



CHARACTERIZATION OF EFFLUENTS FROM CHLORINE DIOXIDE SUBSTITUTION BLEACHING AND OXYGEN-REINFORCED EXTRACTION

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ABSTRACT

The effects of chlorine dioxide substitution for elemental chlorine in the chlorination stage, aimed at the minimization of chlorinated organics and subsequent oxygen reinforcement in the proceeding extraction stage on the characteristics of bleaching effluents have been examined. The characteristics of the effluents were assessed in terms of molecular weight distribution by gel filtration, so that alternatives for the treatment of these effluents can be proposed. The analysis of chlorination and extraction stage effluents with different chlorine dioxide substitution levels and varying available chlorine charges by using a Sephadex G-50 column have indicated that indeed a marked change in the molecular weight distribution of chlorinated organic compounds have occurred. The molecular size of chlorinated organic compounds in the chlorination stage has increased with the chlorine dioxide substitution, while that in the extraction stage has decreased when compared with the molecular size of these compounds in original bleaching effluents with only elemental chlorine used in the chlorination stage and followed by extraction stage. Molecular size of the chlorinated organic compounds in the chlorination stage effluents was not seriously affected by the chlorine dioxide substitution level; while it was increased greatly by the increased total chlorine dosage. In the extraction stage effluents, chlorine dioxide substitution level has not appeared to be an important parameter influencing the molecular size distribution. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Pulp bleaching; chlorine dioxide; oxidative extraction; gel filtration; molecular weight distribution analysis.

INTRODUCTION

Bleaching of kraft pulp is a lignin removal process applied to the cooked pulp to remove any residual lignin in order to brighten the finished paper. Chlorine has historically been used as the primary agent in kraft pulp bleaching. It completes the process of lignin removal. Alkaline extraction completes solubilization of chlorine-treated lignin fragments. Therefore the effluents from these bleaching processes are all characterised by their high chlorinated organics contents. These compounds are known to have the potential to induce long-term chronic toxicity at very low sub-lethal concentrations (Axegard and Renberg, 1989). Serious efforts are now being spent to limit discharges of organic halides to receiving basins. Limits on emissions of these chlorinated compounds are usually set in terms of absorbable organic halide (AOX) which is a generic measurement of a wide range of organic material possessing one or more chlorine atoms (Jackson *et al.*, 1992).

There are a number of process options to reduce the generation of AOX bleachery effluents: improved brown stock washing, extended delignification, O₂ delignification, substitution of ClO₂ for elemental chlorine, and oxidative extraction (Schwantes and McDonough, 1994). In fact, all of these primarily rely on reducing the amount of elemental chlorine used in the initial chlorination stage since the vast majority of organically bound chlorine is produced through the electrophilic addition of chlorine to the aromatic ring of the residual lignin (Singh, 1979). In techniques such as extended delignification, oxygen delignification etc., chlorine use is reduced by lowering the unbleached Kappa number. Substitution of chlorine with ClO₂ (DC) appears as another promising option. ClO₂, too, produces organically bound chlorine, but only one-fifth of the same amount of the elemental chlorine when compared on an active chlorine basis (Basta *et al.*, 1982; Axegard and Renberg, 1989).

In Dalaman Pulp and Paper mill owned by SEKA, softwood kraft pulp is normally bleached by a CEHDED (chlorination, extraction, hypochlorite, chlorine dioxide, extraction, chlorine dioxide) bleaching sequence. The mill is now considering using chlorine dioxide together with molecular chlorine in the chlorination stage (DC) and to adopt an oxidative extraction alkali stage (EO) to follow up. The investigations carried out under laboratory conditions have indicated that the proposed process modification can provide a 77% decrease in the DC-AOX, and a 82% decrease in the EO-AOX (Yetis *et al.*, 1996). However, the characteristics of the effluents from these processes remained uncertain. The objective of this study is therefore to characterize the chlorine dioxide bleached effluents in terms of molecular weight distribution and to compare these characteristics with those of the already existing chlorine-bleaching process. The need for this study arose from the fact that chlorine dioxide substitution changed the overall chemistry of the effluent which would in turn affect the effluents from the subsequent stages and globally affect the linked treatment system.

