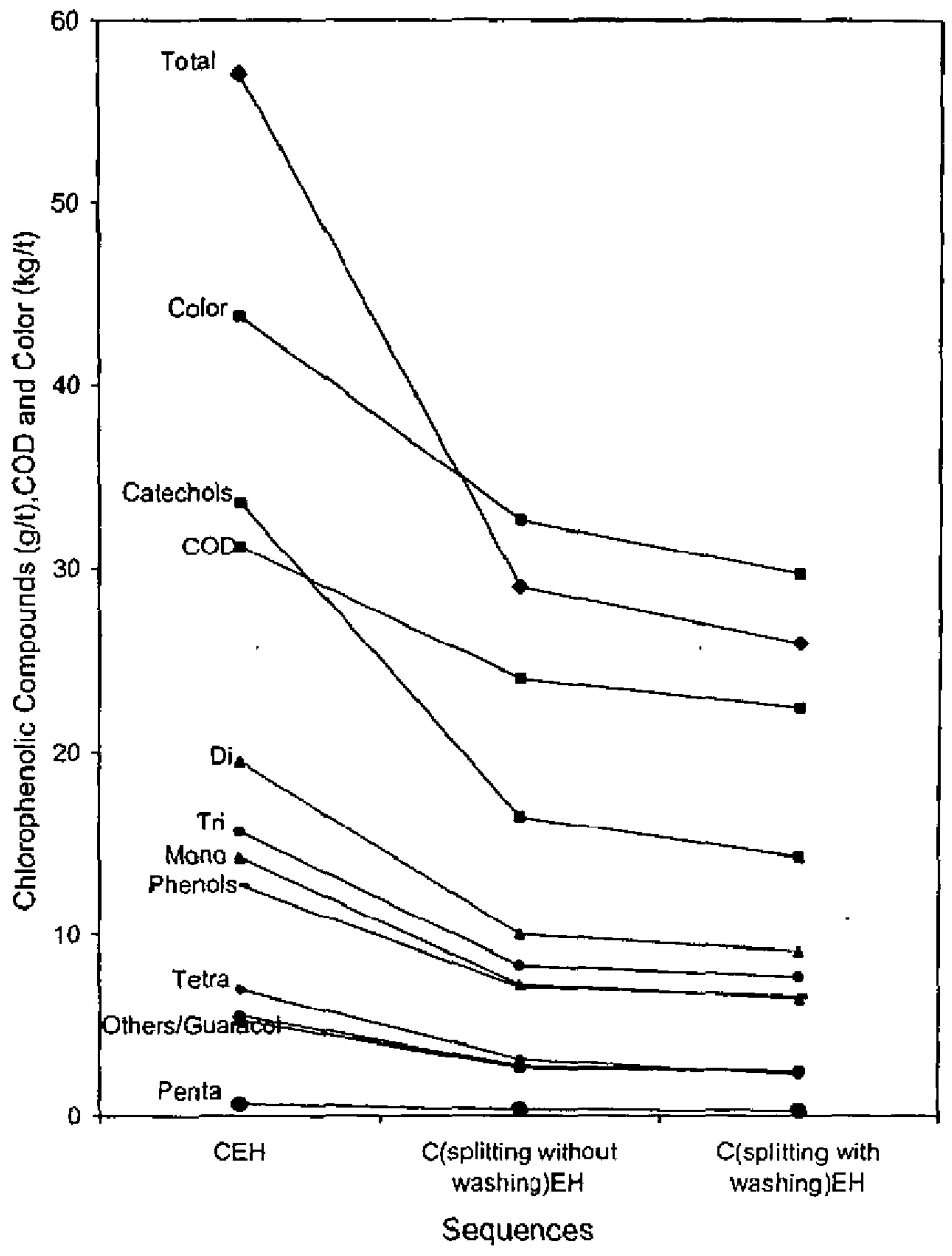


Fig 4.27 Effect of splitting of chlorine dose in C stage (with and without washing) on the generation of chlorophenolics, COD and color in C stage effluent.

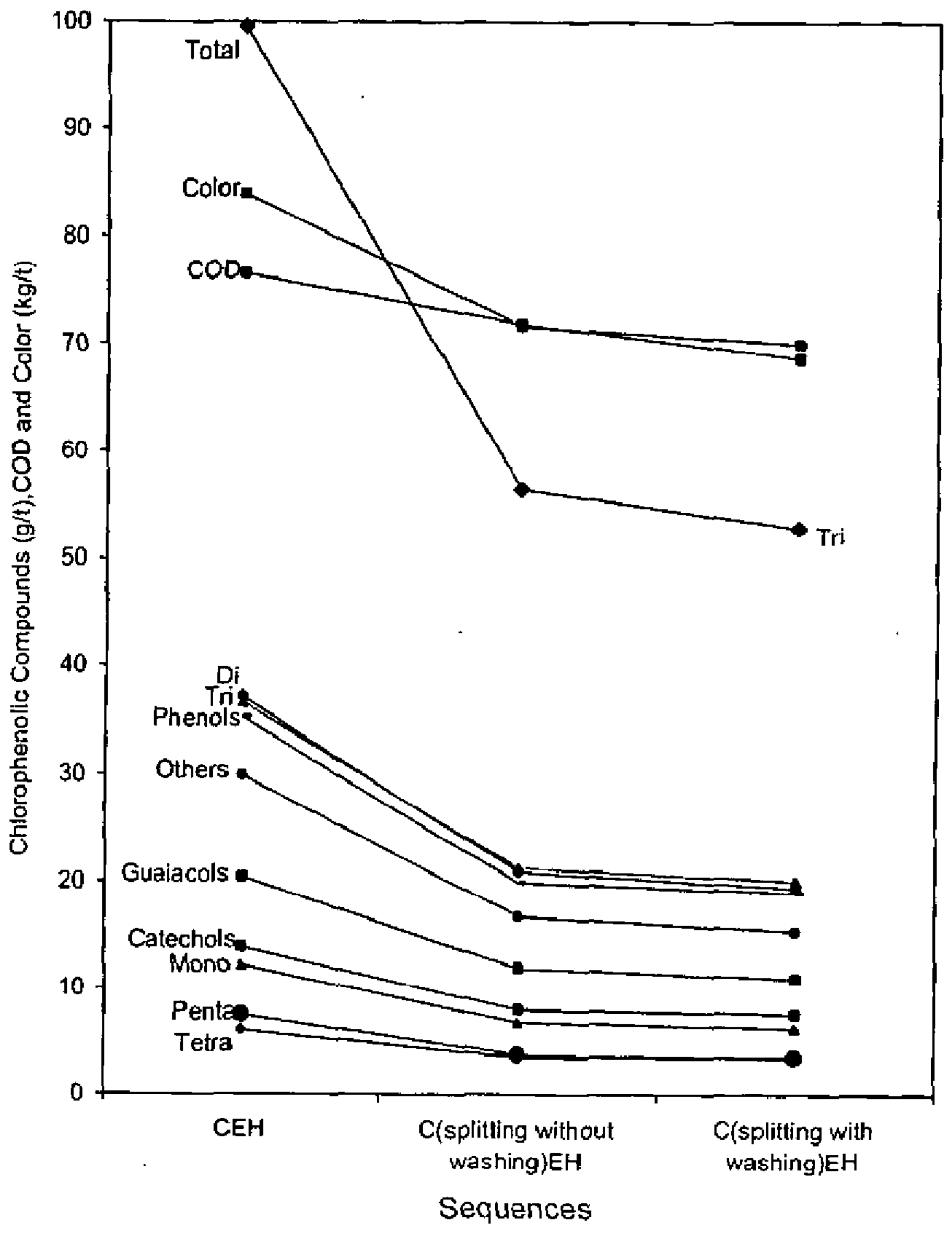


Fig 4.28 Effect of splitting of chlorine dose in C stage (with and without washing) on the generation of chlorophenolics, COD and color in E stage effluent.

