A New Perspective (Sorption/Desorption) on the Question of Chlorolignin Degradation to Chlorinated Phenolics

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■ A "monomer-free" (i.e., predominantly high molecular weight chlorolignin) solution prepared from spent liquor collected from the alkali extraction stage of a softwood kraft pulp mill bleach plant was examined for its ability to release monomeric chlorinated phenolic compounds when stored under sterile conditions at pH 7. The major chlorinated phenolics released from the chlorolignin solution, after 28 days of storage at 50 °C, were 4,5-dichloroguaiacol, 3,4,5-trichloroguaiacol, 6-chlorovanillin, and 5,6-dichlorovanillin. These four compounds were found to reach maximum concentrations over the storage period, which corresponded to only 2.3–3.6% of their concentrations in the original E-stage effluent. The remaining chlorinated phenolics normally present in spent bleach liquors did not reach concentrations of >1 μg/L over the course of the experiment. A spiking experiment using ^{13}C-labeled 4,5-dichloroguaiacol demonstrated that the chlorinated phenolics which are released from the chlorolignin over time may be the result of the slow desorption of chlorinated phenolics which had become associated with the chlorolignin during the bleaching process and not necessarily due to chlorolignin degradation as previously hypothesized.

Introduction

The use of chlorine bleaching agents for the manufacture of bleached chemical pulp inevitably leads to the formation of a wide range of chlorinated organic compounds in the spent bleach liquors. These compounds are produced primarily as a result of complex reactions occurring between the chlorine bleaching agent and the residual (5–10%) lignin remaining in the wood pulp after the preceding chemical (kraft or sulfite) pulping process. Approximately 10% of the chlorine applied to the pulp in the first bleaching stage appears in the effluent as organically bound chlorine [measurable, for example, as adsorbable organic halogen (AOX)] while the remainder (~ 90%) ends up as chloride ions (*1–5*).

The bulk, as much as 80% or more, of the chlorinated organic matter which is dissolved in the spent wash liquors during the bleaching of softwood kraft pulp comprises relatively high molecular weight (MW >1000) chlorinated material, commonly referred to as chlorolignin (*6*).

The chlorolignin which remains after bleaching is decidedly different in nature from unchlorinated lignin. Extensive structural analyses (*4, 6–10*) of chlorolignin have shown it to be virtually nonaromatic with a high carbonyl and carboxyl content, low methoxyl and phenolic hydroxyl content, and only 10% chlorine content by weight.

The high molecular weight chlorolignin is generally not believed to be of immediate concern for aquatic organisms since the size of the molecules precludes them from crossing biological barriers (e.g., the gills of fish) limiting their bioavailability (*6*). Nonetheless, concern has been expressed (*6*) about the possibility of chlorolignin being broken down in the recipient waters to form low molecular mass chlorinated compounds which may give rise to detrimental biological effects.

Such a concern has been heightened by recent reports by Swedish researchers that a portion of the chlorolignin material may undergo chemical (*11*) and microbial degradation (*11–14*) to low molecular weight chlorinated organic compounds. For example, Eriksson et al. (*11*) have reported that chlorolignin, from C- and E-stage bleaching liquors of softwood kraft pulp, when held under sterile conditions for up to 40 days at pH 7.2, appears to undergo chemical degradation to various chlorinated guaiacols and catechols.

The present study was undertaken to investigate whether the release of chlorinated phenolics under sterile conditions at neutral pH from chlorolignin material, which had previously been interpreted (*11*) as being due to "chemical decomposition", may be accounted for by other pathways, such as simple sorption/desorption type mechanisms.

Materials and Methods

Alkali Extraction (E-Stage) Liquor. E-Stage liquor was obtained from a pulp mill producing bleached softwood kraft pulp using a conventional CdEoDED bleaching sequence with 10% chlorine dioxide substitution in the chlorination stage. The E-stage liquor was sampled on two separate occasions. The liquor from the first sampling date was used for a storage experiment at 27 °C. The second sample of E-stage liquor was utilized for a storage experiment at 50 °C and for the ^{13}C-labeled 4,5-dichloroguaiacol spiking experiment.

Preparation of Chlorolignin Solutions from E-Stage Liquor. Two different methods were used to remove as much as possible of the low molecular weight material from the E-stage liquors in order to prepare a "monomer-free" (i.e., predominantly high molecular weight chlorolignin) liquor fraction for the subsequent storage experiments.

