Polarographic Determination of Some Pesticides. Application to a Study of Their Adsorption on Lignin

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Polarographic reduction of the nitro group in acifluorfen and of the disulfidic bond in thiram as well as the anodic waves of mercury salt formation of dazomet can be used to follow adsorption of pesticides on lignin. Within this group, thiram was adsorbed most strongly, then dazomet, and weakest was the adsorption of acifluorfen. The adsorption depends on the pH of the medium, because of both the acid–base equilibria involving the pesticide and the equilibria involving acidic groups on lignin. The effect of variations in spatial arrangement (tertiary structure) of lignin with pH, indicated in previous studies, cannot be excluded. In all cases, the adsorption on kraft lignin used in this study was weaker than that on natural lignins. The greater part of the sulfur-containing pesticides (dazomet, thiram) was bound to lignin irreversibly. This decreases the bioavailability of the pesticide in forest litter and forest soil.

INTRODUCTION

The polarographic method was successfully applied to the analysis of various pesticides, herbicides, and other chemicals used in agriculture (Březina and Zuman, 1958a; Nangniot, 1970; Rowe and Smyth, 1979). The main advantage that polarographic methods offer in this area is the possibility to use them—often without preliminary separations—for analysis of complex biological materials. In particular, it is often possible to take advantage of polarographic methods for the analysis of colored materials or samples containing dispersed solid particles. Direct polarographic analysis can be carried out on samples for which direct use of spectrophotometry is not possible and the use of optical methods would involve preliminary separations. Polarographic methods do not show the selectivity of chromatographic ones, but they are in general faster and can be carried out in turbid solutions. As the determination of agrochemicals usually does not involve complex mixtures of structurally closely related substances, the limited selectivity of polarographic analysis is often sufficient. Moreover, as metabolic changes often either involve the electroactive group or result in an introduction of a substituent, the reduction potential of the electroactive group of the metabolic product often differs from that of the agrochemical.

The study of the binding of pesticides by lignin is one type of application for which the advantages of polarographic methods have been demonstrated. The strong absorbance by colored solutions in which lignin is dispersed combined with the light scattering due to the presence of small particles results in a large background absorbance which prevents spectrophotometric measurements below about 300 nm. The presence of small particles and the occurrence of artifacts in the course of chromatographic separations, resulting in an apparent shift of the adsorption–desorption equilibria, limit the usefulness of chromatographic techniques and would require time-consuming preseparation procedures. Among polarographic methods, the use of dc polarography proved superior to differential pulse techniques (DPP). The sensitivity of dc polarography (DCP) allows sufficiently accurate determinations in the concentration range studied (from 1×10^{-5} to 5×10^{-4} M). Adsorption phenomena involved in the reduction of some studied agrochemicals affect the peak currents in DPP but not the limiting currents measured in DCP. Moreover, the studied samples contain a variable amount of surface active substances which can affect the peak currents in DPP but not the limiting currents in DCP.

EXPERIMENTAL PROCEDURES

Instrumentation. The dc current–voltage curves were recorded using a Sargent Mark XVI polarograph using a dropping mercury electrode with a natural drop time, a Sargent-Welch Mark 4001 polarograph with a controlled drop time of 1 s or a EC 225[IA] voltammetric analyzer and 7424MT X-Y-T recorder (IBM Instruments, Inc.). DPP curves were recorded using the Sargent-Welch Mark 4001 polarograph and controlled drop times. The dropping mercury electrode had $m = 1.87$ mg/s and $t_1 = 3.85$ s at $h = 100$ cm in 0.1 M KCl at 0.0 V (SCE) or $m = 2.1$ mg/s and $t_1 = 5.3$ s. Preliminary studies were carried out in a Kalousek cell using as reference a saturated calomel electrode separated by a liquid junction. Adsorption studies were carried out in an H-type cell with a thermostating jacket and a bottom stopcock for replacing the studied solution. pH measurements were obtained using a PHM 84 research pH-meter (Radiometer) with a 202B glass electrode or a EXTECH 651 digital meter.