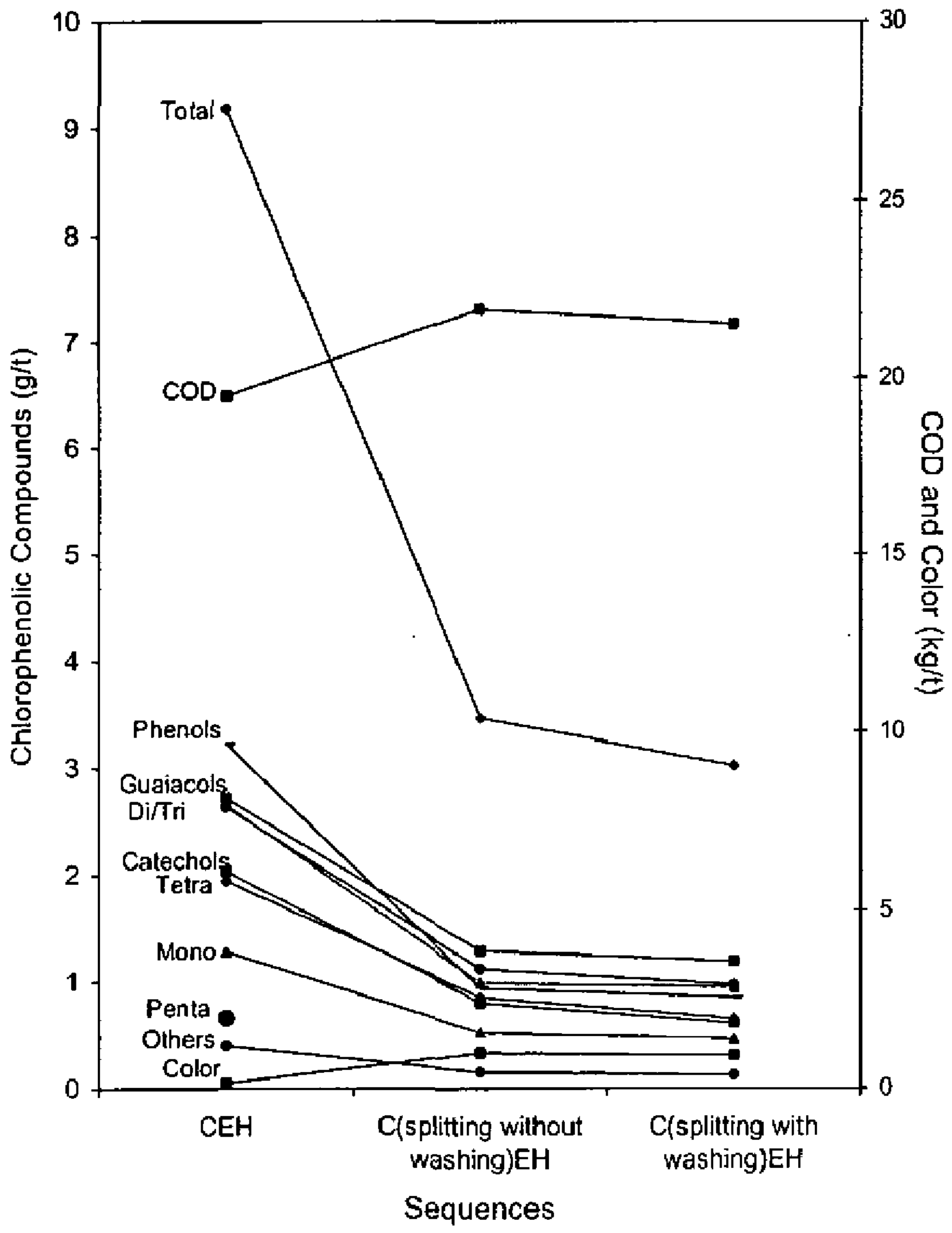


Fig 4.29 Effect of splitting of chlorine dose in C stage (with and without washing) on the generation of chlorophenolics, COD and color in H stage effluent.

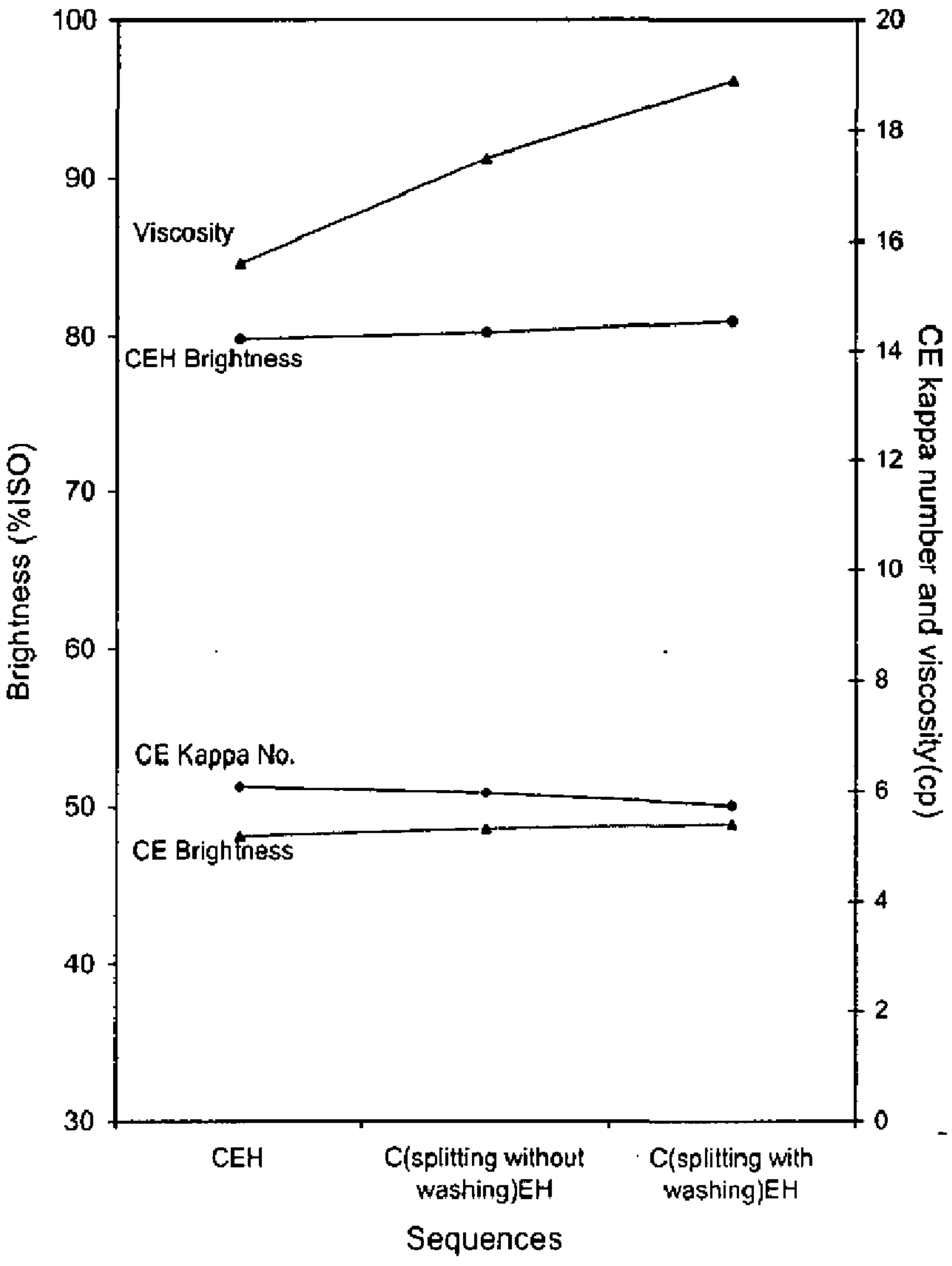


Fig 4.30 Effect of splitting of chlorine dose in C stage (with and without washing) on brightness, viscosity and CE kappa number.

Table 4.25 Effect of changed sequence on the formation of chlorophenolic compounds in various effluents

Name of the Compound	Chlorophenolic compounds (g/t OD pulp) at different sequences														
	Normal CEH			CED			CE_pH			OCEH			ODED		
	C	E	H	C	E	D	C	E_p	H	C	E	H	D	E	D
2,4 Dichlorophenol	2.94	4.24	1.53	2.94	4.24	0.38	2.94	0.74	0.31	0.73	1.17	0.36	0.25	1.03	0.19
2,5 Dichlorophenol	1.04	1.19	-	1.04	1.19	-	1.04	0.22	-	0.27	0.32	-	0.08	0.28	-
2,3-Dichlorophenol	0.22	-	-	0.22	-	-	0.22	-	-	0.06	-	-	-	-	-
3-chloroguaiacol	-	0.37	-	-	0.37	-	-	0.07	-	-	0.10	-	-	0.08	-
2,6 Dichlorophenol	0.32	3.92	-	0.32	3.92	-	0.32	1.73	-	0.08	1.08	-	0.03	0.96	-
4-chlorophenol	0.64	-	-	0.64	-	-	0.64	-	-	0.16	-	-	0.05	-	-
3-chlorophenol	0.78	2.16	0.28	0.78	2.16	0.07	0.78	1.01	0.05	0.20	0.61	0.07	0.07	0.57	0.04
4-chloroguaiacol	0.06	-	0.34	0.06	-	0.09	0.06	-	0.08	0.02	-	0.01	-	-	-
5-chloroguaiacol	-	1.78	0.18	-	1.78	0.03	-	0.34	0.02	-	0.48	0.05	-	0.34	0.04
6-chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-chlorophenol	0.26	-	-	0.26	-	-	0.26	-	-	0.07	-	-	0.03	-	-
2,3,5-Trichlorophenol	0.18	3.73	-	0.18	3.73	-	0.18	0.67	-	0.05	1.06	-	0.02	0.82	-
2,4,6-Trichlorophenol	2.79	4.94	0.76	2.79	4.94	0.17	2.79	1.25	0.13	0.68	1.33	0.18	0.21	1.15	0.16
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.96	6.91	-	0.96	6.91	-	0.96	1.38	-	0.26	1.86	-	0.09	1.72	-
3,6 Dichloroguaiacol	0.11	-	-	0.11	-	-	0.11	-	-	0.03	-	-	-	-	-
3,4 Dichloroguaiacol	0.33	5.37	-	0.33	5.37	-	0.33	1.07	-	0.09	1.53	-	0.03	1.28	-
3,4-Dichlorocatechol	4.65	2.34	-	4.65	2.34	-	4.65	0.45	-	1.22	0.65	-	0.39	0.55	-
3,4-Dicholorophenol	0.99	-	-	0.99	-	-	0.99	-	-	0.26	-	-	0.09	-	-
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.45	0.14	-	0.45	0.04	-	0.01	-	-	0.12	-	-	0.08	-
5-Chlorovanillin	2.14	3.66	-	2.14	3.66	-	2.14	1.21	-	0.53	1.01	-	0.17	0.83	-
5,6 Dichloroguaiacol	-	3.18	0.27	-	3.18	0.07	-	1.03	0.03	-	0.99	0.67	-	0.64	0.31