Method 1: Diafiltration and Solvent Extraction. E-Stage bleaching liquor (500 mL) was adjusted to pH 7 and diafiltered (2.5-L wash volume) with deionized water using an Amicon YM2 membrane (nominal molecular weight cutoff 1000). To ensure a more complete removal of the low molecular weight material, the diafiltered E-stage liquor (400 mL) was then adjusted to pH 2 and solvent extracted (5 × 200 mL) with methyl *tert*-butyl ether (MTBE). After the last solvent extraction, residual quantities of MTBE in the E-stage liquor were removed

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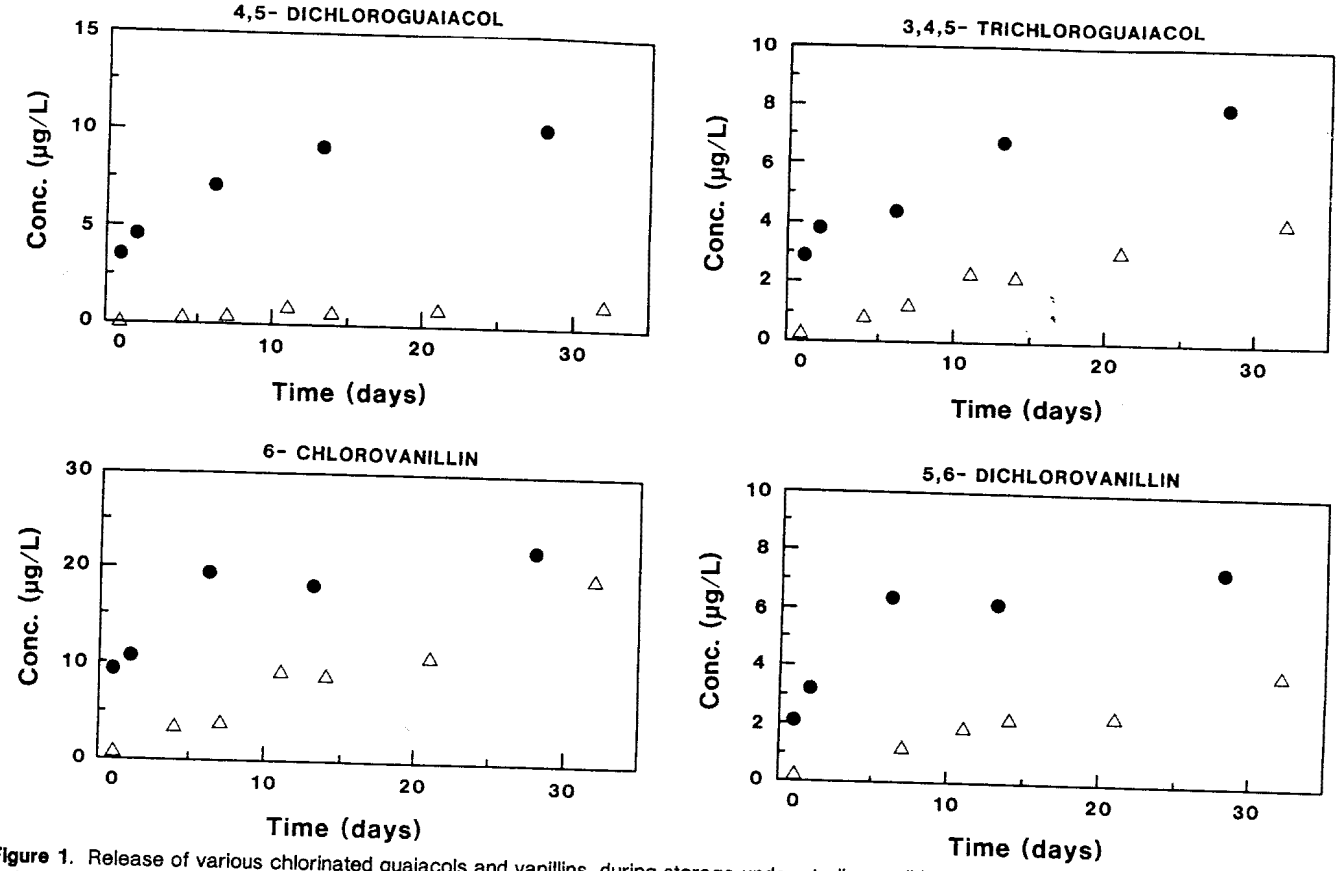

Figure 1. Release of various chlorinated guaiacols and vanillins, during storage under sterile conditions at pH 7, from monomer-free chlorolignin isolated from softwood kraft alkali extraction (E-stage) liquor. Storage at 50 (●) and 27 °C (△).

release of chlorinated phenolics resulting from the storage of monomer-free chlorolignin solutions was first investigated for the chlorolignin solution prepared according to method 1. The temperature for this experiment was approximately the same as the highest storage temperature (28 °C) investigated by Eriksson et al. (*11*) where the release of chlorinated guaiacols was found to be the greatest.

