

Kraft Lignin Adsorption of Alachlor and Chloramben as a Controlled-Release Function Evaluation

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The experimental nonsulfonated kraft lignin, PC940C, had similar adsorption patterns for both [¹⁴C]alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide] and [¹⁴C]chloramben (3-amino-2,5-dichlorobenzoic acid) as measured over a 60 min holding time. In the first 10 min, both compounds were rapidly adsorbed to the lignin, suggesting adsorption to readily available surface sites, while from 10 to 60 min, approximately one-third more [¹⁴C]chloramben, of the total available in solution, was adsorbed as compared to [¹⁴C]alachlor. On the basis of these results and in view of an earlier desorption study that found approximately 60% more of the total available [¹⁴C]-chloramben was desorbed from PC940C as compared to [¹⁴C]alachlor, the following is proposed. The chloramben aromatic amino group formed ionic bonds with the lignin's carboxylic and phenolic groups. This allowed for more adsorption of chloramben by the lignin and allowed for a more rapid desorption of chloramben through an ion-exchange mechanism. The adsorption/desorption characteristics for alachlor suggest hydrogen bonding to the lignin.

Keywords: *Controlled release; adsorption; chloramben; alachlor; kraft lignin*

INTRODUCTION

Kraft lignin has been evaluated as a controlled-release agent for a number of pesticides. Evaluated pesticides include pentachloronitrobenzene, 2,4-D [(2,4-dichlorophenoxy)acetic acid], ethoprop (phosphorodithioic acid *O*-ethyl *S,S*-dipropyl ester) (DelliColli, 1977, 1980), metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one], alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide], and chloramben (3-amino-2,5-dichlorobenzoic acid) (Riggle and Penner, 1988). Kraft lignin has also been shown to adsorb carbendazim (1*H*-benzimidazol-2-ylcarbamic acid methyl ester), triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone], fenarimol, [α -(2-chlorophenyl)- β -(4-chlorophenyl)-5-pyrimidinemethanol] (Barak *et al.*, 1983), atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] (Dunigan and MacIntosh, 1971), and metribuzin (Riggle and Penner, 1992). Kraft lignin has been found to contain hydroxy, carboxy, keto, and phenoxy groups (Glasser *et al.*, 1983). These functional groups have the potential to adsorb different classes of pesticides by hydrogen-bonding, ionic-bonding, and/or van der Waals forces. In addition, tests have suggested that drying processes used in lignin preparations may expose more functional groups for adsorptive purposes (Goring, 1971). Kraft lignin polymers have been found to be spherical in shape and may function as micelles (Goring, 1971). Lignin micelles are believed to attract one another by secondary bonding to form larger macromolecules (Goring, 1971). If a pesticide were attached to these micelles and in turn these micelles formed stable macromolecules, it is possible that macromolecules may function as diffusion barriers for the entrapped pesticide. Evidence for this was demonstrated using three different nonsulfonated kraft lignins in conjunction with [¹⁴C]metribuzin (Riggle and Penner, 1992). Using soil thin layer chromatography (STLC), Riggle and Penner

(1987) found that the experimental kraft lignin PC940C reduced the mobility of both [¹⁴C]metribuzin and [¹⁴C]alachlor in soil and that ³H-labeled PC940C was relatively immobile. PC940C was also found to control the release of [¹⁴C]metribuzin, [¹⁴C]alachlor, and [¹⁴C]chloramben as measured by the amount desorbed from soil leaching columns (Riggle and Penner, 1988). Additional evidence for controlled-release properties of PC940C was the reduction of metribuzin-related phytotoxicity for both greenhouse- and field-grown soybeans [*Glycine max* (L.) Merr.] with no adverse effects on metribuzin-related weed control (Riggle and Penner, 1989). The purpose of this study was to determine if adsorption patterns of [¹⁴C]alachlor and [¹⁴C]chloramben could explain how the controlled-release function of the lignin, PC940C, operates for nonionic and ionic herbicides.

MATERIALS AND METHODS

Kraft Lignin. The pine kraft lignin, PC940C, was provided by Westvaco, Polychemicals Department, Charleston Heights, SC. PC940C is an oxygen rich, nonsulfonated kraft lignin that was derived from the commercial nonsulfonated kraft lignin Indulin AG (personal communication with Westvaco personnel). In aqueous suspensions, the lignin has a pH greater than 9. The lignin used was a dark brown, dry powdered, grainy material and was stored at room temperature in an airtight plastic bottle.