4-Chlorocatechol	3.72	-	-	3.72	-	-	3.72	-	-	0.98	-	-	0.36	-	-
3,5-Dichlorocatechol	6.15	2.10	-	6.15	2.10	-	6.15	0.84	-	1.62	0.60	-	0.54	0.52	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.92	0.68	-	0.92	0.68	-	0.92	0.03	-	0.24	0.19	-	0.08	0.11	-
3,5,6-Trichloroguaiacol	-	0.50	-	-	0.50	-	-	0.10	-	-	0.13	-	-	0.07	-
3,4,6-Trichloroguaiacol	-	2.27	-	-	2.27	-	-	0.95	-	-	0.75	-	-	0.65	-
3,5-Dichlorosyringol	-	1.60	0.35	-	1.60	0.09	-	0.43	0.07	-	0.66	0.09	-	0.54	-
3,4,5-Trichloroguaiacol	2.41	3.34	0.96	2.41	3.34	0.22	2.41	1.18	0.14	0.61	0.92	0.23	0.21	0.82	0.10
3-Chlorocatechol	4.78	-	-	4.78	-	-	4.78	-	-	1.22	-	-	0.43	-	-
6-Chlorovanillin	0.68	2.01	-	0.68	2.01	-	0.68	0.52	-	0.19	0.57	-	-	0.28	-
3,6-Dichlorocatechol	0.94	0.62	-	0.94	0.62	-	0.94	0.15	-	0.24	0.18	-	0.09	0.07	-
4,5,6-Trichloroguaiacol	0.62	0.48	-	0.62	0.48	-	0.62	0.09	-	0.16	0.13	-	0.06	0.05	-
2-Chlorosyringaldehyde	1.19	2.18	0.48	1.19	2.18	0.16	1.19	0.49	0.10	0.29	0.62	0.12	0.09	0.59	0.09
4,5-Dichlorocatechol	0.85	-	-	0.85	-	-	0.85	-	-	0.21	-	-	0.10	-	-
Pentachlorophenol	0.69	7.51	0.66	0.69	7.51	0.09	0.69	-	-	-	2.08	-	-	-	-
3,4,5-Trichlorocatechol	7.18	6.10	-	7.18	6.10	-	7.18	1.22	-	1.75	1.90	-	0.56	1.63	-
Tetrachloroguaiacol	1.75	2.70	0.83	1.75	2.70	0.21	1.75	-	-	0.48	0.75	0.20	0.17	0.70	0.13
Trichlorosyringol	0.50	8.89	-	0.50	8.89	-	0.50	1.58	-	0.13	2.46	-	0.04	1.94	-
3,4,6-Trichlorocatechol	1.03	-	0.92	1.03	-	0.23	1.03	-	0.16	0.14	-	0.23	0.04	-	-
2,6-Dichlorosyringaldehyde	0.29	7.18	-	0.29	7.18	-	0.29	1.38	-	0.08	1.99	-	-	1.62	-
5,6-Dichlorovanillin	0.71	4.46	0.37	0.71	4.46	0.09	0.71	0.96	0.05	0.18	1.31	0.10	0.07	1.05	-
Tetrachlorocatechol	4.32	2.70	1.12	4.32	2.70	0.28	4.32	0.51	0.11	1.12	0.74	0.19	0.36	0.51	-
Total	**57.14**	**99.56**	**9.19**	**57.14**	**99.56**	**2.22**	**57.14**	**21.61**	**1.25**	**14.35**	**28.29**	**2.5**	**4.71**	**21.48**	**1.06**

C stage bleaching conditions: Temperature 30 - 70°C, Consistency 3 - 10% and $C_{end\ pH} \geq 2-4$.

Table 4.26 Effect of changed sequence on COD generation

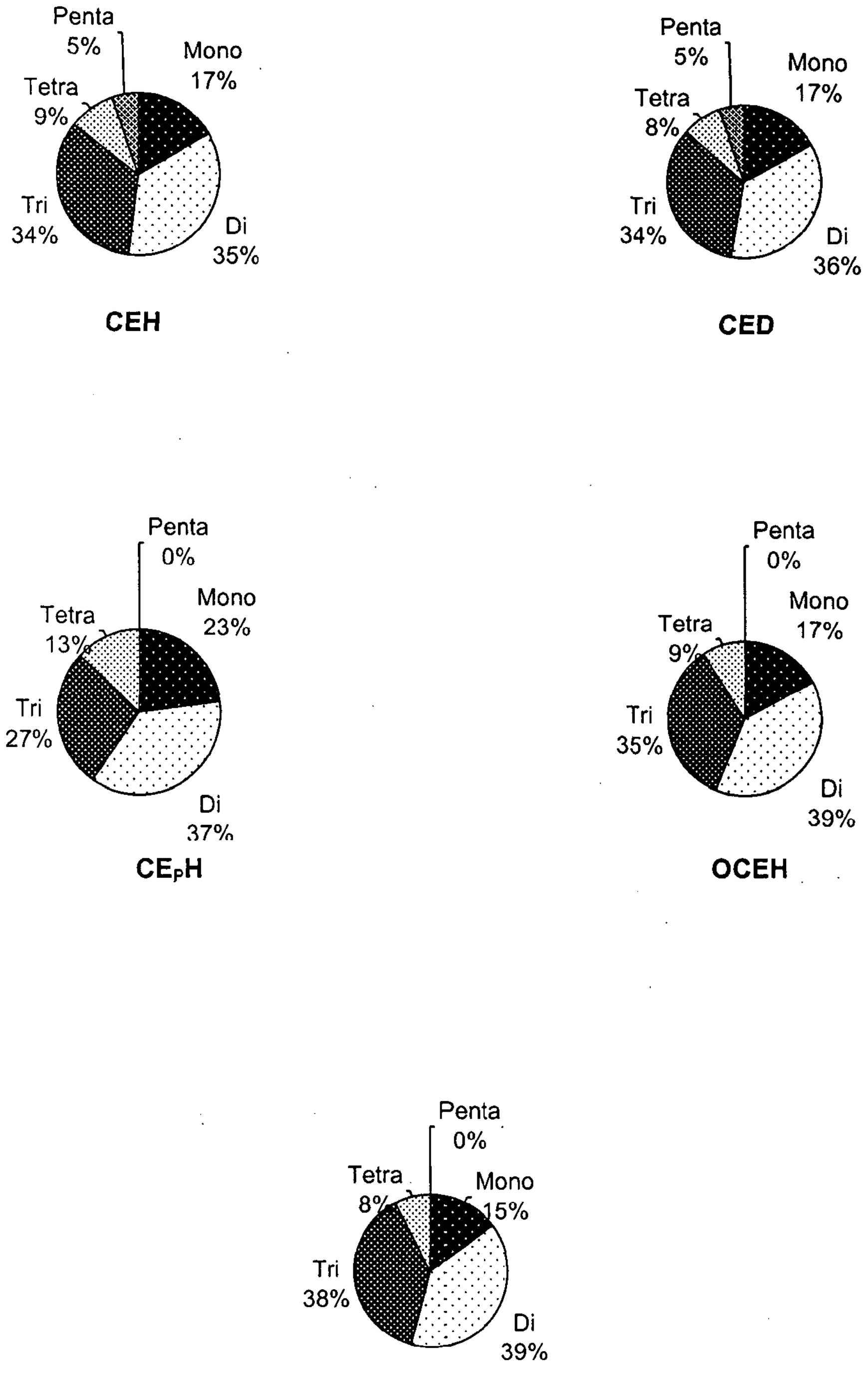
Stage/sequences	COD (kg/t OD pulp) at different sequences				
	Normal CEH	CED	CE_pH	OCEH	ODED
C	31.3	31.3	31.3	15.9	8.1
E	76.5	76.5	46.7	63.4	50.4
H	24.6	19.5	15.4	15.7	5.9
Total	**132.4**	**127.3**	**93.4**	**95.0**	**64.4**

Table 4.27 Effect of changed sequence on color generation

Stage/sequences	Color (kg/t OD pulp) at different sequences				
	Normal CEH	CED	CE_pH	OCEH	ODED
C	43.8	43.8	43.8	30.9	27.8
E	83.9	83.9	42.4	40.3	29.6
H	2.4	0.2	1.2	0.9	0.5
Total	**130.1**	**127.9**	**87.4**	**72.1**	**57.9**

Table 4.28 Effect of changed sequence on CE kappa no, brightness, and CED viscosity

Parameter/sequences	Different parameter at different sequences				
	Normal CEH	CED	CE_pH	OCEH	ODED
CE Kappa No	6.0	6.0	5.2	4.8	4.5
CE Brightness(%ISO)	48.1	48.1	55.9	60.1	62.4
CEH Brightness(%ISO)	79.8	82.1	81.0	87.0	89.6
Viscosity(cp)	15.6	21.3	16.4	14.8	15.0



CEH **CED** **CE$_P$H** **OCEH** **ODED**

Fig. 4.31 The contribution of different chlorophenolic compounds in different sequences