Interestingly, of all the chlorinated phenolics monitored, the only ones whose concentrations were found to increase to levels of >1 μg/L over the course of the 32-day storage experiment were 4,5-dichloroguaiacol (1.3 μg/L), 3,4,5-trichloroguaiacol (4.1 μg/L), 6-chlorovanillin (19.3 μg/L), and 5,6-dichlorovanillin (3.9 μg/L). The time courses of the concentrations for these four compounds are shown in Figure 1. In contrast to the findings of Eriksson et al. (*11*), the levels of 4,5,6-trichloroguaiacol and tetrachloroguaiacol did not increase very significantly over our storage period. From our storage experiment at 27 °C, the compound showing the greatest increase in concentration was 6-chlorovanillin. Unfortunately, a comparison of this finding with the work of Eriksson and co-workers was not possible because the latter workers did not analyze for chlorinated vanillins in their study.

At the end of the 32 days of storage in sealed gas-tight containers, the net increase in the concentrations of the four prominent chlorinated guaiacols and vanillins amounted to only 1.5–3.6% of their concentrations in the original E-stage liquor (Table I). Eriksson et al. (*11*, *17*) in their exposure experiment at 28 °C observed a similar small increase (1.5%) of chlorinated guaiacols (4,5-di, 3,4,5-tri, 4,5,6-tri, and 3,4,5,6-tetra) above the amounts detected in the original E-stage liquor.

For our experiment conducted at 27 °C (and the experiment of Eriksson et al. at 28 °C), the shape of the various release curves seemed to suggest that chlorinated guaiacols and vanillins would perhaps continue to be released if the storage time were increased. In an attempt to accelerate the release of the chlorinated phenolics and investigate whether their release could be made to reach a maximum, an additional experiment was conducted in which the chlorolignin was stored at 50 °C. As was shown previously, the solvent extraction procedure (method 2) used to prepare the chlorolignin solution for the 50 °C storage experiment was not quite as effective in removing

Table I. Chlorinated Phenolic Content of the Alkali Extraction (E-Stage) Effluents Used for the Storage Experiments

	chlorinated phenolic concn, μg/L			
	method 1		method 2	
	original	monomer-free chlorolignin[a]	original	monomer-free chlorolignin[a]
phenols				
2,4-dichloro-	27	ND	50	0.4
2,4,6-trichloro-	63	ND	52	0.2
2,3,4,6-tetrachloro-	4	0.1	7	0.1
pentachloro-	3	0.1	3	0.3
guaiacols				
4,6-dichloro-	2	ND	32	ND
3,4-dichloro-	9	ND	141	ND
4,5-dichloro-	33	0.1	259	3.6
3,4,6-trichloro-	8	ND	10	0.1
3,4,5-trichloro-	207	0.2	141	2.9
4,5,6-trichloro-	91	ND	92	1.1
tetrachloro-	44	ND	35	0.3
catechols				
4,5-dichloro-	4	0.1	5	0.6
3,4,5-trichloro-	0	ND	2	0.2
tetrachloro	2	0.1	2	0.1
vanillins				
6-chloro-	672	0.7	419	9.4
5,6-dichloro-	253	0.2	235	2.1
total	1422	1.6	1485	21.4

[a] ND, not detected, detection limit estimated to be 0.05 μg/L.

under reduced pressure at 30 °C.

Method 2: Solvent Extraction. In the preparation of this monomer-free chlorolignin solution, the diafiltration step was omitted and the E-stage liquor was only solvent extracted as outlined above.

Storage under Sterile Conditions. The chlorolignin solutions were adjusted to pH 7 and sterilized by filtration through a 0.45-μm membrane filter (*12*). Two storage experiments were conducted, one at 27 °C using the chlorolignin solution prepared according to method 1 above and the other at 50 °C using the chlorolignin solution prepared as per method 2. For each storage experiment, portions (50 mL) of the appropriate monomer-free E-stage liquors were placed in sterilized bottles, sealed gas tight, stored at 27 or 50 °C, and analyzed for chlorinated phenolics over periods of 32 and 28 days, respectively.

