

THE REMOVAL OF PESTICIDES
FROM AQUEOUS SOLUTION
BY TREATED PEAT

by

Kamel Djebbar

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemistry).

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ABSTRACT

This research involved the use of cation exchangers produced by chemical modification of peat, (i.e. peat reacted with concentrated sulfuric acid). The resulting product has been found to be superior to the untreated peat since it has enhanced cation exchange capacity, has a granular form useful for column operation, and is resistant to leaching. The modified peat was used as an absorbent for removing a variety of pesticides from water. The treated peat was found to be very effective for the removal of cationic and basic pesticides. The objectives of this research were as follows:

- (i) To determine the effectiveness of the treated peat for removing various pesticides from aqueous solution.
- (ii) To determine the capacity of the treated peat for various pesticides.
- (iii) To determine the effect of pH, ionic strength and flowrate on the efficiency of pesticide removal and,
- (iv) To compare peats obtained from different locations with respect to the above properties.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.	iii
LIST OF FIGURES	viii
LIST OF TABLES.	ix
ACKNOWLEDGMENTS	xi
INTRODUCTION.	1
BACKGROUND INFORMATION.	2
Classification of Pesticides	2
Nature of the Soil Organic Matter: Peat	5
Types of Interaction Occurring Between Pesticides and Soil Organic Matter	6
Brief Discussion of Mechanism of Pesticide- Binding to Soil Organic Matter	8
Cation Exchange and Acid-Base Reactions	8
Hydrogen Bonding.	10
Non-Polar Van Der Waals Forces.	10
Ligand Exchange	11
OBJECTIVES.	12
EXPERIMENTAL.	13
Preparation of the Treated Peat.	13
Description of the Apparatus	14
Determination of Ion Exchange Capacity	14
Effect of pH on the Physical Form of the Treated Peat	16

	<u>Page</u>
Development of Experimental Procedures for the Removal of Cationic Species (Dyes and Pesticides) from Solution by Treated Peat.	17
Cationic Dyes	17
Pesticides.	19
Neutral Pesticides.	19
Cationic Pesticides	20
Colorimetric Determination of Paraquat and Diquat.	22
Standard Solutions of Paraquat and Diquat	23
Removal of Paraquat and Diquat by Treated Peat.	30
Effect of pH, Ionic Strength and Flowrate on Efficiency of Pesticide Removal.	31
Influence of pH.	31
Effect of Ionic Strength	31
Effect of the Flowrate	32
Elution of Pesticides from the Treated Peat	33
Basic Pesticides.	34
Colorimetric Determination of Amitrole	35
Standard Solutions of Amitrole	35
Removal of Amitrole from Aqueous Solution by Treated Peat	37
Effect of pH, Flowrate and Ionic Strength on Efficiency	39
Effect of pH	39
Effect of Flowrate	40

	<u>Page</u>
Effect of Ionic Strength	40
Elution of Amitrole by 3M NaCl.	40
Capacity of the Chemically Modified Peat for Various Cationic Pesticides.	41
Determining Isotherms for Paraquat and Diquat Binding to Treated Peat.	43
Determining Capacity of the Treated Peat for Binding Diquat by the Column Method	45
Determining Isotherm for Amitrole Binding to Treated Peat	45
RESULTS AND DISCUSSION.	50
Preparation of the Treated Peat.	50
Cation Exchange Capacity of the Chemically Treated Peat	51
Efficiency of Pesticide Removal by the Treated Peat	51
Efficiency of Paraquat, Diquat and Amitrole Removal from Aqueous Solution.	53
Mechanism of Pesticide Removal	54
Effect of pH, Ionic Strength and Flowrate on the Efficiency	55
Influence of pH and Ionic Strength	55
Influence of Flowrate.	55
Elution of Paraquat, Diquat and Amitrole from Treated Peat.	56
Capacity of the Chemically Modified Peat For Various Pesticides	56
CONSIDERATION OF PESTICIDE TOXICITY HAZARD.	58

	<u>Page</u>
CHEMICALS USED.	59
CONCLUSIONS AND SUMMARY	60
REFERENCES.	74

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Type of Structure Which Has Been Proposed for Humic Acid.	7
2.	Model Proposed in the Literature for Adsorption of Diquat at Ionizable Carboxyl Groups of Soil Organic Matter or Weakly Cation Exchange Resins.	9
3.	Apparatus for Column Experiments.	15
4.	Visible Spectrum of Reduced Diquat.	24
5.	Visible Spectrum of Reduced Paraquat.	25
6.	Beer's Law Plot for Reduced Paraquat at 390 nm.	27
7.	Beer's Law Plot for Reduced Paraquat at 596 nm.	28
8.	Beer's Law Plot for Reduced Diquat at 380 nm.	29
9.	Visible Spectrum of Amitrole Complex.	36
10.	Beer's Law Plot for Amitrole complex at 625 nm.	38
11.	Classification of Adsorption Isotherms According to Giles.	42
12.	Adsorption Isotherm for Paraquat Binding to Treated Peat.	46
13.	Adsorption Isotherm for Diquat Binding to Treated Peat.	47
14.	Adsorption Isotherm for Amitrole Binding to Treated Peat	49

LIST OF TABLES

<u>Table</u>	<u>Page</u>
I. Cation Exchange Capacities of Treated Peat (Irish and Colorado Peat) for Ba ²⁺ and Na ⁺	63
II. Absorbances of Standard Solutions of Reduced Paraquat at 390 nm.	63
III. Absorbances of Standard Solutions of Reduced Paraquat at 596 nm.	64
IV. Absorbances of Standard Solutions of Reduced Diquat at 380 nm.	64
V. Results of Elution of Paraquat by 5.5 M NaCl.	65
VI. Results of Elution of Diquat by 5.5 M NaCl	65
VII. Results of Elution of Paraquat by 5.5 M NH ₄ Cl	66
VIII. Absorbances of Standard Solutions of Amitrole Complex at 625 nm	66
IX. Results of Elution of Amitrole by 3 M NaCl.	67
X. Data Related to the Adsorption Isotherm of Paraquat.	67
XI. Data Related to the Adsorption Isotherm of Diquat.	68
XII. Data Related to the Adsorption Isotherm for Amitrole After Standing for 48 Hours.	68
XIII. Data Related to the Adsorption Isotherm of Amitrole After Standing for 72 Hours.	69
XIV. Efficiency of Removal of Pesticides by Irish Peat and Colorado Peat.	69
XV. Influence of pH and Ionic Strength on Removal of Paraquat from Solution by Treated Irish Peat.	70
XVI. Influence of pH and Ionic Strength on Removal of Diquat from Solution by Treated Irish Peat	70

<u>Table</u>		<u>Page</u>
XVII.	Influence of pH and Ionic Strength on Removal of Amitrole from Solution by Treated Irish Peat.	71
XXVIII.	Effect of Flowrate on Removal of Paraquat from Solution by Treated Irish Peat	71
XIX.	Effect of Flowrate on Removal of Diquat from Solution by Treated Irish Peat.	72
XX.	Effect of Flowrate on Removal of Amitrole from Solution by Treated Irish Peat	72
XXI.	Capacity of the Treated Irish Peat for Amitrole, Paraquat and Diquat as Determined from Isotherms.	73
XXII.	Moisture Content for Irish Peat and Colorado Peat.	73