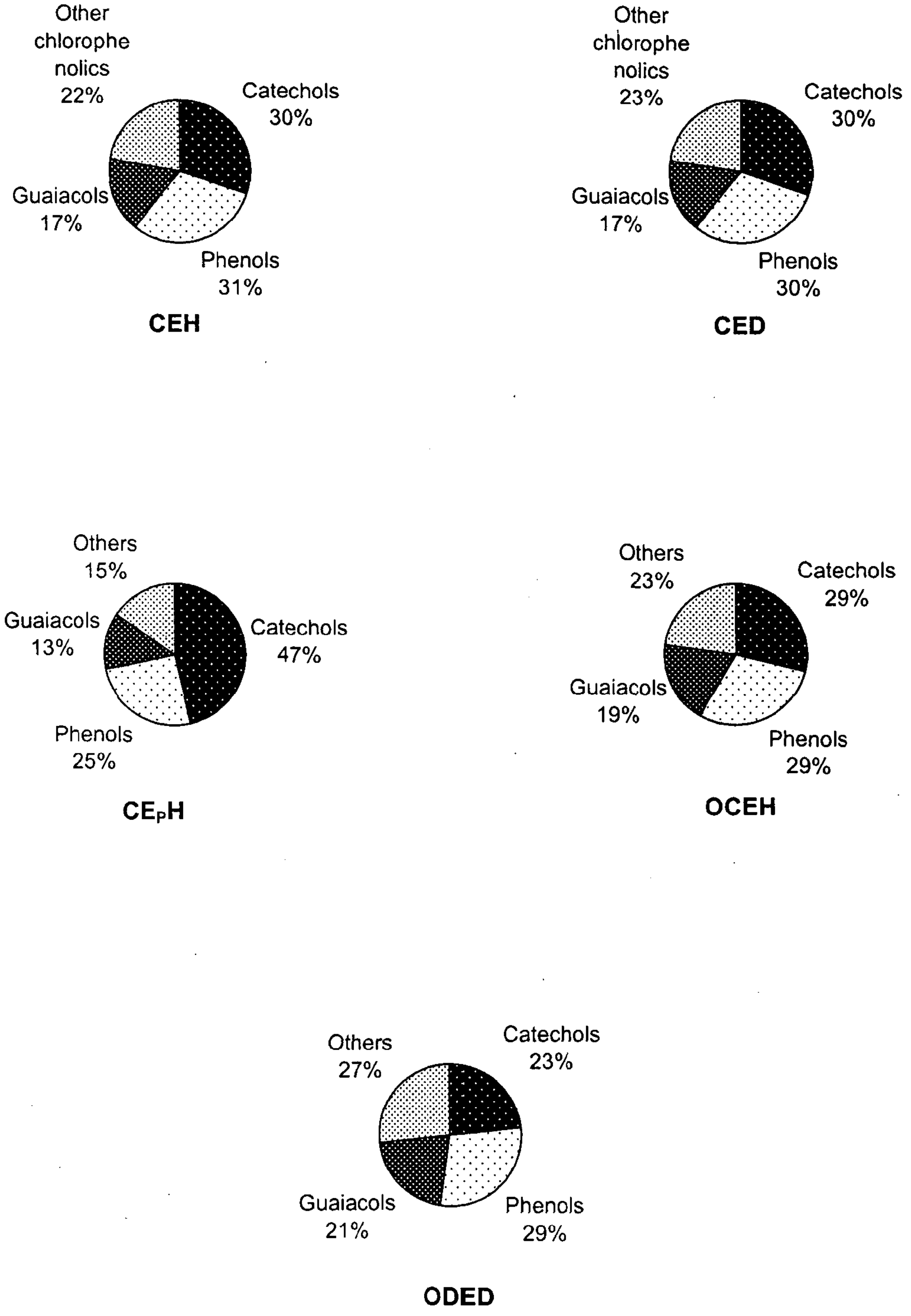


Fig. 4.32 The contribution of different chlorophenolic compounds in different sequences

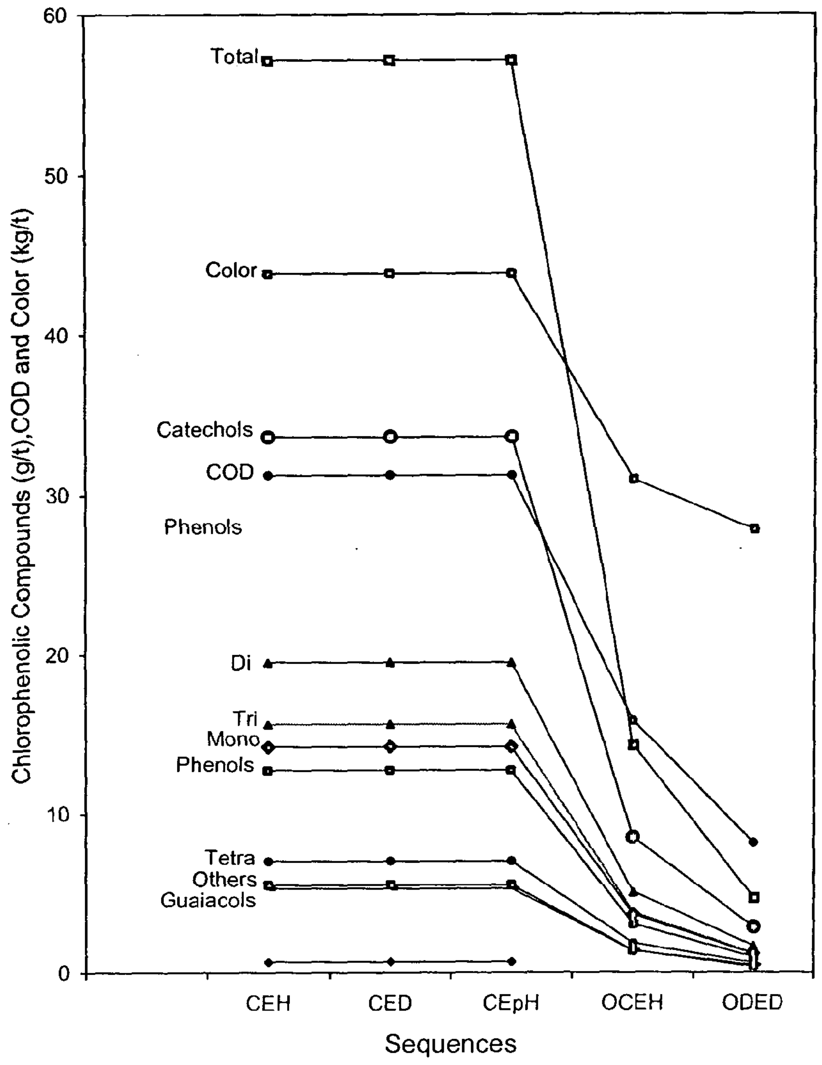


Fig 4.33 **Effect of changed sequences on the generation of chlorophenolics, COD and color in C stage effluent.**

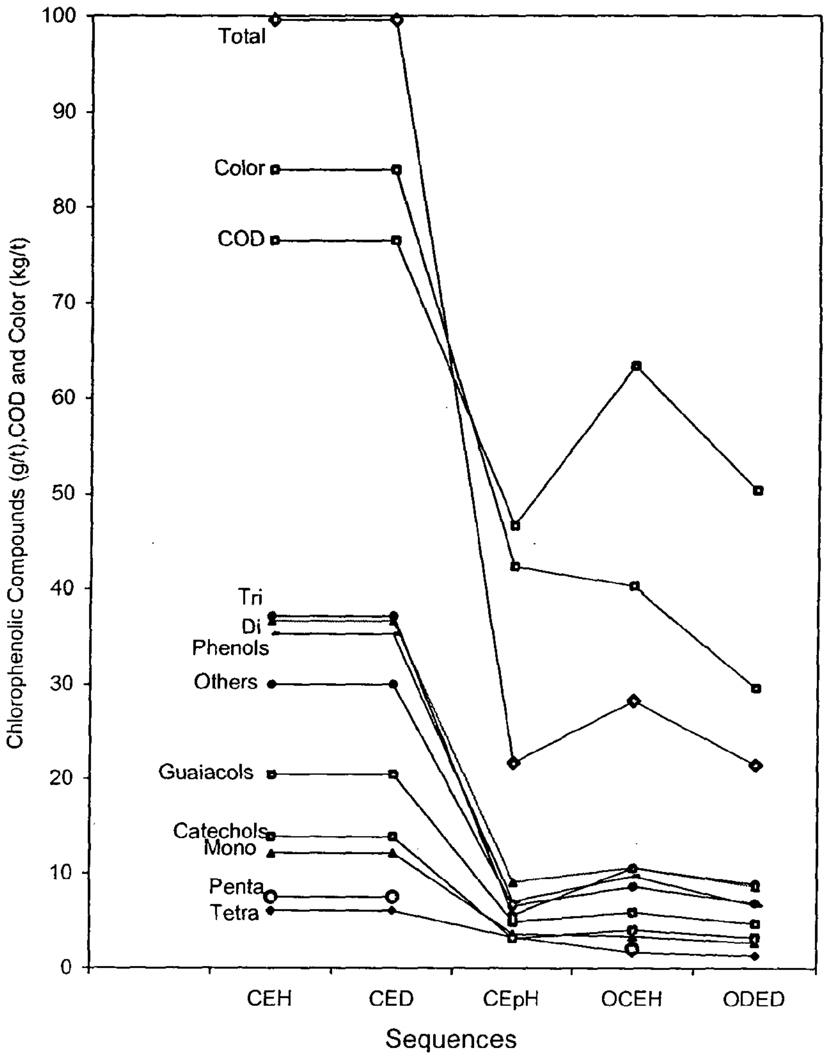


Fig 4.34 **Effect of changed sequences on the generation of chlorophenolics, COD and color in E stage effluent.**