Synthesis of ^{13}C-Labeled 4,5-Dichloroguaiacol. ^{13}C-Labeled 4,5-dichloroguaiacol was prepared from 4,5-dichlorocatechol (obtained from Helix-Biotech, Vancouver, BC) by methylation of one hydroxyl group of the starting material with ^{13}C-labeled diazomethane generated from *N*-methyl-[^{13}C]-*N*-nitroso-*p*-toluenesulfonamide ([^{13}C]-Diazald, available from MSD Isotopes). A solution of 4,5-dichlorocatechol (5.3 mg) in diethyl ether (1.5 mL) and methanol (0.1 mL) contained in a conical test tube was methylated by bubbling continuously generated ^{13}C-labeled diazomethane through the solution for 30 min. The ^{13}C-labeled diazomethane was prepared from [^{13}C]Diazald (100 mg), diethyl ether (4 mL), 2-(2-ethoxyethoxy)ethanol (2 mL), and 11 N KOH (2 mL) in a diazomethane-generating system similar to that described by Levitt (*15*). The resulting mixture was found to contain 3.9 mg of ^{13}C-labeled 4,5-dichloroguaiacol (72% yield), a small amount of ^{13}C-labeled 4,5-dichloroveratrole, and unreacted 4,5-dichlorocatechol. This solution of ^{13}C-labeled 4,5-dichloroguaiacol was used without further purification in subsequent experiments.

Spiking of Monomer-Free Chlorolignin with ^{13}C-Labeled 4,5-Dichloroguaiacol. About 500 mL of monomer-free chlorolignin solution prepared according to method 2 above was readjusted to the original E-stage effluent pH of 10, spiked with ^{13}C-labeled 4,5-dichloroguaiacol (500 μg), covered, and then stirred at 50 °C for 18 h. After being cooled to room temperature, the spiked solution was adjusted to pH 2 and extracted with MTBE (5 × 200 mL). The storage experiment for the resulting solution was conducted according to the procedure described above.

Chemical Analyses. (1) Chlorinated Phenolic Compounds. The chlorinated phenolic contents of the original E-stage liquors were determined according to the method described by Voss et al. (*16*) for the analysis of pulp mill effluents. This involved in situ acetylation and analysis of the resulting acetate derivatives by capillary gas chromatography with electron capture detection (GC/ECD). The lower level analyses required for the chlorinated phenolics present in the monomer-free chlorolignin solutions were carried out according to the alternate procedure described by Voss et al. (*16*) for the analysis of receiving waters by direct acetylation and extract concentration.

(2) Gas Chromatography/Mass Spectrometry (GC/MS). GC/MS analyses for the determination of the relative amount of the ^{13}C-labeled and unlabeled (native) 4,5-dichloroguaiacol in the spiking experiment were performed using a Hewlett-Packard Model 5985A GC/MS system fitted with a 30-m DB-5 capillary column (0.25-mm i.d., 0.25-μm film thickness) under selected ion monitoring (SIM) conditions. Electron impact mass spectra were obtained at 70-eV ionizing energy. The ions selected for monitoring were m/z 193.0 and 195.0 for the ^{13}C-labeled 4,5-dichloroguaiacol and m/z 192.1 and 194.0 for the native 4,5-dichloroguaiacol. Two ions were monitored for each compound to verify that the isotopic ratios expected for two chlorine substituents were correct, thus assuring that the compounds were properly identified and that there were no coeluting contaminants present. The m/z 192.1 and 193.0 masses were used for quantitation purposes. In order to account for the naturally occurring carbon-13 (0.0111 × number of carbons) from the native 4,5-dichloroguaiacol which would contribute to mass 193 peak area for the ^{13}C-labeled guaiacol, the following equation was used to calculate the fraction of the total 4,5-dichloroguaiacol concentration determined from GC/ECD analysis which corresponded to the ^{13}C-labeled 4,5-dichloroguaiacol:

$$\text{labeled fraction} = \frac{\text{area } 193 - (0.0779 \times \text{area } 192.1)}{\text{area } 192.1 + \{\text{area } 193 - (0.0779 \times \text{area } 192.1)\}}$$

The fraction corresponding to unlabeled, native 4,5-dichloroguaiacol would then be equal to 1 − the labeled fraction, calculated using the above equation. The GC conditions were as follows: column, 45 °C (held for 1 min) and then programmed to 120 °C at 15 °C/min, followed immediately by a 2 °C/min temperature increase to 200 °C; injector, 250 °C, carrier gas, helium at 70 kPa, splitless injector.