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INTRODUCTION

Since 1945, organic pesticides have been reported in drinking water (1), agricultural water (1) and in aquatic organisms (1). It is known that these pesticides enter water directly as a result of their application to the environment for the control of insects on land, and in natural water (lakes, rivers) and also from the discharge of industrial waste water (2). Many of these pesticides resist biological degradation (3) and thus may persist for a long time in the environment (3). This source of pollution has been of major concern to scientists for a long time. Methods to remove pollutants of all types from water have been studied extensively. The chemical oxidants, ozone, KMnO_4 , etc . . . have shown an ability to reduce the concentration of some pesticides (4,5,6). Ionizing radiation (7), adsorption by mineral clays (8), adsorption by active carbon (9) and by synthetic resins (10) have also been used to destroy pesticides or remove them from solution. It is desirable to develop simple and inexpensive methods for the treatment of polluted water. Peat, a natural and abundant substance (11) having a native cation exchange capacity, has been shown to be successful in removing organic pollutants (12) and in the purification of water by filtration (13). Smith et al. (14) established that peat, treated by concentrated sulfuric acid (1.2g of dried

peat for 4.0 ml of concentrated sulfuric acid) exhibits enhanced cation exchange capacity, and that leaching problems are considerably reduced in the treated peat. (Leaching meaning a passage into solution of some organic constituents of the peat). The increased capacity seems to be due primarily to the oxidation of some aliphatic chains and, to a lesser extent, sulfonation at some aromatic sites (14). The use of this chemically modified peat for the removal of a variety of pesticides from aqueous solutions was studied in this research

BACKGROUND INFORMATION

Classification of Pesticides

Pesticides are defined as chemical poisons capable of destroying pests. In the context of this thesis it is logical to classify pesticides into three categories on the basis of their charge: cationic, anionic and neutral. Examples of cationic and neutral pesticides are listed below. Anionic pesticides were not investigated in this research as they were expected not to interact with the negatively charged matrix of the treated peat.

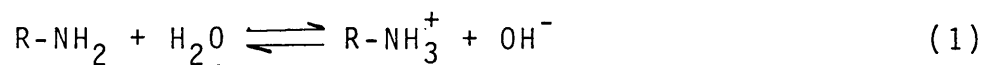
Cationic Pesticides

Paraquat dichloride: $C_{12}H_{14}Cl_2N_2$ (15)

Molecular weight: 257

In aqueous solution, amitrole behaves as a weak bases,

$$pK_b = 9.83:$$



where $R-NH_2$ represents amitrole and the equilibrium relation is shown in equation:

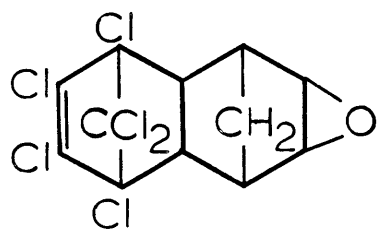
$$\frac{[R-NH_3^+][OH^-]}{[R-NH_2]} = K_b \quad (2)$$

Neutral Pesticides

Dieldrin: $C_{12}H_8Cl_6O$ (15)

Molecular weight 237

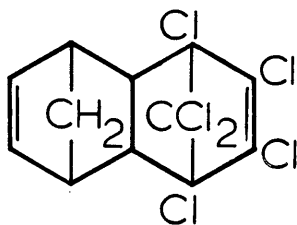
Structure:



Aldrin: $C_{12}H_8Cl_6$ (15)

Molecular weight 364.9

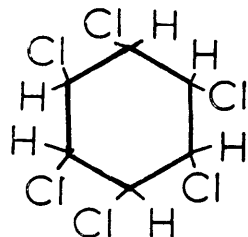
Structure:



Lindane: $C_6H_6Cl_6$ (15)

Molecular weight: 290.8

Structure:



The above three neutral pesticides are insoluble in water but are soluble in ethanol and acetone.

Nature of the Soil Organic Matter: Peat

This thesis involves the study of pesticide interactions with chemically modified peat. However, in order to develop a feeling for the possible nature of these interactions, it is appropriate to first survey the literature concerning the nature of the interactions between these pesticides and untreated peat or soil organic matter. This is desirable as there is relatively little information available on the chemistry of the treated peat,

Peat is a type of soil organic matter consisting of two main groups of compounds: non-humic substances and humic substances (16). Non-humic substances are represented by discrete organic compounds like proteins, carbohydrates, organic acids, sugars, fats, waxes, resins, lignin, pigments, and low molecular weight compounds (16). These compounds exist in relatively small quantity in soil organic matter. Stevenson (17) has reported that the content of fats, waxes, and resins in organic matter varies from 2% to 20%.

Humic substances consist of a highly complex mixture of organic components which is resistant to microbial attack. As a result they persist in the environment for extended periods. They are commonly subdivided into three categories according to their solubilities as a function of pH. Fulvic acid, which is soluble in both acidic and alkaline media; humic acid which is soluble in alkaline medium but not in acidic medium; and humin which is insoluble in both acidic and basic media.

Martin and Haider (18) have shown that humic acid is the most abundant constituent of humus. Humic acid has been described (16) as an ensemble of polymeric compounds having an essentially aromatic structure which is bridged by -O-, -NH-, -N= and S, and containing the following functional groups: carboxyl, phenolic, hydroxyl, and carbonyl. These functional groups are of considerable importance in the interaction between pesticides and soil organic matter. A type of structure which has been proposed for humic acid is shown in figure 1 (16).

Types of Interaction Occurring between Pesticides and Soil Organic Matter

The interactions occurring between pesticides and soil organic matter are extremely complicated because of the complex nature of the soil organic matter. Several mechanisms