Chemicals. Acifluorfen (I) (97.0%) and dazomet (II) (99.0%) were obtained from Chem Services. A sample of technical sodium acifluorfen (I) (41.8%) was kindly donated by BASF Corp., Chemicals Division, Research Triangle Park, NC. Thiram, tetramethylthiuram disulfide or bis(dimethylthiocarbamoyl) disulfide (III) (97%, mp 148–148 °C) was supplied by Aldrich Co. All other reagents used were of analytical grade; ethanol was USP (200 proof). The compounds were used as supplied, and 9.9×10^{-3} to 0.105 M stock solutions were prepared by dissolving the compounds in 95% ethanol. Stock solution of thiram (III, 0.01 M) was prepared in ethanol containing 20% (v/v) dimethylformamide.

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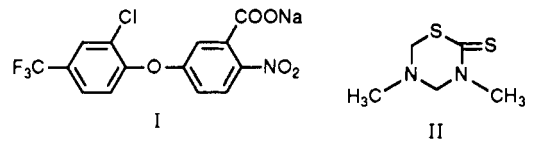
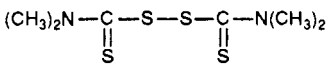


I

II



III

Chemicals used for preparation of the buffers were of reagent grade. Phosphate, acetate, and borate buffers (0.1 M) were used for the pH range 2–11.5. Sulfuric acid of concentration 0.01–2.0 M and sodium hydroxide of concentration 0.01–1 M were also used. Sufficient sodium sulfate was added to solutions less than 0.1 M to make them 0.1 M in sodium ions.

For 33% (w/w) ethanol solutions, similar buffers were prepared using a pH-meter which had been standardized using 33% (w/w) ethanol standards at pH 2.77 and 4.99. These standards were prepared as described by Perrin and Dempsey (1974).

For adsorption studies involving acifluorfen (I), 0.2 M buffers were used, sodium acetate/acetic acid for pH 5 and potassium dihydrogen phosphate/dipotassium hydrogen phosphate for pH 7. Solutions of the components (0.2 M) were prepared and mixed to obtain the desired pH. For the adsorption studies involving dazomet (II), 0.2 M acetate buffers of pH 4.6 and 3.7 were prepared. The samples with pH 3.7 were mixed with 0.2 M sodium acetate (2:3) to obtain a pH of 4.7 for polarographic investigations.

Solutions of acifluorfen in both aqueous and ethanolic (33% w/w) buffers were stable for at least 24 h. Potentiometric titration of a 0.001 M solution of acifluorfen containing 1% ethanol with a 0.02 M sodium hydroxide solution yielded $pK_a = 3.2$. In acidic solutions, pH < 3.7, acifluorfen is present partly as the undissociated acid and is volatile. When such solutions are bubbled with nitrogen, the compound is removed in the gas phase.

Preparation of Lignin Samples. One commercial and two natural lignins were used in this study. Each of the materials was submitted to several different treatments.

Indulin ATR-CK1 from Westvaco was prepared from precipitated softwood kraft lignin by heat coalescence and spraying: C_9 formula, $C_9H_{8.40}O_{2.39}S_{0.09}(OCH_3)_{0.79}$ (64.5% C, 5.82% H, 27.7% O, 1.6% S); unit weight 180; pH 3.68; ash 1.65%; acetone solubility 68.8%; carboxylic acid content 0.42 mol kg^{-1}; methoxy group content 4.50 mol kg^{-1}; phenolic hydroxide content 4.2 mol kg^{-1}. The surface area is about 100 $m^2 g^{-1}$ (BET). This material was treated in two ways: One sample (C) was washed 4 times with 0.25 M HCl and washed further 18 times with distilled water. The lignin dispersed in the washing liquid was stirred until homogenized. The resulting suspension was allowed to separate by gravity, usually overnight. The material was then collected on Whatman No. 5 filter paper in a Büchner funnel and air-dried. A second sample (L) was washed only twice with distilled water and dried before use.

Indulin AT from Westvaco was kraft pine lignin which produced a pH of 6 in a 2% water slurry and had a specific gravity of 1.3. It was treated in a manner similar to that for the indulin ATR-CK1: Sample (E) was washed 4 times with hydrochloric acid and then washed 18 times with distilled water.

The natural materials were first ground with a mortar and pestle and then passed through a screen with 0.14-cm openings before being washed with distilled water.