Results and Discussion

Preparation of Monomer-Free Chlorolignin Solutions. The methods used in this study to prepare monomer-free (chlorolignin) solutions from spent bleaching liquors for the storage experiments were similar to those employed previously by Eriksson et al. (*11*) and Neilson et al. (*12, 13*). Our method 1 (see Materials and Methods) differed from the approaches utilized by the Swedish researchers (*11, 13*) in that we used diafiltration in the first (ultrafiltration) stage. Eriksson et al. (*11*) carried out their water washing on an E-stage liquor sample, which was first concentrated by ultrafiltration, and then they diluted the sample back to its original volume before proceeding with solvent extraction. Prior to solvent extraction, Neilson and co-workers (*12*) concentrated their effluent samples (40–60-fold) by ultrafiltration. Our second method used for preparing a monomer-free, high molecular weight chlorolignin solution from E-stage liquor was very similar to the procedure more recently employed by Neilson et al. (*13*) except that the Swedish workers used continuous liquid–liquid extractions with diethyl ether, whereas we carried out sequential batch extractions with methyl *tert*-butyl ether.

Although the E-stage effluents used for this study were collected at two different times, their chlorinated phenolics content were fairly consistent as is evidenced by the data in Table I. Consistent with the previous reports (*6, 16*) that chlorinated catechols occur primarily in chlorination-stage spent bleaching liquors, the E-stage effluents were found to contain only minor amounts of these compounds.

The procedures employed in methods 1 and 2 for the preparation of the monomer-free chlorolignin effectively removed 99.9% and 98.6%, respectively, of the chlorinated phenolics content of the original E-stage liquor (see Table I).

Release of Chlorinated Phenolics from Monomer-Free E-Stage Chlorolignin Solutions. The pattern of

but of simple desorption of monomeric chlorinated phenolic compounds associated with the dissolved chlorolignin material.

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Registry No. Chlorolignin, 8068-02-8; 4,5-dichloroquaiacol, 2460-49-3; 3,4,5-trichloroquaiacol, 57057-83-7; 6-chlorovanillin, 18268-76-3; 5,6-dichloroavanillin, 18268-69-4.

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the monomeric chlorinated phenolics as compared to the diafiltration/extraction procedure (method 1). This difference between the two isolation procedures was also visually evident from a comparison of the starting concentrations of the various chlorinated phenolics for the two storage experiments, as shown in Figure 1.

The results of the storage experiment at 50 °C again demonstrated that after 28 days of storage the only chlorinated phenolics which were released in concentrations of >1 μg/L were 4,5-dichloroguaiacol (10.3 μg/L), 3,4,5-trichloroguaiacol (8.0 μg/L), 6-chlorovanillin (22 μg/L), and 5,6-dichlorovanillin (7.4 μg/L). However, in contrast to the experiments conducted at 27 °C, the results of the storage at 50 °C suggest that at this temperature the four predominantly released chlorinated phenolics were all approaching a maximum concentration after 28 days (Figure 1). The final concentrations in all four cases were found to correspond to only 2.3–3.6% of their original E-stage concentrations (Table I). Again, our experiments, in contrast with the findings from the study by Eriksson et al. (*11*, *17*), did not reveal the release of any significant amounts of 4,5,6-trichloroguaiacol or tetrachloroguaiacol. This apparent discrepancy may have been due to our more efficient preparation of monomer-free chlorolignin [for example, the initial concentration of 4,5-dichloroguaiacol in the chlorolignin solution used by Eriksson et al. (*11*) for their storage experiments was 20 μg/L] or to differences in the composition of each E-stage liquor.

Our results, together with those obtained previously by Eriksson et al. (*11*), illustrate that relatively small amounts of certain chlorinated phenolics can be slowly released from monomer-free E-stage chlorolignin under sterile conditions at pH 7. When one is attempting to draw conclusions about the possible environmental significance of this minor release, however, it is important to keep in mind that the bulk of these compounds released to the environment could be accounted for by the original concentration in the spent bleaching liquors.