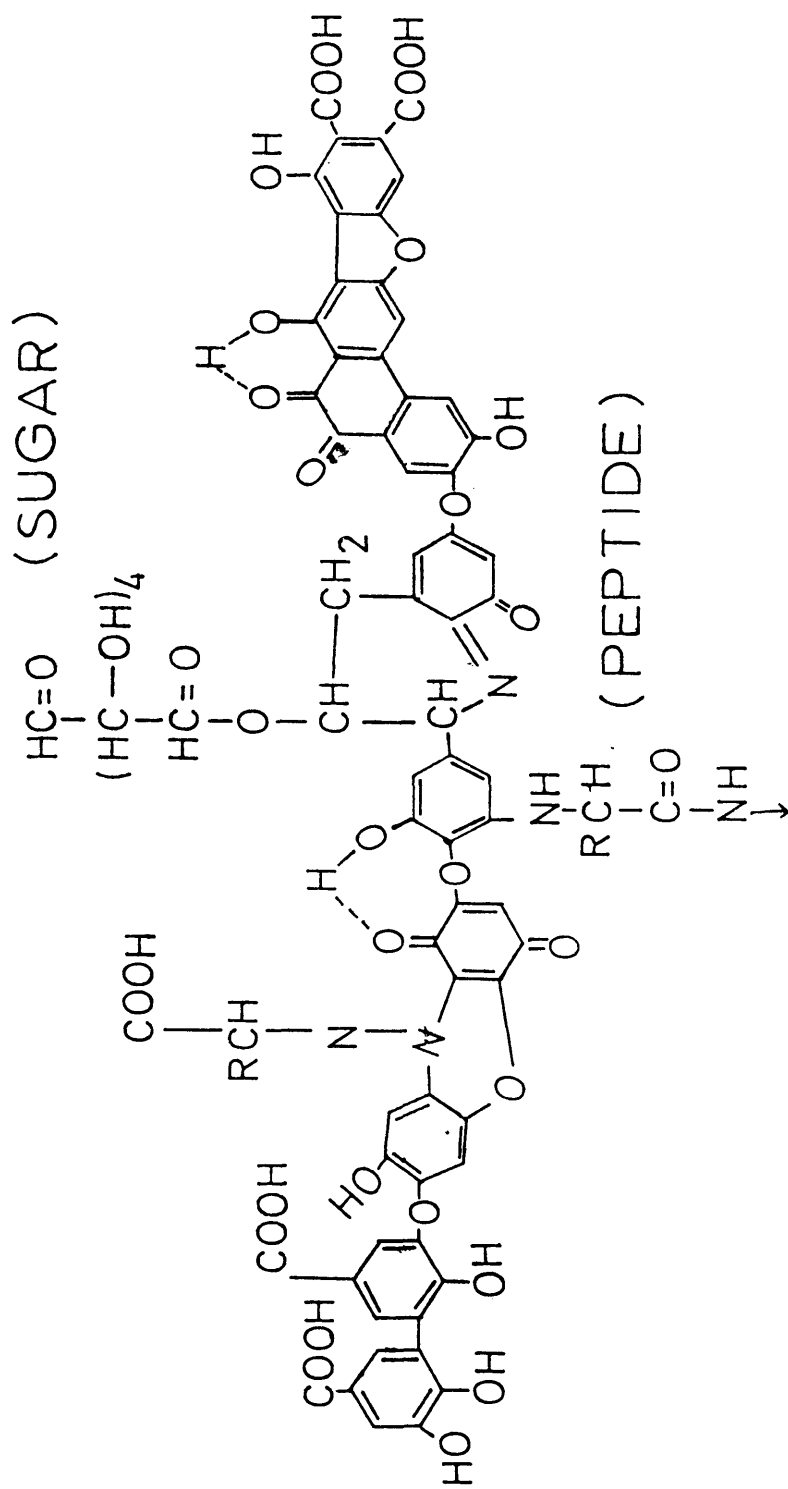


FIG. 1. TYPE OF STRUCTURE WHICH HAS BEEN PROPOSED FOR HUMIC ACID (16).

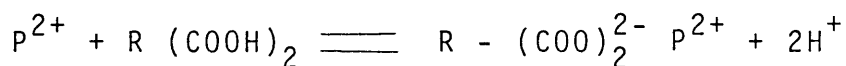
have been proposed (19) in the past for the retention of pesticides by organic matter. These include:

- (a) cation exchange and acid-base reactions
- (b) hydrogen bonding
- (c) non-polar Van der Waals forces
- (d) ligand exchange

Brief Discussion of Mechanisms of Pesticide Binding to Soil Organic Matter

(a) Cation Exchange

It is known that cationic pesticides, such as diquat and paraquat are absorbed by the organic matter in soil (20). They presumably interact with the negatively charged sites on soil humic substances such as carboxylate. This can be illustrated by the following figure (Fig. 2), which has been proposed in the literature (21). The process involved is best described by the following equation (2):



P^{2+} being the cationic pesticide, and $R-(COOH)_2$ being the cation exchanger (the treated peat).

Basic pesticides, such as amitrole are not cationic in themselves, but become cationic through accepting a proton. The reactions leading to adsorption of basic pesticides are described by Weber et al. (22) in the following equation:

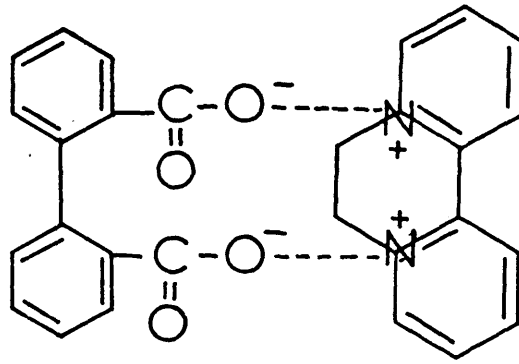
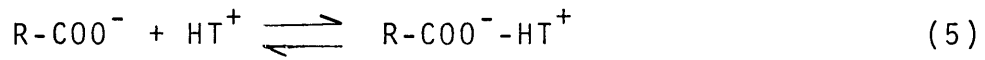
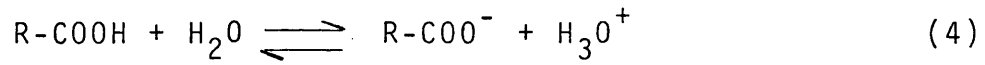


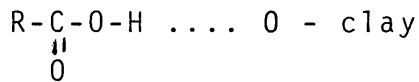
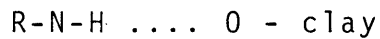
FIG. 2. MODEL PROPOSED IN THE LITERATURE FOR ADSORPTION OF DIQUAT AT IONIZABLE CARBOXYL GROUPS OF SOIL ORGANIC MATTER OR WEAKLY CATION EXCHANGE RESINS (21).



Where R-COOH represents the ion-exchanger, T the amitrole molecule and HT⁺ the protonated amitrole molecule.

(b) Hydrogen Bonding

Hydrogen bonding is primarily an electrostatic effect that involves interaction between molecules having a dipole moment and in which the hydrogen atom serves as a bridge between two electronegative atoms. The following examples are given by Bailey (23):



The abundance of carboxyl and hydroxyl functional groups on organic matter can lead to a bonding mechanism for organic molecules containing similar groups.

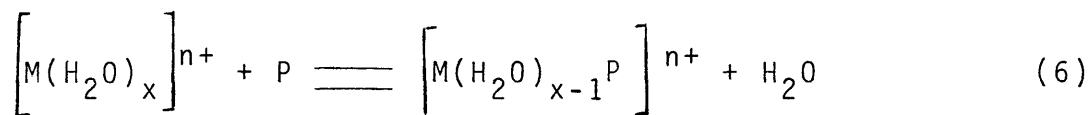
(c) Non-polar Van der Waals Forces

In the context of solute adsorption, Van der Waals attraction may be the principal force causing adsorption of non-ionic molecules on soil organic matter even though

individually these forces are relatively weak compared to other types of interaction (24).

(d) Ligand Exchange

Hayes (25) has shown that transition metals may act as sites for ligand exchange adsorption, and has shown also that water of hydration, acting as a ligand, may be displaced by the pesticide solution. The process involved can be illustrated by the following equation:



where P is the pesticide having a lone pair of electrons.

OBJECTIVES

The purpose of this study was to evaluate the potential of chemically modified peat for removing pesticides from aqueous solution. The research involved the following aspects:

(1) Preparation of the cation exchangers, and determination of their cation exchange capacities for Na^+ and Ba^{2+} ions.