The first natural material (P) came from the Clarkson University campus and was gathered from a rotten maple log lying on the surface of the ground. The material was of a light brown color, resembling indulin ATR-CK1, but still had some structure of the original wood. It was brittle and crumbled when pressed by fingers. It was brought to the laboratory in chunks and dried before grinding and screening.

The second natural material (Q) was obtained from a rotten stump in the Manistee National Forest in Michigan. It was similar to that obtained from the Clarkson University campus and was treated in an analogous way.

Methodology of Adsorption Studies. *Acifluorfen (I).* As the compound is stable in aqueous solutions at pH 5 and 7, 0.3 g of a lignin preparation was dispersed in 15 mL of a 0.2 M aqueous buffer, pH 5 or 7, in a 35-mL centrifuge tube. To this suspension, varying volumes (0.01–0.4 mL) of ethanolic stock solution of compound I were added, and the container was placed on an Erbach 6460 Kahn shaker (38-mm stroke, 280 excursions/min) and shaken for approximately 21 h. The tubes were then placed in an IEC clinical centrifuge (maximum speed 4500 rpm) and centrifuged for 3 min; 5 mL of the supernatant was transferred into the polarographic H-cell, and 3.45 mL of 95% ethanol was added to yield a final concentration of 33% (w/w) of ethanol. The buffer used during the establishment of the adsorption equilibrium also served as supporting electrolyte. These solutions were purged with nitrogen for 3 min and polarographic current–voltage curves recorded.

Dazomet (II). At pH higher than about 7, dazomet undergoes rapid cleavage. Therefore, the adsorption on lignin was studied in solutions with pH ≤ 4.7, where the decrease in dazomet concentration due to cleavage was less than 5% over a 3-h period. Dazomet is best determined polarographically using its anodic wave, corresponding to a mercury salt formation. As this wave at pH < 4 is overlapped by the current of mercury dissolution, the determination is best carried out at pH 4.2–4.7, where the anodic wave is measurable and cleavage is negligible over the duration of polarographic analysis.

To establish the adsorption equilibrium, 0.3 g of lignin was dispersed in 15 mL of 0.2 M buffer containing dazomet in concentrations varying from 2×10^{-5} to 1×10^{-3} M, the mixture was shaken for 3 h, and the solid lignin particles were separated by centrifugation for 3 min at 4500 rpm. Two buffers, pH 4.7 and 3.7, were used for the adsorption studies. For the former, 15 mL of the supernatant was transferred to the polarographic cell. For the latter, 9 mL of 0.2 M sodium acetate was added to 6 mL of the supernatant to adjust the pH to 4.7, and this pH-adjusted solution was transferred into the polarographic cell. In both cases, the anodic waves of dazomet were recorded after a 3-min deaeration with nitrogen.

In both cases, calibration curves for dazomet were constructed using the same procedure and the same concentration range of dazomet but without the added lignin. By shaking the solutions of dazomet with buffers pH 3.7 and 4.7 for 3 h, correction was made for any losses due to the cleavage reaction.

For dazomet, the investigation was extended to a study of desorption. For this purpose, 0.3 g of lignin C (ATR-CK1, acid wash) was suspended in 15 mL of acetate buffer, pH 4.6, containing 6×10^{-4} M dazomet. The suspension was shaken for 80 min and centrifuged for 3 min. The decrease in concentration of dazomet in the supernatant was determined to establish the amount of bound dazomet. The lignin with bound dazomet was separated by decantation, dispersed in 15 mL of acetate buffer, pH 4.6, and placed in the shaker. Samples were taken every 20 min and analyzed polarographically for dazomet.

In a second set of experiments, 0.0, 0.3, and 0.6 g of lignin C (ATR-CK1, acid wash) were suspended in 15 mL of acetate buffer, pH 4.6, containing 6×10^{-4} M dazomet and shaken for 60 min. The suspensions were centrifuged for 3 min, and the supernatant was decanted and saved for analysis to determine the amount of bound dazomet. An additional 15 mL of acetate buffer was added to each sample of lignin, the mixture was shaken for 50 min, and the amount of dazomet released from the lignin was determined. This desorption process was repeated twice.