Chlorinated Organics

Of the 300 different compounds that have been identified in bleachery effluents, about 200 are chlorinated (Basta *et al.*, 1990). Approximately 75 to 80% of the chlorinated organics in kraft mill effluent is high molecular weight material (MW>1000) (Kringstad and Lindström, 1984). High MW compounds provide much of the colour associated with the bleach plant effluents, but are thought to be biologically inactive. However, it is possible that these high MW compounds might be broken down in recipient waters or in sediments and converted into smaller, more biologically-active compounds (Reeve and Earl, 1989). Also, such materials are of environmental importance, because they carry chromophoric structures that cause bleaching plant effluents to impart light-absorbing qualities to receiving waters (Kringstad and Lindstrom, 1984). These compounds are stable against biodegradation, thus they can not be removed by conventional primary and secondary treatment. Low MW compounds are major contributors to mutagenicity and bioaccumulation due to their hydrophobicity and ability to penetrate cell membranes of target organisms (Afonso *et al.*, 1992).

MATERIALS AND METHODS

Gel Filtration: For the determination of the molecular weight distribution, the method called "gel filtration" has been used. In this method, separation of substances is accomplished by the use of columns packed with gels. The gels which have a very open, three dimensional network formed by cross-linking long polymeric chains, separate molecules primarily on the basis of their sizes. Depending on the extent of cross-linking, there will be a critical size of a molecule that will just penetrate the interior. Thus, for a given gel, the distribution of a particular solute between the inner and outer pores of the gel is defined by a distribution coefficient (K_d), which is a function of molecular size (Plummer, 1987). The elution volume, V_e of a given solute depends on the volume external to the gel particles, V_o ; the distribution coefficient, K_d ; and volume inside the gel matrix itself, V_i :

$$V_e = V_o + K_d \cdot V_i \quad (1)$$

The V_i can be calculated from the dry weight of the gel, a ; and the water regain value, W_r :

$$V_i = a.W_r \quad (2)$$

Then, K_d which is independent of the geometry of the column is:

$$K_d = (V_e - V_o) / a.W_r \quad (3)$$

Table 1. Molecular weights and extinction wavelengths of calibration materials

Material	MW	Extinction wavelength, nm
Potassium chromate	194	370
Polyethylene glycol methyl ether	5 000	275
Lysozyme	14 300	280
Blue dextran	2 000 000	660

Column Preparation: Six grams of Sephadex G-50 was stirred into an excess volume of eluant solution (0.1 N LiOH-NaCl) and was allowed to swell for 3 h and to settle. The excess eluant containing the fines was decanted and the gel was resuspended in the excess eluant again. When it had settled, the supernatant was decanted until a volume of not more than 30% of the gel volume remained above the gel.

A column which is 60 cm long with a diameter of 1 cm was used. A piece of cotton was placed as the bed support. Then the column outlet tubing was closed and gel slurry was transferred into the column. The space above the gel was filled with eluant since the gel could never be allowed to dry. The column was connected to a pump which provided a constant eluant flowrate of 70 ml/h. The column was calibrated with the markers shown in Table 1. The effluent was collected as 2 ml fractions while the pump operated. The markers were detected in the collected samples using ultraviolet spectroscopy at the wavelengths shown in Table 1. Knowing V_e , K_d of each material was determined by using Eq. 3. Then a semi logarithmic plot of K_d against MW was prepared and used in the analysis.

Wastewater Samples: As stated above, the samples characterized in this study were obtained from a previous study in which an experimental design approach was adopted (Yetis *et al.*, 1996). In the study, three different chlorine dioxide substitutions and three different total chlorine application rates were examined and nine (total of 18 with their parallels) experiments were performed (Table 2). Pulp samples were initially bleached and then subjected to oxidative extraction under the conditions mentioned by Yetis *et al.* (1996). Since the target was to obtain the MW distribution of chlorinated organic compounds, the parallels for each set were combined for this study.