(2) Evaluation of the effectiveness of the treated peat for the removal of different types of pesticides from aqueous solution. Cationic and basic pesticides were studied in detail, and preliminary experiments were conducted with neutral pesticides. The effect of the pH, ionic strength and flowrate on efficiency of pesticide removal were investigated.

3) Evaluation of the capacity of the exchanger for each type of pesticide. This was achieved by determining the adsorption isotherms for the various pesticides on the chemically treated peat. The exchange capacity for diquat was also determined by the column method.

4) Comparison of samples of peat from Ireland and from the State of Colorado in regard to the quality of the adsorbents obtained. Most of the work was carried out using Irish peat.

EXPERIMENTAL

The raw peat materials used in this study were obtained from the Irish Peatlands Experimental Station, Glenamoy, County Mayo, Ireland (14) at about 3½ ft. depth. Peat samples were also obtained from the Guannala Pass located above Georgetown in the State of Colorado. The peat was dug at approximately 15 to 20 inches. The moisture content of both types of peat was determined by weighing. Four batches of each material containing 10 g of wet peat were put in an oven at 110 °C for drying. The samples were dried to a constant weight, and the moisture content was determined by difference. The results are provided in Table (XXII).

Peat in its natural form is impervious to water flow, and readily leaches organic matter which can be a source of pollution in itself. This problem can be minimized by treating the peat with concentrated sulfuric acid at elevated temperatures (14).

Preparation of the Treated Peat

Both types of peat (Irish and Coloradoan) were treated in the identical manner. The peat samples were dried for 24 hours in an oven at 110 °C in order to remove water. Concentrated sulfuric acid was added to weighed samples of dried peat according to Smith et al. (14) in the ratio of 4.0 ml

of concentrated H_2SO_4 to 1.2 g of dried peat. The experiment was carried out in a large beaker, and the mixture was heated for two hours at $150^\circ C$ on a hot plate located in a fume hood. The reaction mixture was then washed with portions of deionized water until the pH of the supernatant solution was close to that of distilled water, in order to remove excess H_2SO_4 . The treated peat was then dried in an oven at $110^\circ C$ for 26 hours. After grinding in a mortar, and sieving, the batches of different particle sizes were stored in labeled jars. All experiments were carried out with particles ranging from 354 microns to 500 microns.

Description of the Apparatus

The use of the column instead of the batch mode is based on the fact that pesticide solution is continuously in contact with the fresh exchanger as it passes through the column, therefore making a more efficient separation of the pesticides from aqueous solution. The apparatus used for removing pesticides from aqueous solutions in this study is very simple, and is illustrated in figure 3.

Determination of Ion Exchange Capacity

A 0.5 gram sample of each type of chemically modified peat was washed with distilled water. A few drops of methanol were added in order to facilitate wetting of the initially dry particles. To ensure that the exchanger was in the hydrogen

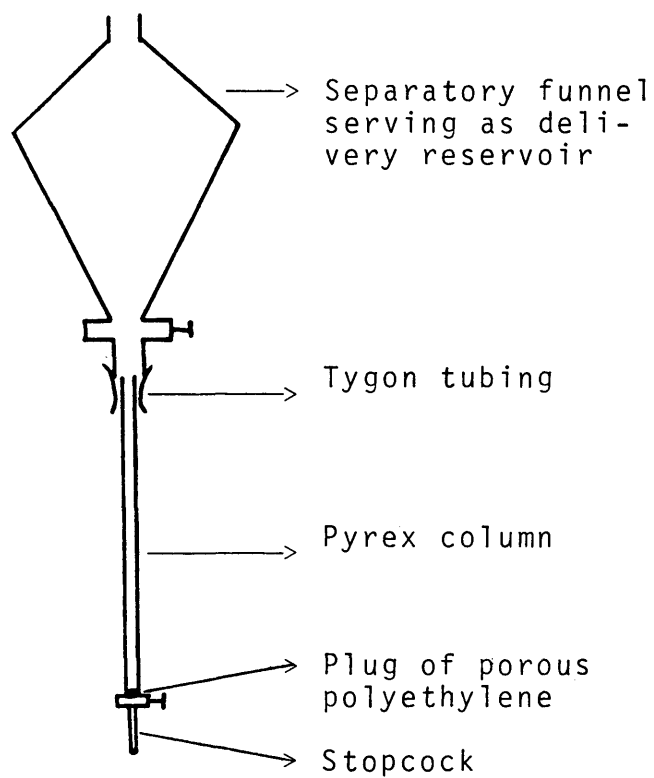


FIG. 3. APPARATUS FOR COLUMN EXPERIMENTS

form, 50 ml of 3N HCl was slowly passed through columns (1.50 ml per minute) followed by a large volume of distilled water in order to remove excess of acid. The exchange capacities were determined according to Smith et al. (14). The process was to run an excess of Na^+ or Ba^{2+} (100 ml of 0.5N NaCl and 100 ml of 0.1N BaCl_2) through columns of treated peat (0.5 g) in the H^+ form at a slow flow rate (1.20 ml per minute). After rinsing the columns with 20 ml of distilled water, the total effluents were titrated to a phenolphthalein end point with standardized base (NaOH).

The cation exchange capacity with Ba^{2+} was greater than the cation exchange capacity with Na^+ , for both types of treated peat (See Table I).

Cation exchange capacity of the treated peat was also determined by the above method using diquat as the displacing cation. That experiment will be described later.

Effect of pH on the Physical Form of the Treated Peat

Previous workers (14) have shown that the chemically treated peat does not leach under acidic or neutral conditions, but that it does leach at high pH values ($\text{pH} > 9$). These results were confirmed in the present experiments. There was no evidence of leaching under acidic condition. The influence of alkaline pH's on the treated peat was determined by equilibrating the exchanger with Clark-Lubs

buffers (26) at pH values of 7.0, 8.0, 9.0, and 10.0. It was necessary to buffer the solutions as the pH values would steadily decrease if simply adjusted by addition of sodium hydroxide solution.

The experiment was carried out by placing 0.2 g of the treated peat in 100 ml of each buffer solution. The samples were inspected visually after standing for 15 days. The leaching was pronounced at pH 9.0 and pH 10.0, as marked by a dark solution; little leaching occurred at pH 7.0 and pH 8.0, as indicated by a light color of the buffer solutions. The Irish peat and the Colorado peat gave similar results in these experiments.

Development of the Experiment for the Removal of Cationic Species (Dyes and Pesticides) from Solution by Treated Peat

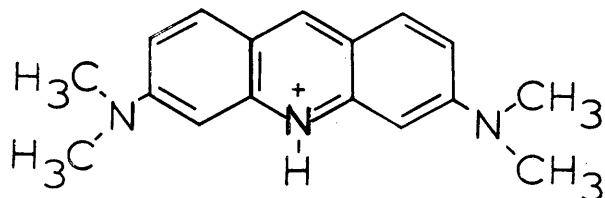
(a) Cationic Dyes

Initial experiments were carried out with three cationic dyes instead of pesticides for two reasons:

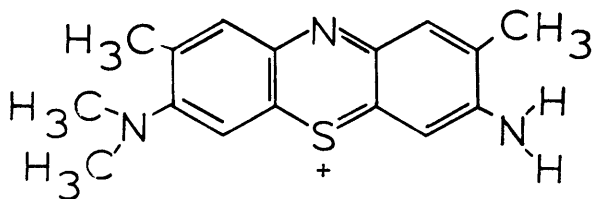
- (i) For safety reasons: contact with pesticides was avoided until the basic experimental methods were developed and refined.
- (ii) In initial trial experiments, the dyes can be directly measured spectrophotometrically, without the need of forming derivatives.