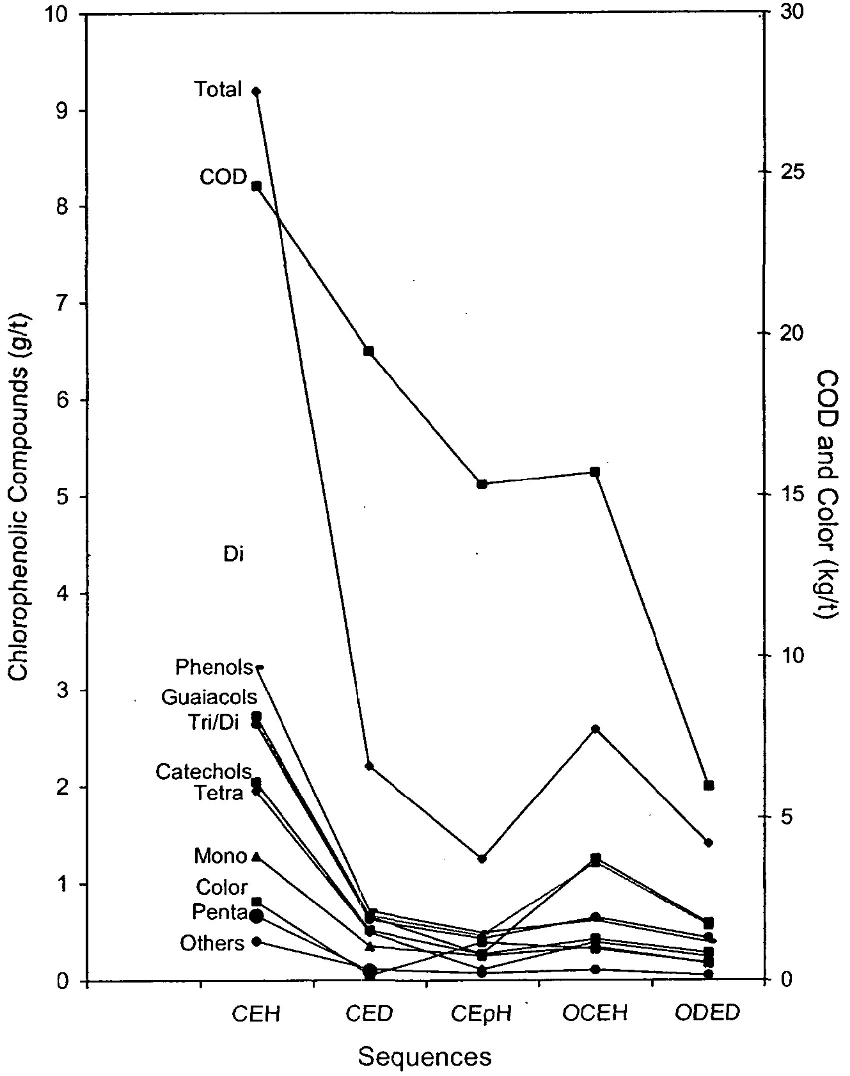


Fig 4.35 **Effect of changed sequences on the generation of chlorophenolics, COD and color in H stage effluent.**

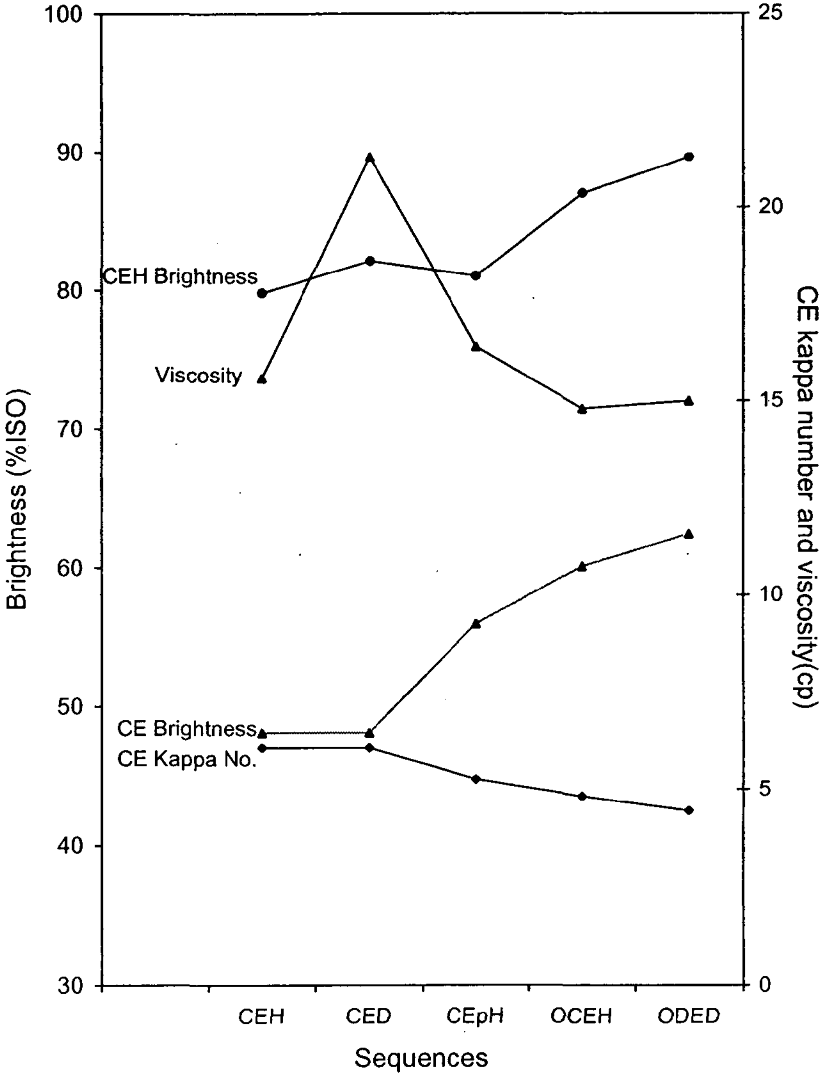


Fig 4.36 **Effect of changed sequences on brightness, viscosity and CE kappa number.**

Table 4.29 Estimation of chlorophenolic compounds in various effluents obtained by bleaching pulp when 80% target brightness achieved by different sequences

Name of the Compound	Chlorophenolics compounds (g/t OD pulp) at different sequences														
	Normal CEH			$D_{50}C_{50}EH$			$C_{splitting}EH$			ODED			Modified CEH		
	C	E	H	$D_{50}C_{50}$	E	H	$C_{splitting}$	E	H	D	E	D	C	E	H
2,4 Dichlorophenol	2.94	4.24	1.53	3.05	2.85	1.09	1.46	2.27	0.60	0.20	0.76	0.16	2.49	3.68	1.41
2,5 Dichlorophenol	1.04	1.19	-	1.37	0.93	-	0.54	0.68	-	0.07	0.22	-	0.77	0.77	-
2,3-Dichlorophenol	0.22	-	-	0.71	-	-	0.09	-	-	-	-	-	0.09	-	-
3-chloroguaiacol	-	0.37	-	-	0.17	-	-	0.20	-	-	0.06	-	-	0.25	-
2,6 Dichlorophenol	0.32	3.92	-	0.34	2.26	-	0.12	2.36	-	0.03	0.81	-	0.23	3.41	-
4-chlorophenol	0.64	-	-	0.56	-	-	0.33	-	-	0.05	-	-	0.52	-	-
3-chlorophenol	0.78	2.16	0.28	0.98	1.18	-	0.32	1.21	0.06	0.07	0.40	0.03	0.56	1.67	0.23
4-chloroguaiacol	0.06	-	0.34	0.15	-	0.06	-	-	-	-	-	-	0.04	-	0.29
5-chloroguaiacol	-	1.78	0.18	-	1.15	0.04	-	0.93	0.06	-	0.12	0.03	-	1.32	0.14
6-chloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-chlorophenol	0.26	-	-	0.11	-	-	0.10	-	-	0.02	-	-	0.13	-	-
2,3,5-Trichlorophenol	0.18	3.73	-	0.17	2.21	-	0.07	2.32	-	0.01	0.59	-	0.12	2.53	-
2,4,6-Trichlorophenol	2.79	4.94	0.76	2.35	3.04	0.38	1.74	2.15	0.18	0.18	0.96	0.12	1.94	3.74	0.65
2,4,5-Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4 Trichlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,6 Trichlorophenol	0.96	6.91	-	1.06	4.87	-	0.42	3.18	-	0.06	1.54	-	0.87	4.56	-
3,6 Dichloroguaiacol	0.11	-	-	0.01	-	-	0.03	-	-	-	-	-	0.09	-	-
3,4 Dichloroguaiacol	0.33	5.37	-	0.23	3.58	-	0.11	3.26	-	0.06	1.12	-	0.25	4.69	-
3,4-Dichlorocatechol	4.65	2.34	-	2.84	1.19	-	1.93	1.15	-	0.28	0.36	-	3.22	1.87	-
3,4-Dicholorophenol	0.99	-	-	1.05	-	-	0.35	-	-	0.10	-	-	0.59	-	-
4,5 Dichloroguaiacol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4,6 Dichloroguaiacol	-	0.45	0.14	-	0.32	0.08	-	0.22	-	-	0.53	-	-	0.26	0.12