Table 2. Chlorine dioxide fractions and active chlorine charges in the chlorination stage

Experiment No.	1	2	3	4	5	6	7	8	9
ClO ₂ substitution level, %	10	10	10	50	50	50	90	90	90
Total available chlorine, kg/ton	10	25	40	10	25	40	10	25	40

Sample Application: Firstly, the eluant above the gel surface was removed and then the sample was applied. As soon as all the sample entered the gel bed, the eluant was applied and the pump was reconnected. Two ml fractions were collected until 100 ml passed through the column. The collected fractions were analysed at 280 nm at which the chlorinated organics containing double conjugated bonds give a high resonance.

RESULTS AND DISCUSSION

In order to assess the changes in the characteristics of the wastewater due to the proposed process modifications, a base-line study in which the effluents from the existing bleaching processes were analysed

was required. For this aim, original pulp bleaching effluents were obtained from the chlorination and extraction stages of SEKA Dalaman Pulp Bleaching Plant. The results of this molecular weight distribution analysis are displayed in Fig. 1. As can be seen, the molecular weights of chlorinated organic compounds in the chlorination stage effluent were quite low as compared to those in extraction stage effluent. The fraction of organic compounds with a MW below 1000 was 80% in chlorination stage, while it was only 5% in extraction stage effluent.

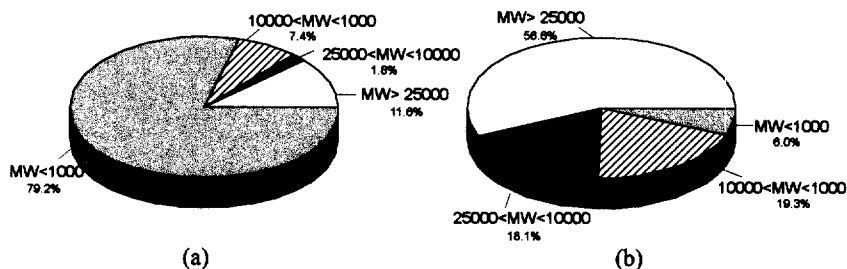


Figure 1. Molecular weight distribution of the organics in SEKA Dalaman Pulp and Paper Mill effluents (a) chlorination stage effluent (b) extraction stage effluent.

Chlorine dioxide bleaching effluents

The results of the molecular weight distribution analysis that was done on the chlorine dioxide bleached effluent samples indicated in Table 2 are presented in Fig. 2. In this figure, the chromatogram obtained with the original chlorination stage effluent is also provided to make the comparative analysis possible. As it is seen, when chlorine was substituted with chlorine dioxide, a considerable change in wastewater characteristics has occurred; total quantity has increased for high MW compounds and decreased for low MW compounds. Further, as total available chlorine charge was increased from 10 kg/ton to 40 kg/ton, the quantity of high MW materials has been observed to decrease. At the lowest chlorine charge tested, the change in the percentage chlorine substitution has not resulted in an appreciable change in the quantity of organics as is obvious from the absorbance values. However, when total available chlorine charge has been increased to 40 kg/ton, chlorine dioxide substitution level seemed to be an important factor influencing both the molecular weight distribution and the quantity of organics.

Quantitative evaluation of the molecular weight distribution of the organics existing in the effluents was also done by simply evaluating the areas under the chromatograms. The results obtained from such an evaluation are presented in Fig. 3. In chlorination with chlorine alone, the majority of the chlorinated organic compounds were from the low MW group while in chlorination with different chlorine dioxide substitution levels, there was relatively an even MW distribution, except for the highest total chlorine charge tested.