The dyes chosen are described in ref. (27):

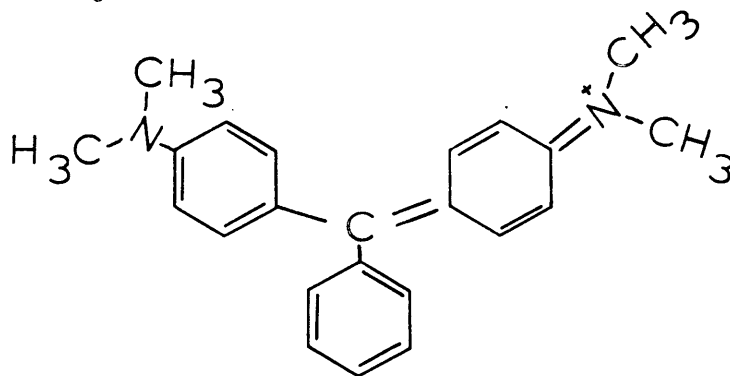
Acridine orange whose structure is:



Tolidine blue whose structure is:



and Machite green whose structure is:



All of these dyes are readily soluble in water. One gram of the chemically modified peat was washed with deionized water. A few drops of methanol were added in order to facilitate wetting of the treated peat particles. The treated peat was then placed into a column (see Figure 3). A 0.25 ml aliquot

of the aqueous dye solution at 0.001% (i.e. 1 mg/100 ml) was run through the columns at slow flow rates (0.5 ml per minute). From these first runs, all three effluents were colorless showing that the exchanger had removed the cationic dyes from solution. All effluent absorbances were essentially zero when measured on a Beckman DU-2 spectrophotometer. However, at higher flowrates (18.5 ml/min) some dye came through the column.

(b) Pesticides

Following familiarization with the column technique, experiments were initiated using pesticides in order to evaluate the efficiency of the treated peat for their removal. A variety of pesticides (neutral pesticides, cationic pesticides, basic pesticides) was studied.

(i) Neutral Pesticides

Peat and treated peat are known to be cation exchangers from previous reports (14) and also from the results of this research. For example Na^+ and Ba^{2+} ions were effective in displacing hydrogen ions from the treated peat. Accordingly, the primary focus of this research was on the removal of cationic pesticides, and also of basic pesticides, from water. The latter species become cationic through acceptance of a proton. However, it was decided to carry out some preliminary experiments with some neutral, hydrophobic pesticides. The

pesticides chosen for this purpose were aldrin, diéldrin and lindane. As these compounds have a very low solubility in water, ethanolic solutions were prepared and passed through columns of the treated peat. In these preliminary experiments, no evidence of significant retention of the pesticides by the treated peat was obtained. Being very insoluble in water, these neutral pesticides were precipitated after addition of water to their ethanolic solutions. This can be used as a qualitative test to detect the presence of these types of pesticides at high concentrations. It should be mentioned that the use of the organic solvent ethanol may have prevented the hydrophobic compounds from binding to the treated peat, whereas the compounds might be removed from extremely dilute aqueous solutions. However, experimentation was not pursued along those lines.

(ii) Cationic Pesticides

Paraquat and diquat are chemically similar to each other and their methods of analysis are also similar. Accordingly, both of these pesticides will be considered jointly in this thesis. The experiments carried out with amitrole will be considered separately. Preliminary investigations revealed that the cationic pesticides, paraquat and diquat, are retained on the treated peat by an ion exchange mechanism. For example, when a solution of paraquat (0.1M) was passed

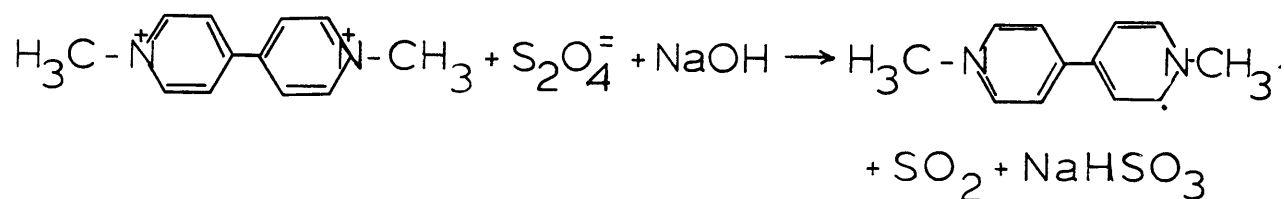
through a column of treated peat, the pH of the effluent solution (pH = 1.60) was considerably lower than that of the initial paraquat solution (pH = 4.30). The pH of the effluent on passing distilled water through the treated peat was 4.2. This indicates that protons are being displaced from the exchanger by the paraquat. A similar result was found with diquat. A similar experiment conducted in a batch mode yielded corresponding results. When a 0.1 M solution of paraquat was added to a beaker containing a sample of treated peat in distilled water, a significant drop in pH occurred. These results indicated that protons were being displaced from the exchanger by the paraquat and diquat, thereby demonstrating an ion exchange mechanism. It was decided to initiate a detailed study of the removal of paraquat and diquat by the treated peat. The above experiments were conducted with high concentrations of pesticide (0.1M) in order to observe the pH effect. However, the remainder of the experiments were carried out with very dilute solutions of pesticides.

A colorimetric method based on reduction by sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) for paraquat (28) and diquat (29) was used in order to analyze the effluent and thereby to determine the efficiency of the removal of the cationic pesticides from aqueous solution by the treated peat.

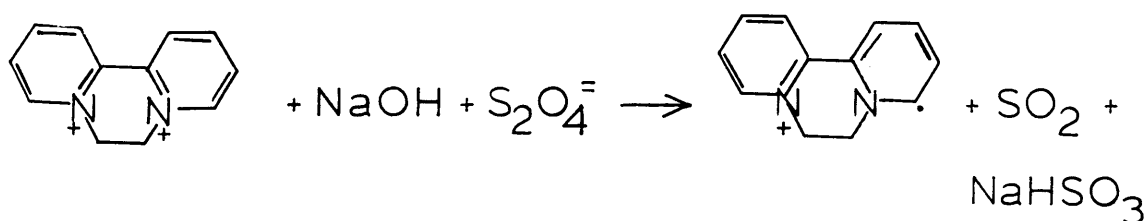
Colorimetric Determination of Paraquat and Diquat

Aqueous solutions of paraquat and diquat were shown to be reduced by alkaline sodium dithionite (28,29) giving colored free radical products:

For paraquat:



and for diquat:



The reduced products are characterized by a deep blue colored solution for paraquat, and an intense green solution for diquat. The proportions of all reagents used were: 10 ml of 0.1 g/l of paraquat solution reacting with 2 ml of 1% sodium dithionite prepared in 1N NaOH, and 10 ml of 0.1 g/l of diquat solution reacting with 2 ml of .1% of sodium dithionite prepared in 3N NaOH. However, by mixing these solutions in other proportions (e.g., 10 ml of 16 ppm of paraquat and 2 ml of 1% sodium dithionite prepared in 1N NaOH and 20 ppm of diquat and 2 ml of .1% of sodium dithionate prepared in 3N NaOH) it has been found in this research that the:

stability of the colored solution of paraquat was relatively good. It was also established in this research that the stability of the colored product for diquat could be improved by a reasonable choice of concentration of sodium dithionite in sodium hydroxide. The following conditions were found to give satisfactory results in this research:

Ten ml of 16 ppm of paraquat reacting with 2 ml of 1% sodium dithionite prepared in 1N NaOH and 10 ml of 20 ppm of diquat reacting with 2 ml of 1% of sodium dithionite prepared in 3N NaOH.