5-Chlorovanillin	2.14	3.66	-	1.11	1.66	-	1.00	1.94	-	0.16	0.69	-	1.71	2.97	-
5,6 Dichloroguaiacol	-	3.18	0.27	-	1.54	0.18	-	1.46	0.12	-	0.41	0.29	-	2.53	0.24
4-Chlorocatechol	3.72	-	-	1.79	-	-	1.78	-	-	0.35	-	-	2.63	-	-
3,5-Dichlorocatechol	6.15	2.10	-	2.92	1.07	-	2.63	1.09	-	0.52	0.33	-	5.42	1.98	-
2,3,5,6-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,5-Tetrachlorophenol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2,3,4,6-Tetrachlorophenol	0.92	0.68	-	0.63	0.33	-	0.44	0.28	-	0.05	0.07	-	0.66	0.52	-
3,5,6-Trichloroguaiacol	-	0.50	-	-	0.25	-	-	0.27	-	-	0.04	-	-	0.41	-
3,4,6-Trichloroguaiacol	-	2.27	-	-	0.98	-	-	1.09	-	-	0.57	-	-	1.68	-
3,5-Dichlorosyringol	-	1.60	0.35	-	0.74	0.18	-	0.85	0.14	-	0.28	-	-	1.19	0.32
3,4,5-Trichloroguaiacol	2.41	3.34	0.96	2.18	1.15	0.57	1.12	1.87	0.30	0.19	0.63	0.08	2.01	2.67	0.81
3-Chlorocatechol	4.78	-	-	3.25	-	-	2.35	-	-	0.30	-	-	4.08	-	-
6-Chlorovanillin	0.68	2.01	-	0.21	0.93	-	0.24	1.14	-	-	0.19	-	0.52	1.84	-
3,6-Dichlorocatechol	0.94	0.62	-	0.49	0.36	-	0.41	0.33	-	0.08	0.06	-	0.46	0.57	-
4,5,6-Trichloroguaiacol	0.62	0.48	-	0.18	0.20	-	0.19	0.25	-	0.06	0.03	-	0.24	0.29	-
2-Chlorosyringaldehyde	1.19	2.18	0.48	0.80	1.15	0.10	0.50	1.16	0.17	0.08	0.38	0.05	0.69	1.61	0.43
4,5-Dichlorocatechol	0.85	-	-	0.63	-	-	0.38	-	-	0.13	-	-	0.28	-	-
Pentachlorophenol	0.69	7.51	0.66	0.24	2.87	-	0.16	3.72	-	-	-	-	0.31	6.75	0.52
3,4,5-Trichlorocatechol	7.18	6.10	-	4.59	3.12	-	2.54	3.44	-	0.47	1.14	-	6.19	5.21	-
Tetrachloroguaiacol	1.75	2.70	0.83	0.62	1.54	0.19	0.63	1.61	0.29	0.15	0.47	0.10	1.28	1.84	0.64
Trichlorosyringol	0.50	8.89	-	0.30	2.81	-	0.27	4.50	-	0.03	1.60	-	0.34	7.13	-
3,4,6-Trichlorocatechol	1.03	-	0.92	0.56	-	0.17	0.42	-	0.25	0.03	-	0.12	0.67	-	0.55
2,6-Dichlorosyringaldehyde	0.29	7.18	-	0.12	4.77	-	0.18	3.68	-	-	1.39	-	0.15	6.16	-
5,6-Dichlorovanillin	0.71	4.46	0.37	0.55	2.19	0.28	0.40	2.41	0.17	.084	0.85	0.06	0.70	3.32	0.26
Tetrachlorocatechol	4.32	2.70	1.12	1.18	0.76	0.16	1.65	1.23	0.38	0.23	0.27	0.08	3.25	2.63	0.93
Total	**57.14**	**99.56**	**9.19**	**37.33**	**52.17**	**3.48**	**24.9**	**52.25**	**2.72**	**4.04**	**16.87**	**1.12**	**43.5**	**80.05**	**7.54**

C stage bleaching conditions: $C_{end\ pH} \geq 2 - 4$, Temperature 30 - 70°C and Consistency 3 - 10%.

Table 4.30 Effect on effluent COD generated during bleaching of pulp to 80% target brightness by different sequences

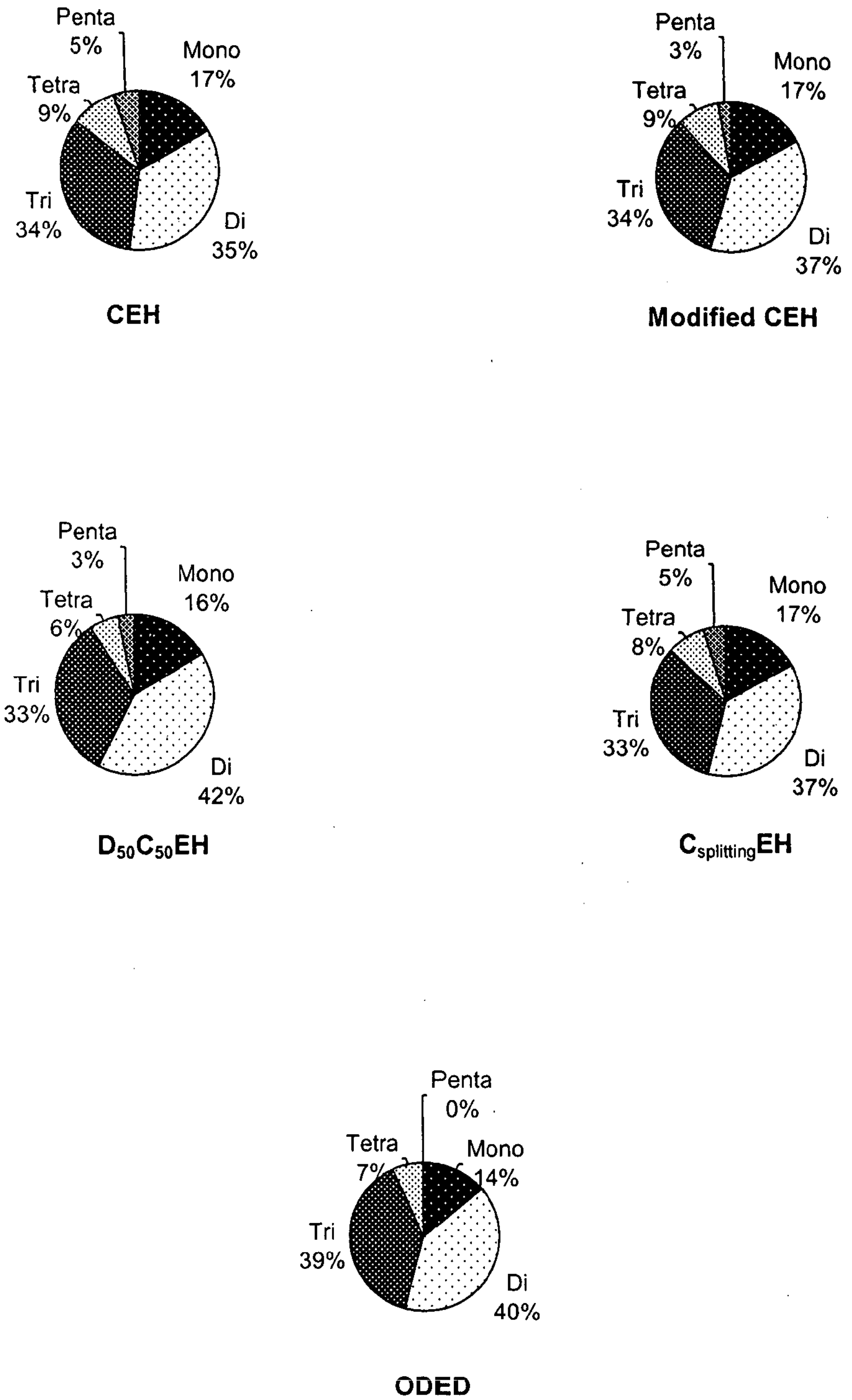
Stage/sequences	COD (kg/t OD pulp) at different sequences				
	Normal CEH	Change parameter	$C_{splitting}EH$	$D_{50}C_{50}EH$	ODED
C	31.3	27.3	22.8	16.5	9.2
E	76.5	73.7	64.3	48.1	35.9
H	24.6	19.2	14.4	11.9	8.5
Total	**132.4**	**120.2**	**101.5**	**76.5**	**53.6**

Table 4.31 Effect on effluent color generated during bleaching of pulp to 80% target brightness by different sequences