Pesticide Solutions. Stock solutions were prepared in distilled water by mixing technical grade chloramben or technical grade alachlor (prepared by crystallization) to approximate maximum solution concentrations at room temperature of 700 and 240 μ g/mL, respectively (Merck Index, 1989). Chloramben used was in the acid form and has a *pK_a* of 4 (Hartley and Graham-Bryce, 1980).

Radiolabeled materials used were carboxyl-labeled [¹⁴C]chloramben (specific activity of 2.18 mCi/mmol) and phenyl-labeled [¹⁴C]alachlor (specific activity of 1.76 mCi/mmol). Purity of ¹⁴C-labeled compounds was confirmed by thin layer chromatography and plates were scanned with a Berthold 2D-TLC scanner LB276 using methane as the ionizing gas.

Adsorption Measurements. Adsorption measurements were made as follows. A sample of lignin (250 mg) was

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combined with one of the two herbicide stock solutions (2.5 mL) and the corresponding ^{14}C -labeled solution (3 μL) in a 50 mL glass centrifuge tube. The ratio of lignin to the combined labeled and unlabeled stock solutions was the same as used in an earlier soil leaching column study (Riggle and Penner, 1988). The control consisted of the two combined stock solutions, which were combined at the same ratio as used for the lignin tests but with no added lignin. Holding times consisted of 0, 10, 40, and 60 min. Each holding time was replicated three to four times. Tubes were shaken by a wrist-action shaker at 200 reciprocations/min, removed from the shaker, and centrifuged at 200g for 2 min. Radioactivity in the resulting clear supernatant was determined by removing 100 μL subsamples, which were then placed in vials containing 10 mL of liquid scintillation counting fluid. Radioactivity levels were determined by liquid scintillation spectrometry using a Beckman liquid scintillation spectrometer. A reduction in radioactivity of the supernatant as compared to the control was attributed to ^{14}C -labeled compound adsorption by the lignin.

Adsorption Determinations. Adsorption data are presented as both a percentage of ^{14}C activity remaining in the container after the solution was removed and as micromoles (unlabeled) of either chloramben or alachlor per gram of lignin remaining in the container after the solution had been removed. Percentage of the total value was determined by calculating radioactivity remaining in the supernatant compared to the total applied. The difference between the original total applied and the amount remaining in the supernatant was determined to be the amount adsorbed by the lignin. This was then calculated as micromoles per gram of lignin. It was assumed that there was no discrimination by the lignin in adsorption between the labeled and nonlabeled pesticides. Linear equations were determined as well as coefficients of variation. Standard errors were determined and are depicted by lines above and below the data points in Figures 1 and 2.

RESULTS AND DISCUSSION

Distilled water was used in measuring the interaction between the lignin PC940C and the two herbicides. Organic solvents, such as dimethylformamide or acetone, would have allowed for higher concentrations of alachlor and chloramben in solution, but these solvents would have also altered both the physical and chemical characteristics of the lignin (personal communication with Dr. Frederick Baker of Westvaco). Another reason for using water was to reproduce the conditions of the earlier cited studies (Riggle and Penner, 1987, 1989, 1992).

The nonsulfonated kraft lignin was not soluble in water and consequently was kept in suspension using the wrist-action shaker. The non-water-soluble characteristic of PC940C is consistent with earlier reported results (Goring, 1971) and with those of other tested kraft lignins (Riggle and Penner, 1987, 1988, 1992).