At low chlorine charges, the percentage of the organics with MWs below 1000 has decreased; and correspondingly, the fraction of bigger molecules has increased. However, at 40 kg/ton, this trend was only observed for the highest chlorine dioxide substitution level. In all cases, as a result of chlorine dioxide substitution, a general increase was observed in the quantity of the compounds having MWs between 1000-25000. On the other hand, an increase in the fraction of compounds with MWs higher than 25000 was observed only at the highest chlorine dioxide substitution level.

Oxygen-reinforced extraction stage effluents

For the qualitative analysis of the MW distribution of the organics in the oxygen-reinforced extraction stage, again the chromatograms of different chlorine dioxide substitution levels at each total chlorine charge were combined with the chromatogram of original extraction stage effluent (Fig. 4). At all total chlorine charges, the chromatogram of the already existing extraction stage effluent appeared to the left of others, indicating the presence of much bigger molecules. However, there was no apparent variation in the MW due to different chlorine dioxide substitution levels.

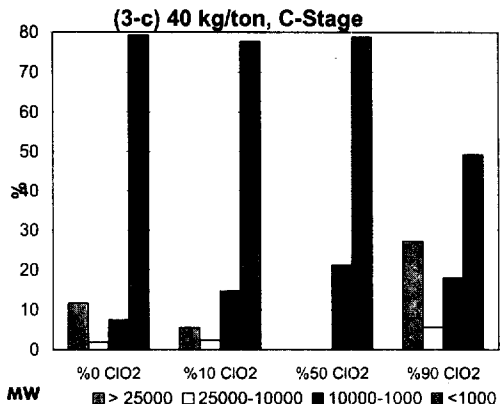
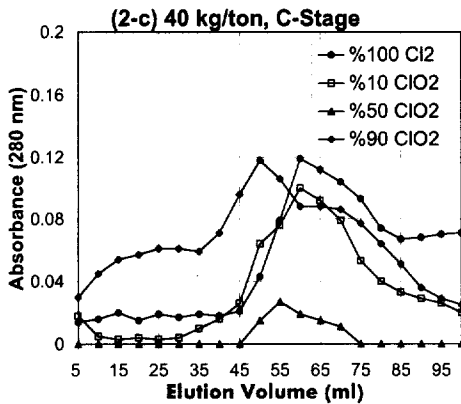
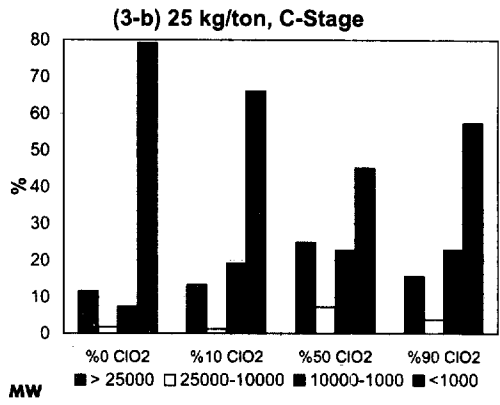
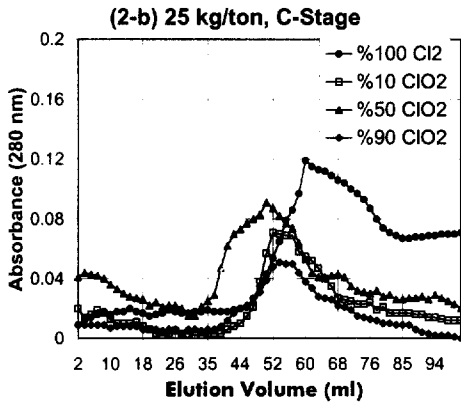
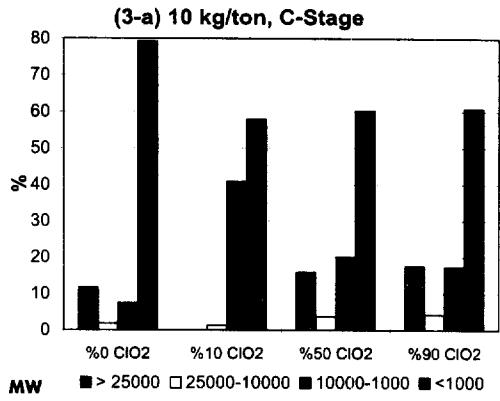
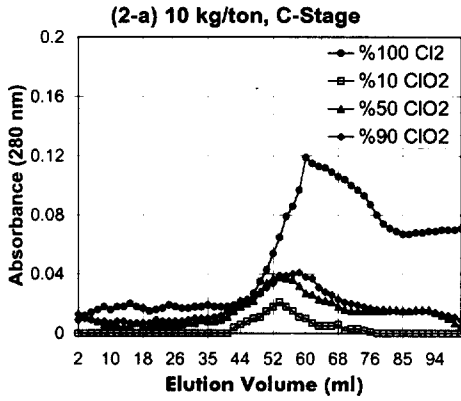