Thiram (III). The compound was reasonably stable for at least 6 h in aqueous solutions of pH 4.7 and 7.0. Lignin (0.3 g) was dispersed in 15 mL of an aqueous buffer in a 35-mL centrifuge tube, and varying volumes (0.01–0.4 mL) of 20% DMF–80% ethanol stock solution of thiram were added. The resulting solutions contained 1×10^{-5} to about 2×10^{-4} M thiram. The tubes were placed for varying times in the Erbach shaker and centrifuged for 3 min, and 7 mL of the supernatant was mixed with 4.83 mL of 95% ethanol to yield a solution containing 33% (w/w) ethanol. A similar set of solutions without lignin was placed in centrifuge tubes and treated in a similar way to establish a calibration curve for the concentration of thiram. The samples were purged for 3 min with nitrogen and the polarographic current–voltage curves recorded.

To study the desorption of thiram, 15 mL of suspensions of lignin in a pH 7.0 buffer containing 1×10^{-4} M thiram were equilibrated for 4 h, and the amount of adsorbed material was

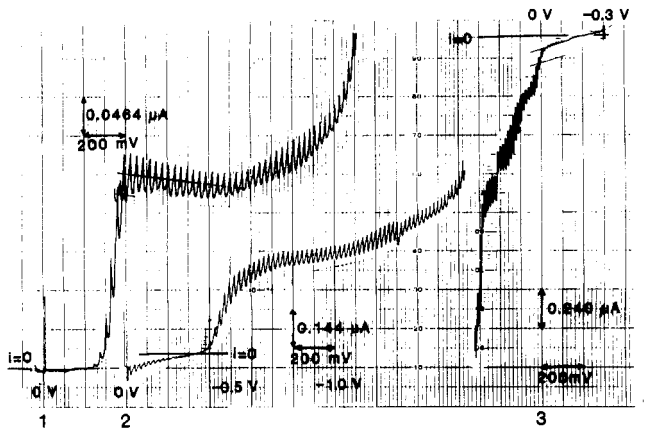


Figure 1. DC polarographic current–voltage curves of studied pesticides. Dropping mercury electrode had the following characteristics: m = 2.1 mg/s; t_1 = 5.3 s at h = 100 cm in 0.1 M KCl. (1) Cathodic wave of 7.9×10^{-5} M thiram in 0.2 M phosphate buffer, pH 7, containing 33% (w/w) ethanol; curve starting at 0.0 V to negative potentials. (2) Cathodic wave of 5×10^{-5} M acifluorfen in 0.2 M phosphate buffer, pH 7, containing 33% (w/w) ethanol; curve starting at 0.0 V to negative potentials. (3) Anodic wave of 1×10^{-4} M dazomet in 0.2 M acetate buffer, pH 4.7; curve starting at −0.3 V to positive potentials.

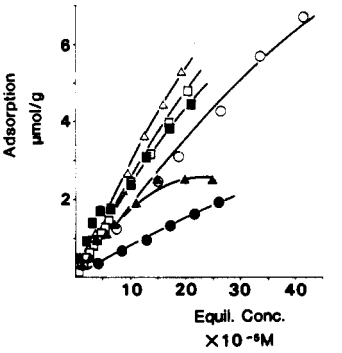


Figure 2. Adsorption of acifluorfen on various lignins equilibrated at two pH values. Amount of acifluorfen (micromoles) adsorbed per gram of indulin ATR-CK1 (L) [(○) pH 7.0; (●) pH 5.0], natural lignin (P) [(□) pH 7.0; (■) pH 5.0], and natural lignin (Q) [(△) pH 7.00; (▲) pH 5.0] is shown as a function of the equilibrium concentration of acifluorfen.

determined. After centrifugation, the solution was decanted from the lignin, and an additional 15-mL aliquot of buffer was again equilibrated with the lignin for varying times (15 min–18.5 h). The suspensions were centrifuged, the supernatant was analyzed for thiram, and the concentration of desorbed material was calculated.