Adsorption test results showed that both herbicides were adsorbed by PC940C (Figures 1 and 2). A higher experimental error was found for ^{14}C chloramben versus ^{14}C alachlor. A common feature was the rapid adsorption that occurred during the first 10 min. This suggests that the initial adsorption was occurring on readily accessible sites of the lignin. Earlier studies (Goring, 1971) suggest that these accessible sites are located on micelles. Goring (1971) reported that as lignin is dried, more surface area is exposed, which in turn increases the accessibility of oxygen-enriched functional groups. The gradual adsorption pattern, which occurred after 10 min, was probably due to an envelopment process that occurred as the micelles were attracted to one another by secondary bonding to form larger macromolecules as described by Goring (1971)

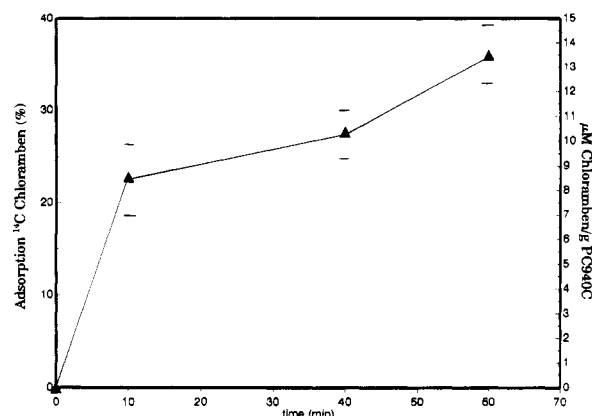


Figure 1. PC940C adsorption of ^{14}C chloramben from an aqueous solution as measured over 60 min. Linear equation for the chloramben measurements was $Y = 8.11 + 0.49X$ ($r = 0.8773$).

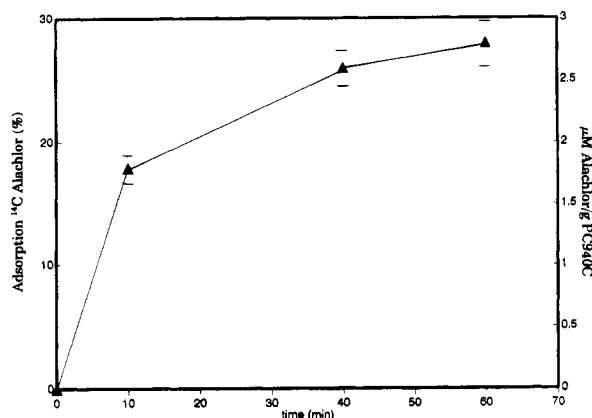


Figure 2. PC940C adsorption of ^{14}C alachlor from an aqueous solution as measured over 60 min. Linear equation for the alachlor measurements was $Y = 6.83 + 0.41X$ ($r = 0.8748$).

and supported by Riggle and Penner (1992) using ^{14}C -metribuzin with PC940C and two other nonsulfonated kraft lignins.

Taking into account the differences in experimental error, a comparison of the amounts of adsorbed ^{14}C -alachlor and ^{14}C chloramben shows chloramben was adsorbed at slightly higher percentages of the total ^{14}C -labeled material available in solution at all holding times as compared to alachlor and that at the end of the 10 and 60 min holding times the amount of total available ^{14}C chloramben adsorbed was 5 times greater than that of total available ^{14}C alachlor. This was not an unexpected result since the chloramben solution concentration was almost 3 times greater than that of alachlor. The amount of ^{14}C chloramben adsorbed by PC940C was also greater than that of ^{14}C metribuzin as measured in an earlier study (Riggle and Penner, 1992), even though the metribuzin solution concentration was almost twice that of chloramben.

At neutral pH conditions, chloramben, with a pK_a of 4, exists in a disassociated state and has a negative charge. It is proposed that under the NaOH alkaline conditions of the kraft lignin the amino group of chloramben formed a close ionic association with the lignin's carboxylic and phenolic groups. There is evidence to suggest that as the dry lignin was hydrated, more oxygen-enriched functional groups were exposed (Goring, 1971) and were available for ionic interaction with chloramben.

While adsorption measurements demonstrated different adsorption patterns for ^{14}C chloramben and ^{14}C -

alachlor, an earlier soil column chromatography study using PC940C nonsulfonated lignin (Riggle and Penner, 1988) showed [^{14}C]chloramben was desorbed at higher percentages and at higher amounts of material applied than [^{14}C]alachlor. These differences demonstrated that while chloramben was more adsorptive to PC940C than alachlor (Riggle and Penner, 1992), chloramben was the more desorptive of the two. The leaching study results suggest that the rapid desorption was due to an ion-exchange mechanism. Results showed that alachlor remained more closely associated with the lignin. The more gradual adsorption/desorption characteristics of alachlor suggest this herbicide experienced hydrogen bonding with the lignin.

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