Figure 2. Chromatograms obtained at different ClO₂ substitution levels and at different available Cl charges for ClO₂ bleaching effluents

Figure 3. Molecular weight distribution of the organics existing in the chlorine dioxide bleaching effluents

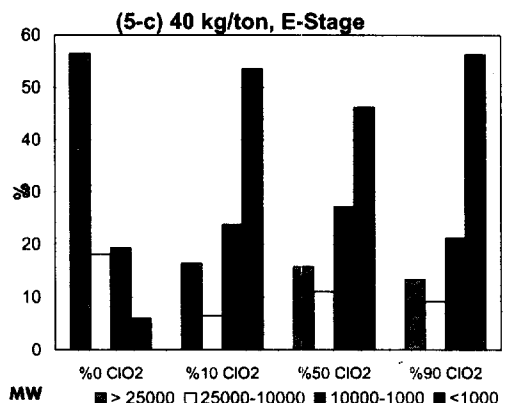
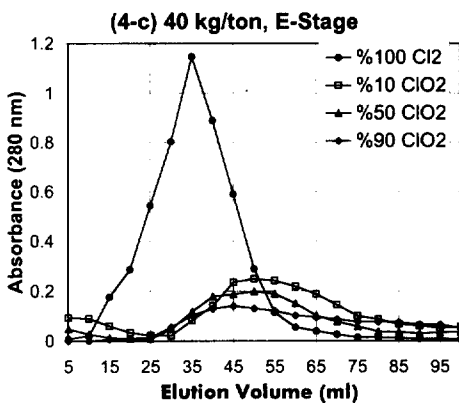
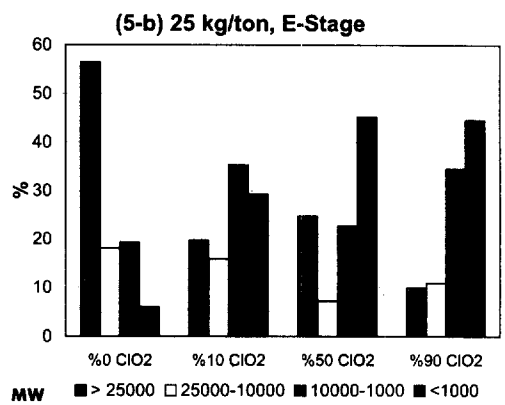
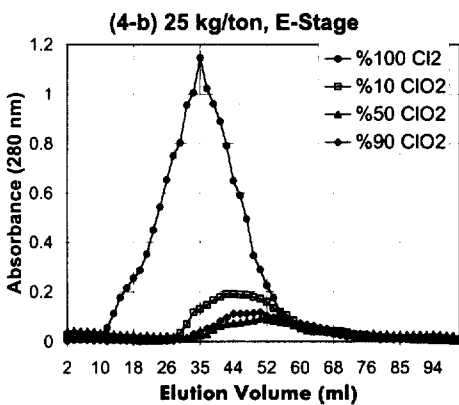
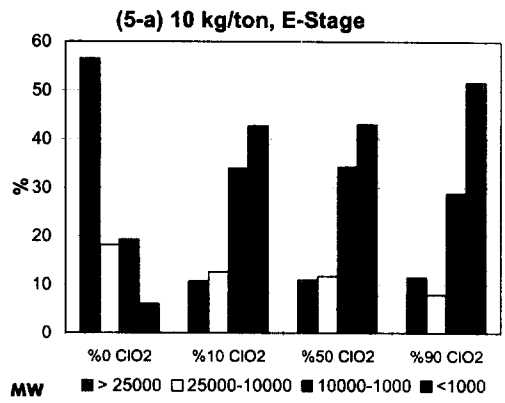
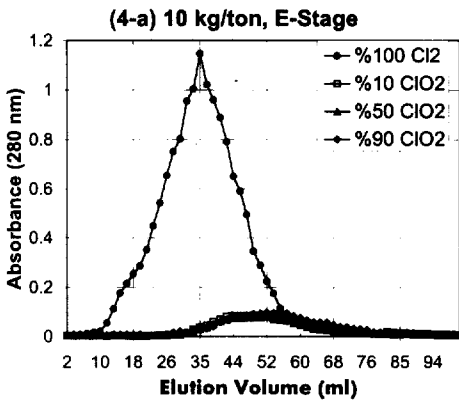