In a second set of desorption experiments, solutions of 1.0×10^{-4}, 1.5×10^{-4}, and 2.0×10^{-4} M thiram were shaken with lignin in a pH 7.0 buffer. The amount of adsorbed material was determined, and the supernatant solutions were decanted. Several 15-mL portions of the buffer were successively equilibrated for 30 min with the samples of lignin bearing adsorbed thiram. The concentration of the desorbed thiram was determined, and from the amount of thiram initially bound to lignin, the relative amount of desorbed thiram was found.

RESULTS AND DISCUSSION

Acifluorfen (I). *Electroreduction.* The reduction of acifluorfen (I) at the DME occurs principally in two steps (Figure 1): In the first, the nitro group is reduced in a four-electron step to a hydroxylamino group (Kemula and Krygowski, 1979; Zuman and Fijalek, 1990; Zuman et al., 1992). This wave occurs over the entire range of pH. In acidic media, this reduction is followed by a two-electron reduction of the hydroxylamino group to an amine. Since only the protonated form is reduced, the height of this wave decreases, at pH greater than about 5.5, with increasing pH, as the rate of the protonation decreases. In aqueous solutions the two waves overlap, so that a single six-electron wave appears in acidic media. Moreover, at pH < 6 the current–voltage curves are complicated by adsorption phenomena. In buffered solutions containing 33% (w/w) ethanol, a separation of two waves occurs at pH > 8, resulting from a decreased rate of protonation of a reduction intermediate. The course of the reduction process is discussed in more detail elsewhere (Rupp et al., 1992).

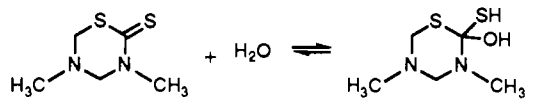
The limiting current of the first wave at pH 4.7–8 was best suited for analytical purposes. In aqueous solutions this current is a linear function of concentration of acifluorfen between 2×10^{-5} and 1.5×10^{-4} M. Extension to higher concentrations is prevented by the limited solubility of the nitro compound. In buffered solutions containing 33% (w/w) ethanol, linear dependence on concentration of acifluorfen was observed for 1×10^{-5} to 5×10^{-4} M solutions, both for limiting currents in dc polarography and for peak currents in DPP.

Adsorption on Lignin. Polarographic analysis was used in the study of adsorption of acifluorfen on three lignin preparations—one commercially available, indulin ATR-CK1 (L), and two natural lignins (P and Q)—at pH 5 and 7. These pH values were chosen to mimic possible conditions in forest soil and litter. A plot of the dependence of the adsorbed amount of the nitro compound on its equilibrium concentration at constant amount of lignin (Figure 2) has the shape of the first part of an adsorption isotherm. The region of equilibrium concentration where the adsorbed amount reaches a limiting value, corresponding to complete surface coverage, is in most cases not accessible due to the limited solubility of the nitro compound in aqueous buffers used. The use of water–ethanol mixtures which would allow studies in a wider concentration range was not adopted, as such a medium would differ from natural conditions. In all instances the adsorption was stronger at pH 7 than at pH 5.

The nature of the lignin also plays an important role: At both pH 5 and 7 the adsorption is weaker on kraft lignin (L) than on natural lignins (P and Q). The adsorption on kraft lignin (L) is affected by the variation of pH, whereas that on natural lignin P shows relative insensitivity to the effect of pH. For natural lignin Q, even the shape of the adsorption isotherm varies with changes in pH. These results indicate that the adsorption depends not only on the ionic state of the adsorbed nitro compound but also on the dissociation of the carboxylic groups of lignin and possibly on changes in its spatial arrangement (tertiary structure) (Zuman et al., 1988; Ainso et al., 1988; Wieber et al., 1988).

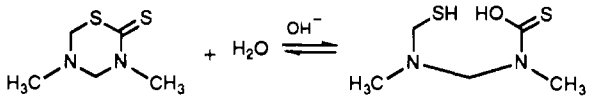
Dazomet (II). *Cathodic Waves.* The polarographic reduction of dazomet (II) takes place at pH 4.5–8 in a single cathodic wave at about −1.1 V (SCE), the height of which is less than 10% of that corresponding to a diffusion-controlled one-electron wave. This is a kinetic wave whose height is independent of mercury pressure (h_{Hg}). Dazomet exists in the solution predominantly in an electroinactive form; the rate of formation of the reducible species governs the limiting current. There is no evidence available for the nature of the chemical reaction involved. The pH independence of the limiting current and of its half-wave potential at pH 4.5–8 indicates that the rate of the chemical reaction in this pH range is neither acid nor base catalyzed.