Stage/sequences	Color (kg/t OD pulp) at different sequences				
	Normal CEH	Change parameter	$C_{splitting}EH$	$D_{50}C_{50}EH$	ODED
C	43.8	34.1	30.9	22.9	18.4
E	83.9	72.3	63.2	35.4	24.8
H	2.4	2.2	1.8	1.3	1.1
Total	**130.1**	**108.6**	**95.9**	**59.6**	**44.3**

Table 4.32 Effect on CE kappa no, brightness, and CED viscosity of pulp bleached to 80% target brightness by different sequences

Parameter/sequences	Different parameter at different sequences				
	Normal CEH	Change parameter	$C_{splitting}EH$	$D_{50}C_{50}EH$	ODED
CE Kappa no	6.0	5.9	5.9	6.0	6.1
CE Brightness(%ISO)	48.1	48.0	48.2	48.1	48.3
CEH Brightness(%ISO)	79.8	80.00	80.3	80.6	80.9
Viscosity(cp)	15.6	12.3	18.7	19.9	13.8



CEH

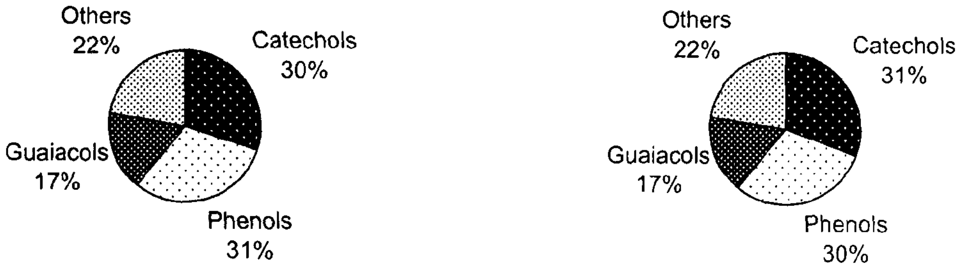
Modified CEH

$D_{50}C_{50}EH$

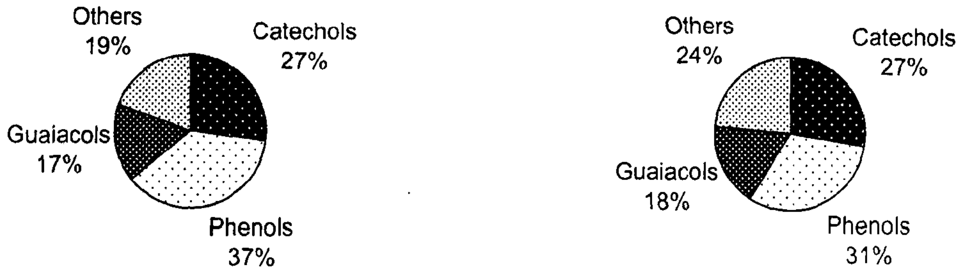
$C_{splitting}EH$

ODED

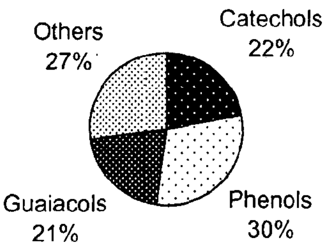
Fig. 4.37 The contribution of different chlorophenolic compounds in different sequences, when target brightness achieved.



CEH **Modified CEH**



$D_{50}C_{50}EH$ $C_{splitting}EH$



ODED

Fig. 4.38 The contribution of different chlorophenolic compounds in different sequences, when target brightness achieved.

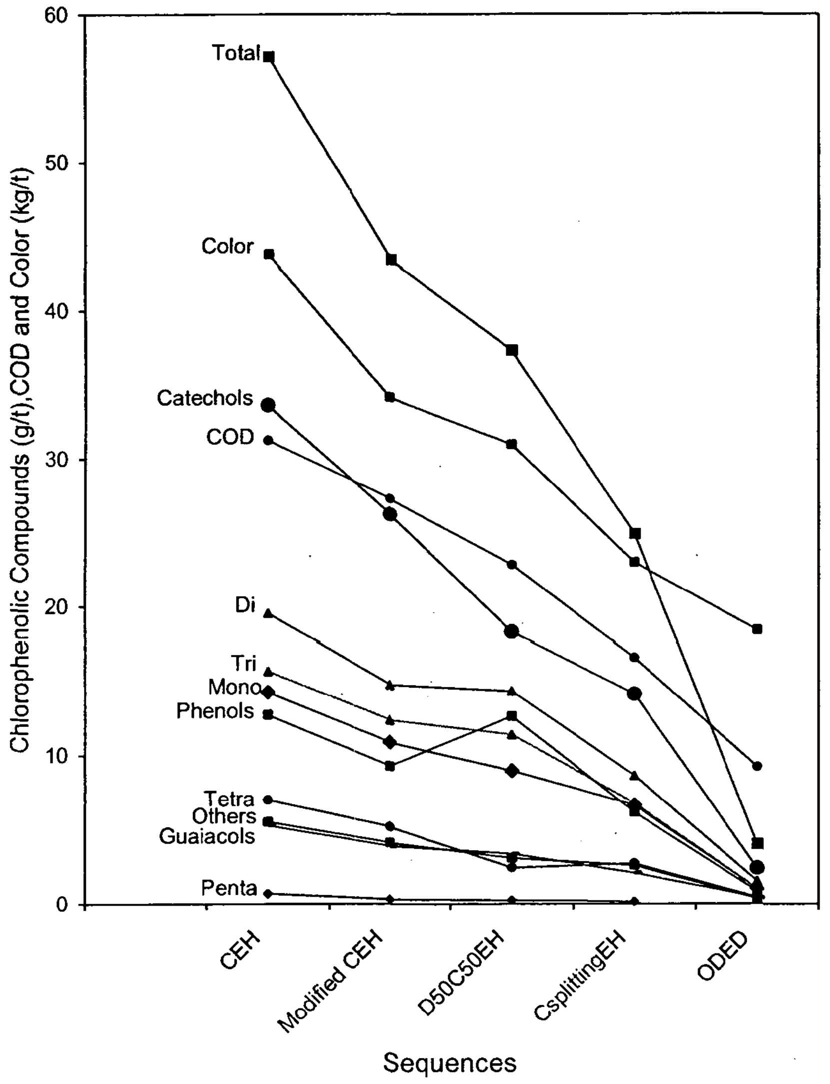


Fig 4.39 Effect of changed sequences on the generation of chlorophenolics, COD and color in C stage effluent, when target brightness achieved.

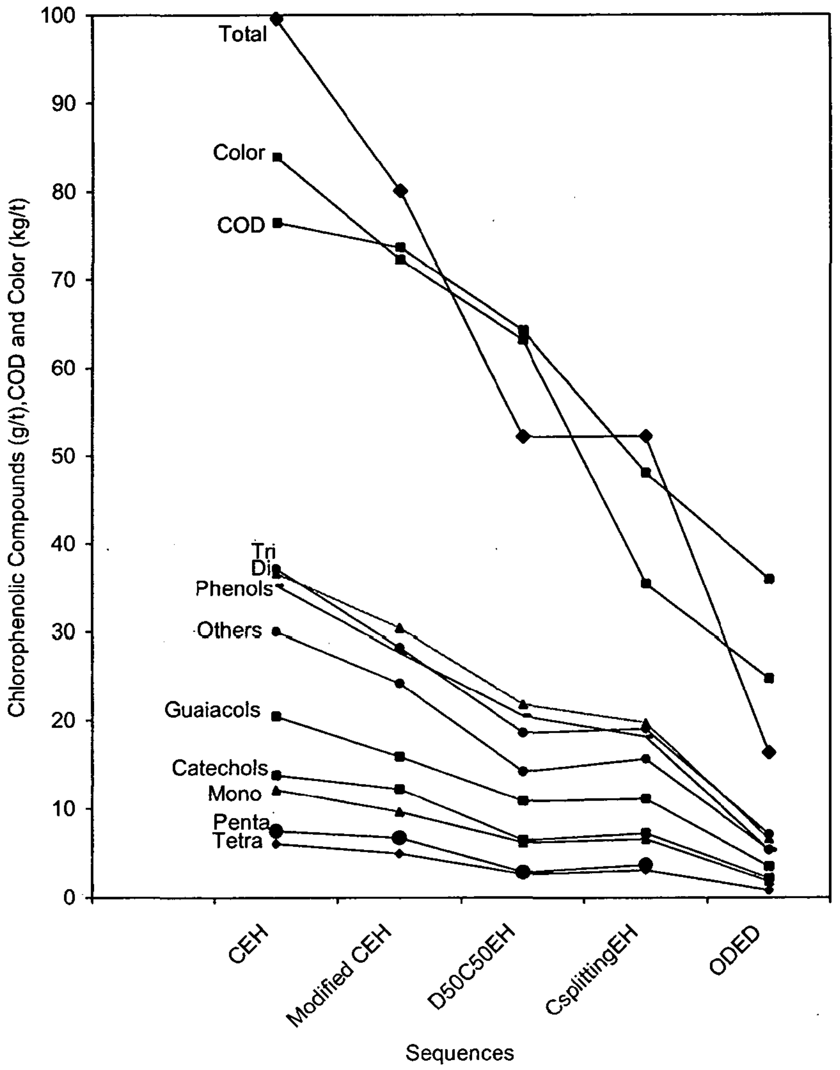


Fig 4.40 Effect of changed sequences on the generation of chlorophenolics, COD and color in E stage effluent, when target brightness achieved.