Figure 4. Chromatograms obtained at different ClO₂ substitution levels and at different available Cl charges for oxidative extraction effluents

Figure 5. Molecular weight distribution of the organics existing in the oxygen reinforced extraction effluents

At 10 kg/ton chlorine (Fig. 4a), the elution curves for different chlorine dioxide substitution levels had almost the same shape indicating that there was not an apparent molecular size variation due to different chlorine dioxide substitution levels. However, at higher total available chlorine charges (25 and 40 kg/ton), variations in MW distributions have been observed. This variation has especially become apparent when the total chlorine charge was 40 kg/ton. At this chlorine rate, although the chromatograms for the three chlorine dioxide substitution levels had a peak almost at the same elution volume, the chromatogram of 90% chlorine dioxide substitution appeared to the left of those with a low absorbance value indicating a very low AOX concentration. There was about a six to seven fold decrease in the absorbance values when chlorine was substituted with chlorine dioxide. Evidently, the AOX concentration of this effluent was determined as about 10 mg/l while those of 50%, 10% and 0% chlorine dioxide substitutions were 22, 30 and 180 mg/l AOX respectively (Yetis *et al.*, 1996).

Figure 5 shows the MW distribution of the organics existing in the extraction stage effluents following chlorine dioxide bleaching. From this figure, it immediately appears that the proposed process modification resulted in a considerable reduction in the fraction of compounds with MWs above 25000, and a corresponding considerable increase in the fraction of compounds with MWs below 1000. Similarly, the fraction of compounds having MWs between 1000-10000 has increased. Although an increase in the applied chlorine charge has not resulted in a significant change in the molecular weight distributions, the increase in the fraction of compounds with MW's below 1000 was the highest at 40 kg/ton.

CONCLUSIONS

In this study the effects of chlorine dioxide substitution in chlorination and oxygen reinforced extraction on the MW distribution of the chlorinated organic compounds in bleaching effluents was assessed. The following conclusions have been drawn from the results obtained:

There was an increase in the quantity of the organics with increased chlorine dosages both in chlorination and extraction stages as expected.

Low MW chlorinated organics dominated both the chlorine dioxide bleaching effluents and the oxygen reinforced extraction stage effluents.

When compared with the current bleaching process, the fraction of low MW organics was found to be decreased when chlorine was substituted with chlorine dioxide at chlorination stage; while the subsequent extraction process with oxygen reinforcement caused a significant reduction in the fraction of compounds with highest molecular weights.

The current bleaching stage effluents are dominated by compounds with molecular weights below 1000, and the extraction stage effluents by compounds above 1000. However, the proposed process modification has resulted in a more even molecular weight distribution considering the fraction of compounds having molecular weights above and below 1000.

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