Tentatively, such behavior could be explained by the hydration of the thiono group:



At pH <4.5 this wave is overlapped by a hydrogen evolution current which is probably catalytic. At pH <8 the height of this reduction wave does not change noticeably with time for up to 30 min. At pH >8 the height of this wave decreases with time. This decrease is accompanied by the increase of a wave at potentials about 0.2 V more negative. The half-wave potential of this wave is pH dependent and is shifted by about −0.03 V/pH unit.

This decrease in current at pH >8 can be tentatively attributed to a base-catalyzed hydrolysis involving ring opening:



The wave at more negative potentials can be attributed to the reduction of the acyclic species.

Anodic Wave. At pH ≈7, dazomet with concentration of 2×10^{-4} M yields two main anodic waves which overlap. The total height of the anodic limiting current ($i_1 + i_2$ at pH <7, i_{1+2} at pH 7–8) is pH independent. At pH >8 a decrease in the limiting current with time is observed. This decrease is attributed to hydrolysis, as mentioned above. The anodic wave is distorted by a desorption step at about +0.3 V; the desorption potential is practically pH independent. All of these waves show characteristics typical of anodic waves corresponding to a dissolution of mercury, producing mercury ions (Březina and Zuman, 1958b; Chambers, 1978; Fijalek and Zuman, 1990). At the electrode surface, these ions react with the sulfur compound present, forming a slightly soluble mercury salt:

$$2Hg \rightleftarrows Hg_2^{2+} + 2e$$

$$Hg_2^{2+} + nL \rightleftarrows (Hg_2L_n)^{2+}$$

Adsorption complications are due to the formation of various adsorbed layers, differing in composition of the adsorbed salt or in the structure of the adsorbed layer, e.g., in the orientation of adsorbed species.

For analytical application, the total anodic current was measured at constant potential. This current in acetate buffer of pH 4.7 is a linear function of concentration between 2×10^{-5} and 6×10^{-4} M. The plot of $i = f(C)$ at concentrations higher than 6×10^{-4} M was curved due to adsorption of the electrolysis product.

Adsorption on Lignin. The adsorption of dazomet was followed at pH 3.7 and 4.7 (the analysis was carried out in both cases at pH 4.7, see Experimental Procedures). At both pH values the kraft lignin indulin AT (E) has shown the lower adsorption capacity (Figure 3). This lignin shows similar adsorption capacity at pH 4.7 and 3.7, whereas kraft lignin indulin ATR-CK1 (C) and the natural lignin P are more strongly adsorbing at pH 4.7 than at 3.7. At both pH values, the differences between the adsorptions on lignins C and P are not significant.

In all instances, dazomet was more strongly adsorbed than acifluorfen. Desorption of dazomet bound on lignin C is practically complete after 20 min of contact with an acetate buffer of pH 4.6 (Table I). About 40% of the adsorbed dazomet is easily desorbed, while the remaining 60% is irreversibly bound.

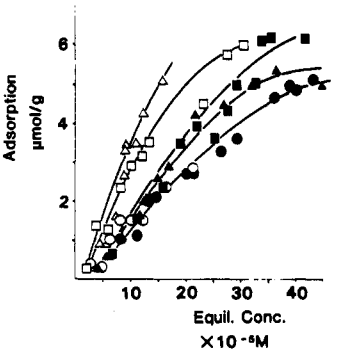


Figure 3. Adsorption of dazomet on various lignins equilibrated at two pH values. Amount of dazomet (micromoles) adsorbed per gram of acid-washed indulin AT (E) [(○) pH 4.67; (●) pH 3.68], acid-washed indulin ATR-CK1 (C) [(△) pH 4.67; (▲) 3.68], and natural lignin (P) [(□) pH 4.67; (■) pH 3.68] is shown as a function of the equilibrium concentration of dazomet. All samples were analyzed at pH 4.7.