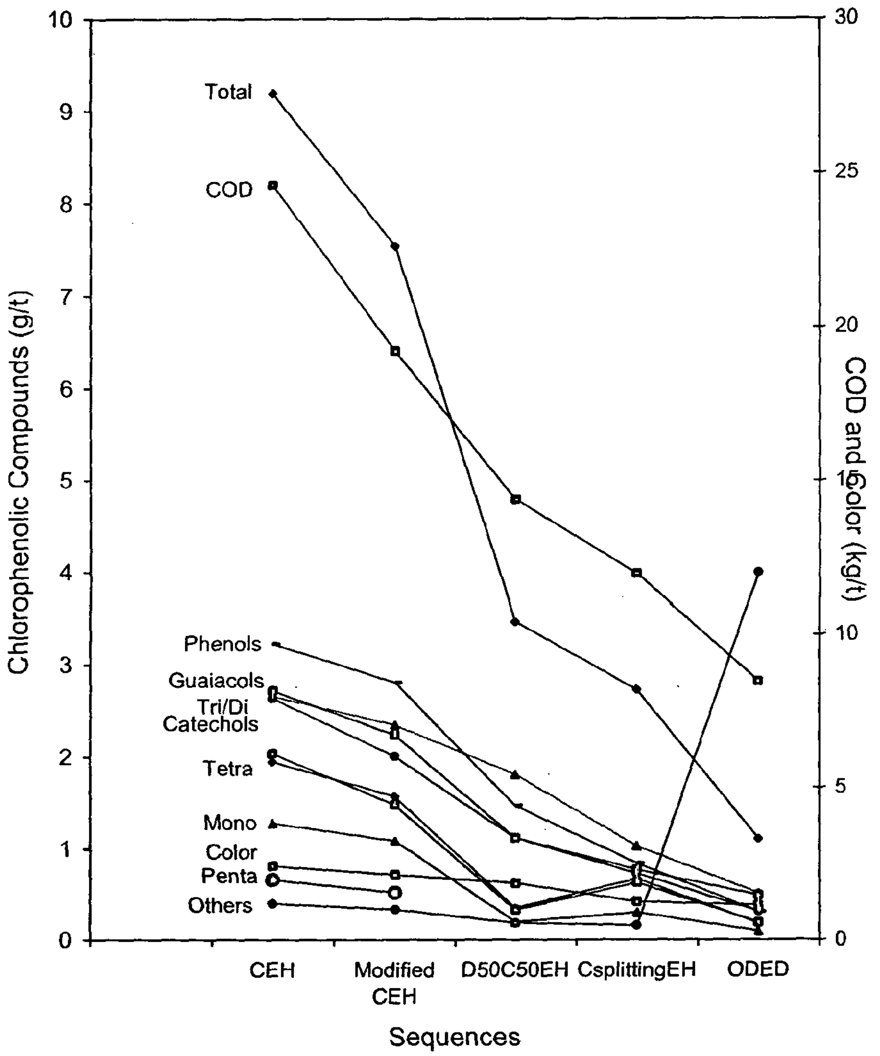


Fig 4.41 **Effect of changed sequences on the generation of chlorophenolics, COD and color in H stage effluent, when target brightness achieved.**

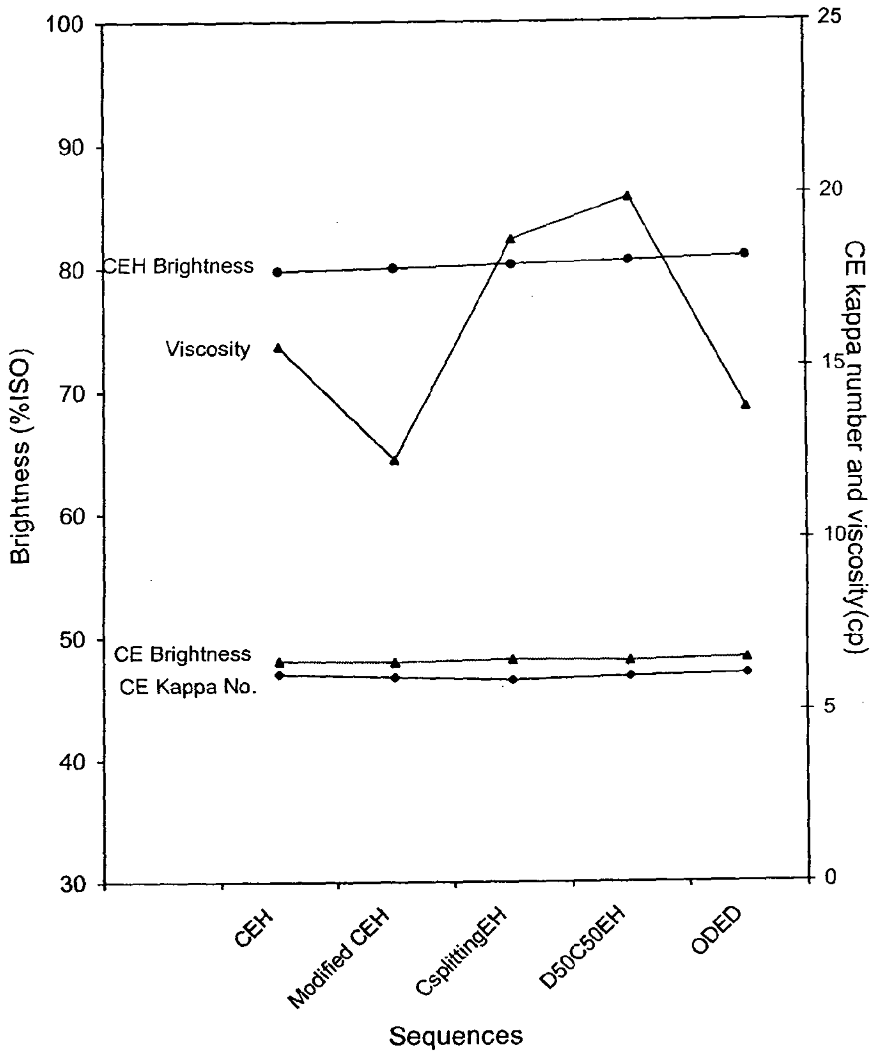


Fig 4.42 **Effect of changed sequences on brightness, viscosity and CE kappa number, when target brightness achieved.**

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Chapter - 5

CONCLUSIONS

5.1 CONCLUSIONS

Splitting of chlorine dose

Splitting of chlorine dose in C stage in two equal portions also reduce the generation of chlorophenolics by 52-57%. The reduction in effluent color is 23-28% and COD is 34-35% with 20-21% improvement in pulp viscosity. This change requires small capital investment in the form an additional C stage tower, pump and chlorine mixer.

Changing C stage to $D_{50}C_{50}$ stage

Changing C stage to $D_{50}C_{50}$ stage gives reduction in chlorophenolics by 52-56%, in color by 42-48% and in COD by 54-67% with improvement in pulp viscosity by 24-28% i.e. stronger pulp. This requires major capital investment in the form of chlorine dioxide plant. The cost of bleaching will also increase as chlorine dioxide much more expensive than chlorine.

Oxygen delignification

Addition of an oxygen delignification stage reduces the formation of chlorophenolics by about 80%. The reduction in color is 28-46% and in COD is 30-45% with small drop (5-8%) in viscosity. The reduction in effluent color and COD is because of the fact that oxygen stage effluent is used for unbleached pulp washing and thus does not go to effluent treatment plant. It is an excellent approach but requires major capital expenditure in the form of oxygen reactor, oxygen manufacturing and storage facility and medium consistency reactor and additional washer and pump. The bleaching costs are reduced. The use of oxygen can also permit the change of C and H stages by D stages – ECF bleaching. Use of oxygen reduces the consumption of costly chlorine dioxide by 50% and the bleaching cost of ODED sequence or $ODE_{OP}D$ sequence becomes competitive.

Chloro-organics generation, COD and color load per unit Kappa number are 30% -50% higher for bamboo pulp than for Jute Cady pulp

With the exception of splitting of chlorine stage other modifications outlined above are being implemented in mill conditions.

ABBREVIATIONS

AOX	:	Absorbable Organic Halides
AQ	:	Anthraquinone
ASB	:	Aerated Stablization Basin
ASP	:	Activated Sludge Process
BCRC	:	British Columbia Research Canada
BOD	:	Biochemical Oxygen Demand
CED	:	Cupriethylenediamine
COD	:	Chemical Oxygen Demand
Cy	:	Consistency
ECD	:	Electron Capture Detector
EMCC	:	Extended Modified Continuous Cooking
EOX	:	Extractable Organic Halides
ETP	:	End of Pipe Treatment
FID	:	Flame Ionization Detector
GC	:	Gas Chromatograph
HPLC	:	High Performance Liquid Chromatography
LC	:	Lethal Concentration
LR	:	Laboratory Reagent
MCC	:	Modified Continuous Cooking
OD	:	Oven Dry
PC No.	:	Post Color Number
PCDF	:	Poly-Chlorinated Dibenzofuran
PCPD	:	Poly-Chlorinated Dibenzodioxin
POX	:	Purgable Organic Halides
RDH	:	Rapid Displacement Heating
RPM	:	Rotation Per Minute
TCDD	:	2,3,7,8-Tetra Chlorodibenzo-p-dioxin
TOCL	:	Total Organic Chlorides