The resulting solutions exhibited intense absorption bands with a maximum at 380 nm for diquat (see figure 4), and two maxima at 390 nm and 596 nm for paraquat (see figure 5).

Under the above-mentioned conditions it has been shown that the reduced diquat and the reduced paraquat species were stable for a period sufficient to permit convenient measurement of absorbance. It was advisable to carry out the reduction within 1 to 2 hours of preparing the alkaline sodium dithionite reagent.

Standard Solutions of Paraquat and Diquat

A 0.1 g quantity of pure paraquat and pure diquat were separately dissolved in distilled water and diluted to 1 liter; thus 1 ml contained 0.1 mg of each compound.

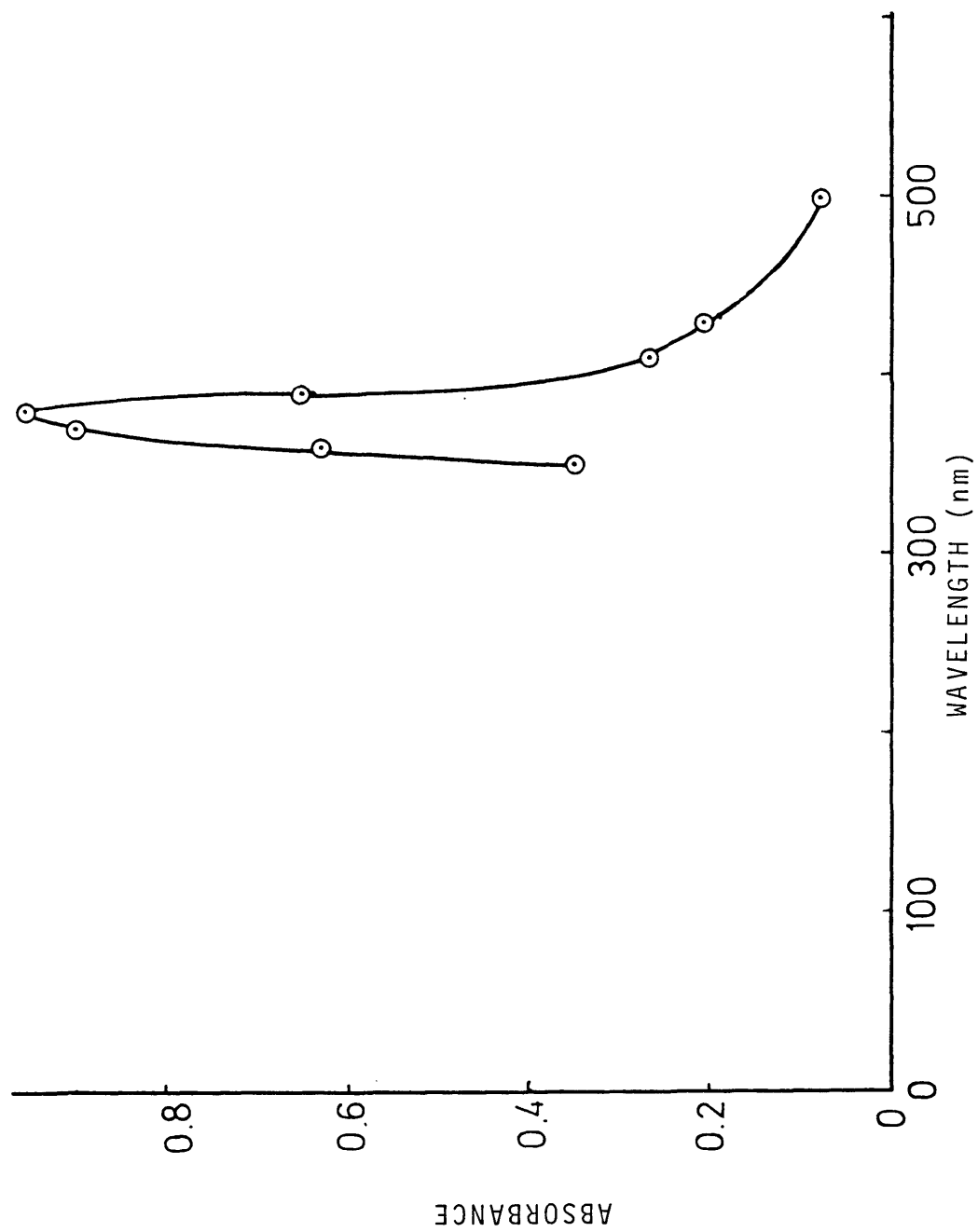


FIG. 4 UV-VISIBLE SPECTRUM OF REDUCED DIQUAT

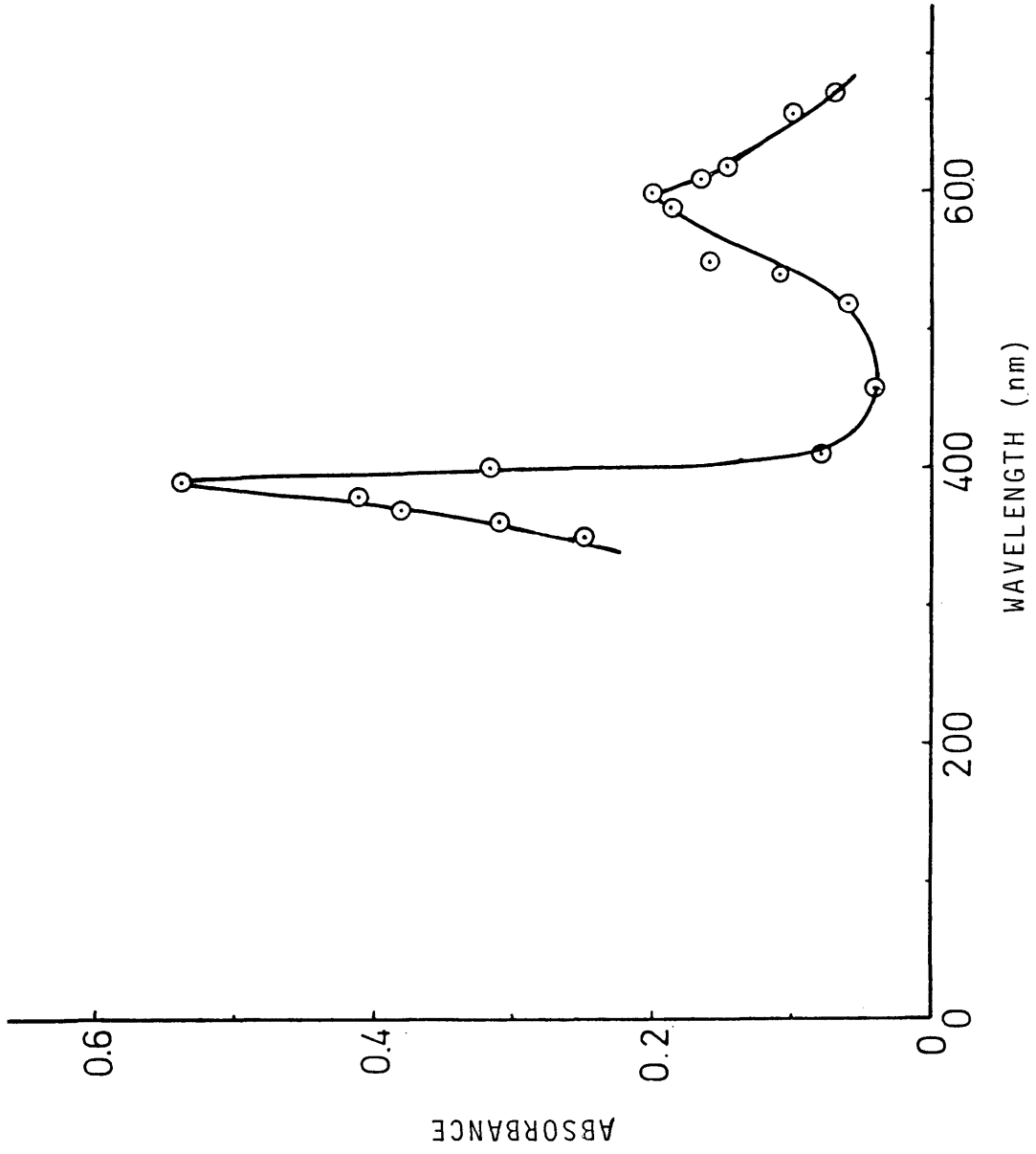


FIG. 5 UV-VISIBLE SPECTRUM OF REDUCED PARAQUAT

Aliquots containing from 0.05 mg to 1.6 mg for paraquat, and containing from .2 mg to 1.6 mg for diquat were transferred from the above stock solutions into volumetric flasks and diluted up to 100 ml, resulting in solutions ranging from 0.5 mg/l to 16 mg/l (i.e. 0.5 to 16 ppm) for paraquat, and ranging from 2 mg/l to 16 mg/l (i.e. 2 ppm to 16 ppm) for diquat. To 10 ml aliquots of each of these later pesticide solutions, 2.0 ml of alkaline sodium dithionite solution was added in order to reduce paraquat and diquat. Within five minutes of the mixing, the absorbances of these samples were measured on a Beckman DU-2 spectrophotometer. (see Tables II, III, and IV). Over these ranges of concentrations for both series of pesticides solutions, Beer's Law was obeyed (see figure 6,7, and 8). Corrections were provided for all measurements by subtracting the blank value of 0.023 for diquat and 0.005 for paraquat from all readings.

It should be noted that the concentrations on the Beer's Law plots for paraquat and diquat refer to the series of stock solutions prior to addition of the dithionite reducing solution. (The dilution factor of 6/5 is ignored). This facilitates the direct determination of the concentrations of unknown solutions from the Beer's Law plots since the identical procedure is used in those determinations and the dilution factor is also ignored there.