Table I. Desorption of Dazomet from 0.3 g of Lignin C (ATR-CK1) in Acetate Buffer, pH 4.6, 60×10^{-5} M Dazomet in Initial Solution

time for desorption, min	dazomet adsorbed, μmol/g	dazomet desorbed, μmol/g	% desorbed
20	2.82	1.11	39.4
40	3.16	1.20	38.0
60	2.93	1.28	43.7
80	2.88	1.16	39.0
100	3.05	1.19	39.0
av	2.97	1.19	40.1

Table II. Desorption of Dazomet at Various pH Values

pH	amount desorbed, μmol/g	% desorbed
2	3.4	18.9
3	3.3	18.3
4.6	3.05	16.9

Table III. Desorption of Dazomet with Several Extractions

lignin, g	dazomet adsorbed, μmol/g	extraction	dazomet desorbed, μmol/g	% desorbed
0.3	8	1	3.4	42.5
		2	1.2	15.0
0.6	5.5	1	2.0	36.4
		2	0.9	16.4

Between pH 2 and 4.6, the desorption was practically independent of the pH (Table II). When 18.4 μmol of dazomet was adsorbed per gram of lignin C, repeated extraction with the same volume of acetate buffer, pH 4.6, indicated that most of the desorption was achieved in the first extract (Table III).

Thiram (III). *Electroreduction.* The reduction of organic disulfides (RSSR) on mercury electrodes often occurs in two steps (Heyrovský and Kůta, 1965): A more positive, steep reversible wave corresponds to a sequence

$$RSSR + Hg \rightleftarrows (RS)_2Hg$$

$$(RS)_2Hg \rightleftarrows Hg^{2+} + 2RS^-$$

$$Hg^{2+} + 2e \rightleftarrows Hg$$

and a more negative, drawn-out irreversible wave corre-

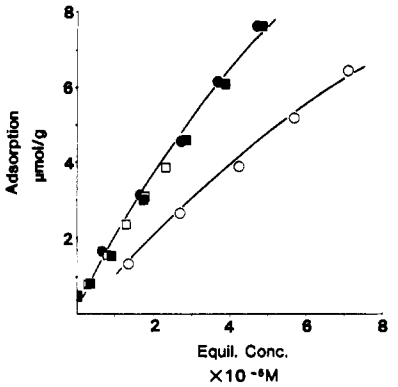


Figure 4. Adsorption of thiram on various lignins equilibrated at two pH values. Amount of thiram (micromoles) adsorbed per gram of indulin ATR-CK1 (L) [(●) pH 7.0; (○) pH 4.7] or natural lignin (P) [(■) pH 7.0; (□) pH 4.7] is shown as a function of the equilibrium concentration of thiram.

sponds to a reductive cleavage of the S–S bond:

$$RS\text{–}SR + 2e \rightarrow 2RS^-$$

For disulfides derived from dialkyl dithiocarbamates (Zuman et al., 1953; Gregg and Tyler, 1950) the first process at positive potentials predominates, corresponding to the sequence

$$R_2N\text{–}C(:S)\text{–}S\text{–}S\text{–}C(:S)NR_2 + Hg \rightleftarrows (R_2NCSS)_2Hg$$

$$(R_2NCSS)_2Hg \rightleftarrows 2R_2NCSS^- + Hg^{2+}$$

$$Hg^{2+} + 2e \rightleftarrows Hg$$

Reversibility of the process, involving the Hg^{2+}/Hg couple (Zuman et al., 1953), is supported by the fact that for a given pH the anodic wave in the presence of dithiocarbamates occurs at the same potential as the cathodic wave in the presence of disulfide (Gregg and Tyler, 1950). In addition, the adsorption waves (cathodic for the disulfide, anodic for the dithiocarbamate) occur at the same potential, with both corresponding to the adsorption of $(R_2NCSS)_2Hg$.

The total height of the adsorption wave and the main cathodic wave is a linear function of the concentration of the disulfide (III) between 1×10^{-5} and 3×10^{-4} M.