Although Eriksson et al. (*11*) have interpreted the results from their chlorolignin storage experiments to mean that the high molecular weight chlorolignin material is "chemically degrading" to form various low molecular weight chlorinated phenolic compounds, there are two considerations which raise doubts about the likelihood of such a process occurring. First, on the basis of the structural features of the chlorolignin material as discussed previously, particularly the near absence of aromatic character, it is inconceivable that this high molecular weight chlorolignin material could extensively break down in the receiving water environment to low molecular weight polychlorinated aromatic compounds such as the monomeric chlorinated phenolics. Second, it is very puzzling that the so-called "chemical degradation" takes place under extremely mild reaction conditions, namely, sterile conditions, neutral pH, and temperatures as low as 5 °C. One might expect that such reactions would have been carried to completion under the much more aggressive reaction conditions encountered in the alkali extraction stage of pulp bleaching, namely, temperatures of 50–60 °C, relatively high alkali content (final pH 10–11), and a residence time of 1–1.5 h.

In light of the above reservations, we undertook some additional studies (described below) to determine if there were some other possible explanations for the chlorolignin "degradation" phenomenon.

Spiking Experiments with ^{13}C-Labeled 4,5-Dichloroguaiacol. We hypothesized that the observed increase in chlorinated phenolics over time may be due to slow desorption of monomeric chlorinated phenolic compounds associated in some way with the dissolved chlorolignin material. This observation is not inconsistent with previous studies, which have documented (*18–21*) the slow sorption or desorption of several types of organic compounds from dissolved organic material.

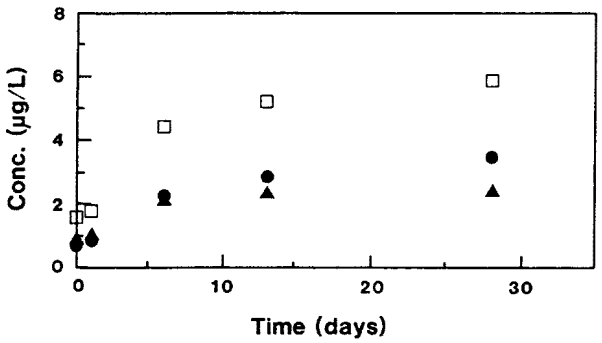

Figure 2. Release of total 4,5-dichloroguaiacol (□), ^{13}C-labeled 4,5-dichloroguaiacol (▲), and native 4,5-dichloroguaiacol (●) from spiked chlorolignin during storage at 50 °C under sterile conditions at pH 7.

In an attempt to verify that the same was possibly occurring for chlorinated phenolics, a spiking experiment (see Materials and Methods) was devised to determine whether chlorinated phenolics could actually be sorbed onto and then slowly released from the dissolved chlorolignin material. The chlorinated phenolic chosen for this experiment was 4,5-dichloroguaiacol since, in both our experiments and those by Eriksson et al. (*11*), the concentration of this compound showed a significant increase with storage time. The proportions of the ^{13}C-labeled and the native 4,5-dichloroguaiacol were determined in duplicate, throughout the storage experiment, by GC/MS analysis.

At the start of the storage experiment, the concentrations of the ^{13}C-labeled and native forms of 4,5-dichloroguaiacol were found to be 0.9 and 0.7 μg/L, respectively. Time–concentration curves (Figure 2) for the total amount of 4,5-dichloroguaiacol released at 50 °C as well as for its constituent ^{13}C-labeled and native forms were similar to the release patterns observed previously (Figure 1) for the unspiked chlorolignin solutions. The similarity of the curves for the ^{13}C-labeled and native forms of 4,5-dichloroguaiacol is particularly noteworthy as its implies that the mechanism for the release of the native compound with time is similar to that for the ^{13}C-labeled compound, where the release of the latter compound with time is a result of desorption from the dissolved chlorolignin material. Over the 28-day storage period, the concentration of the labeled 4,5-dichloroguaiacol was found to increase from 0.9 to 2.4 μg/L, whereas the concentration of the native 4,5-dichloroguaiacol grew from 0.7 to 3.5 μg/L.

The increase in the concentration of the ^{13}C-labeled 4,5-dichloroguaiacol clearly demonstrated that 4,5-dichloroguaiacol can be reversibly sorbed onto dissolved chlorolignin material and then slowly desorb over time. Although these experiments do not irrefutably exclude the possibility that the compounds arise from degradation, they nonetheless illustrate the likelihood of what in our view is a more plausible explanation for the release of chlorinated phenolics from aged chlorolignin solutions.

Conclusions

These investigations demonstrated that the amount of chlorinated phenolics which are released over time, under sterile conditions and pH 7, are relatively minor in comparison with the measurable concentrations of these same compounds in the original spent bleaching liquors, and that their release may be the result not of chemical degradation