In alkaline solutions, thiram undergoes nucleophilic cleavage, as do other disulfides (Reid, 1960; Danehy, 1966; Kolthoff and Stricks, 1951; Stricks and Kolthoff, 1951). The cleavage products produce anodic waves when mercury electrodes are used. Solutions (3×10^{-4} M) of thiram at pH 5 and 7 were stable for at least 30 min. An increase in the anodic waves, accompanied by a decrease in the cathodic waves, occurs slowly at pH 9.4 and rapidly at pH 12 (0.01 M KOH). Analyses and adsorption studies were, therefore, limited to pH ≤7.

Adsorption on Lignin. The adsorption of thiram was followed at pH 4.7 and 7.0 using the decrease of the reduction waves of the disulfidic bond. For natural lignin P there was no significant difference between the adsorptions at pH 4.7 and 7.0 (Figure 4), which is in agreement with the fact that the adsorbed substance does not contain groups which would be protonated or dissociated in this pH range. For kraft lignin L the adsorption is somewhat stronger at pH 7.0 than at pH 4.7. This reflects the role of dissociation of carboxylic groups on lignin and/or changes in its tertiary structure with pH. In all instances, thiram was the most strongly adsorbed of the three compounds compared.

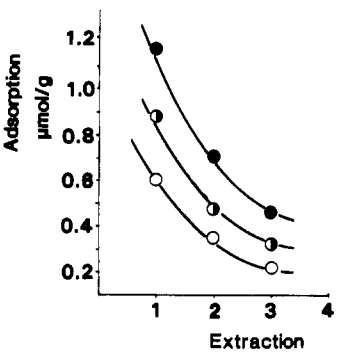


Figure 5. Desorption of thiram from lignin at pH 7.0 as a function of number of desorption steps. Each desorption step equilibrated for 30 min with indulin ATR-CK1 (L) which had an initial bound amount of (○) 3.05, (◑) 4.62, and (●) 6.33 µmol/g thiram.

Table IV. Desorption of Thiram from 0.3 g of Lignin L (ATR-CK1) in Phosphate Buffer, pH 7.0

initial soln concn $\times 10^{-5}$ M	thiram adsorbed, µmol/g	thiram desorbed[a] extraction 1, µmol/g	2, µmol/g	3, µmol/g	total, %
10.06	3.05	0.609 (20.0)	0.355 (14.5)	0.196 (9.4)	38
15.03	4.62	0.888 (19.2)	0.482 (12.9)	0.316 (9.7)	37
20.14	6.33	1.174 (18.6)	0.708 (13.8)	0.459 (10.3)	37

[a] Relative percent desorbed in individual step is in parentheses.

The desorption of the bound thiram was followed in a phosphate buffer of pH 7.0. The desorption equilibrium was essentially established within 10 min of mixing of the lignin with bound thiram and the buffer solutions. With a single extraction, only about 20% of the thiram was desorbed, indicating that most of the thiram is irreversibly bound. Repeated extractions resulted in gradually decreasing amounts of thiram desorbed (Figure 5). Three successive equilibrations with phosphate buffer of pH 7.0 resulted in a total thiram decrease of about 37% (Table IV).

Conclusions. All of the pesticides studied are adsorbed on lignin. For dazomet and thiram, which contain thiono groups and other sulfur-containing functional groups, the binding is partly irreversible. Only about 40% of the pesticide can be released under batch conditions in aqueous buffered systems of pH 4–7. This has considerable practical consequences. First, the bioavailability of the pesticide is affected: 100% larger dosage of the pesticide is needed in the presence of lignin to achieve the same concentration in the underground water system as would be needed in the absence of lignin. Second, since more than 60% of the pesticides are adsorbed on naturally occurring organic matter, the potential for these agrochemicals to reach groundwater supplies is greatly reduced. For decomposition products of lignin, humic acids, adsorption of some pesticides has been reported [DDT (Wershaw et al., 1969; Carter and Suffel, 1982)].

Our results also stress that conditions of the medium in which the pesticide is dissolved, in particular pH, affect the adsorption capacity of lignin. Moreover, the nature of the lignin plays a considerable role. For lignins currently studied, the natural lignins obtained from rotten wood proved to have higher adsorption capacity than the commercial lignins. The lignins studied differ not only in the chemical nature of the building units of the polymer

but also in the spatial arrangement of these units (tertiary structure). Our experiments indicate that studies of three-dimensional structure of lignins deserve more attention in the future.

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