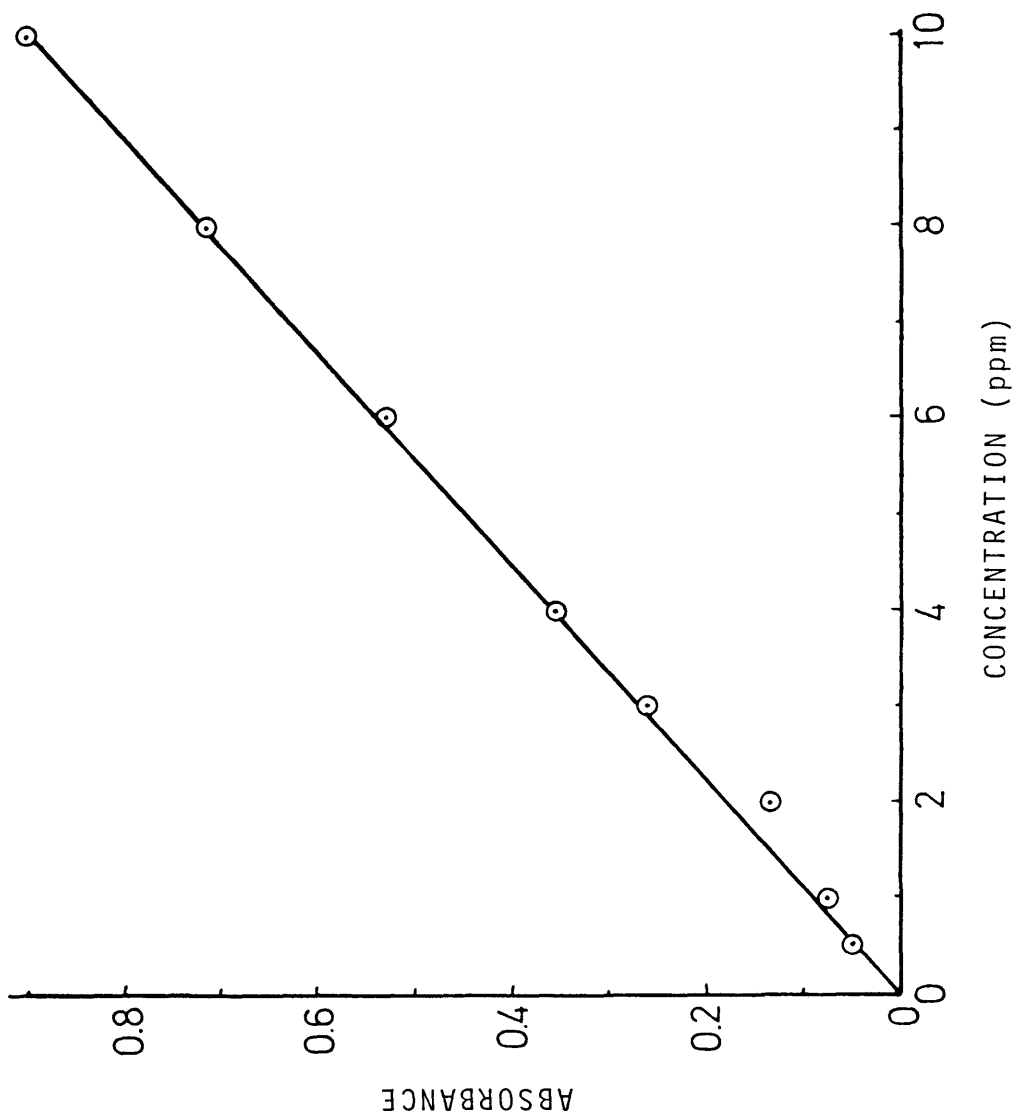


FIG. 6 BEER'S LAW PLOT FOR REDUCED PARAQUAT AT 390 nm

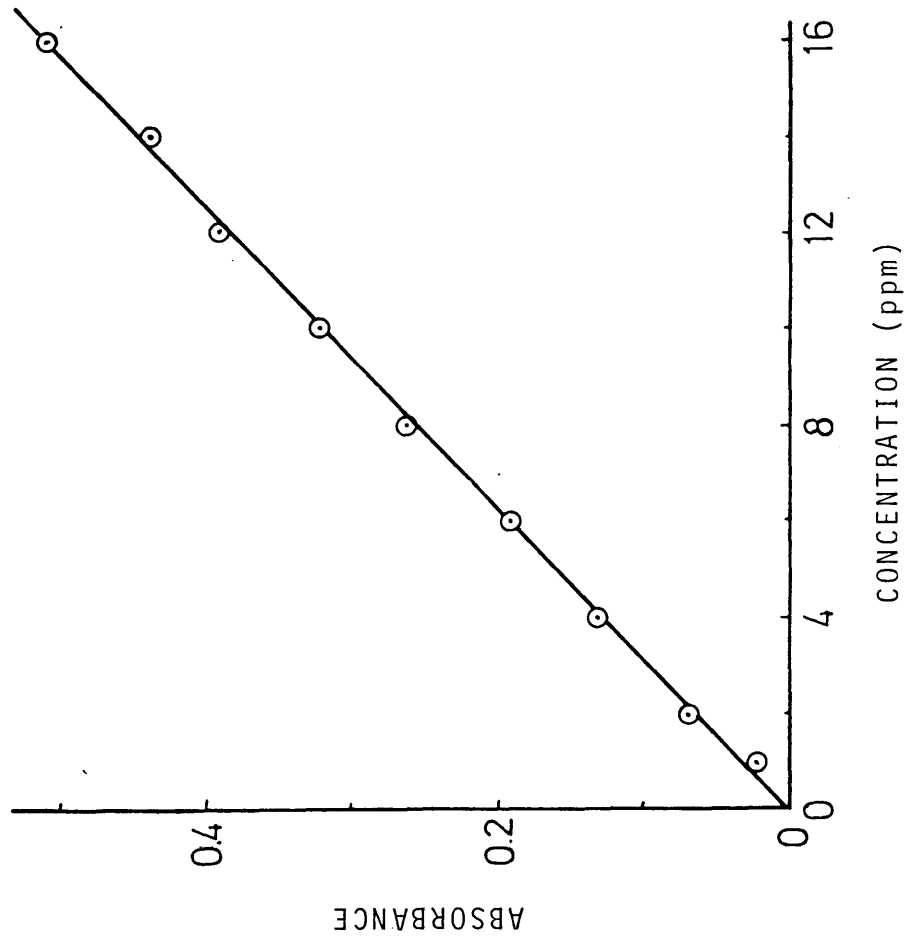


FIG. 7 BEER'S LAW PLOT FOR REDUCED
PARAQUAT AT 596 nm

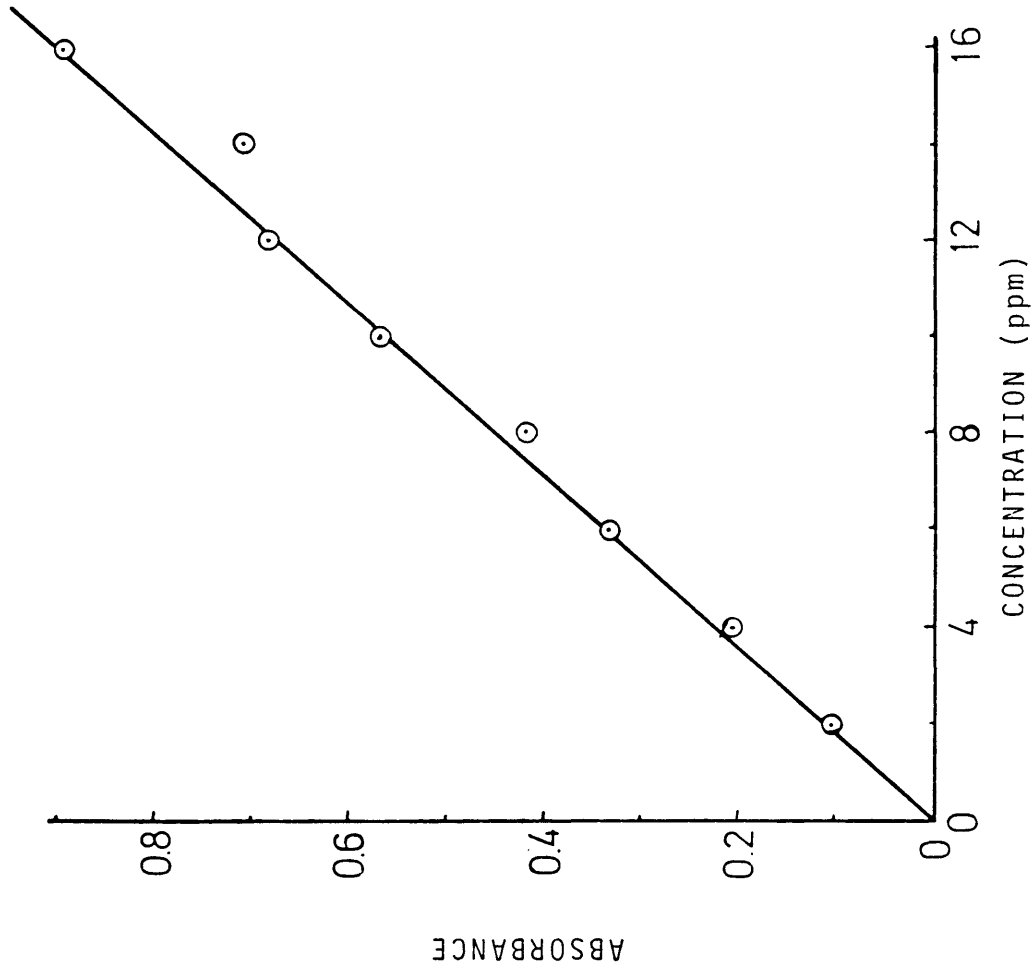


FIG. 8 BEER'S LAW PLOT FOR REDUCED DIQUAT AT 380 nm

Removal of Paraquat and Diquat by Treated Peat

A series of experiments was then carried out using 16 ppm paraquat solution and 16 ppm of diquat solution at ambient pH (pH = 5.85 for paraquat solution and pH = 6.15 for diquat solution), in order to establish the efficiency of the treated peat for the removal of these pesticides from aqueous solutions.

A 0.7g quantity of the treated peat was weighed and washed with distilled water. A few drops of methanol were added in order to facilitate wetting of the treated peat. After that, the treated peat was placed into the column (figure 3). Then a volume V_1 of each pesticide solution was run through the column ($V_1 = 45$ ml for paraquat and $V_1 = 50$ ml for diquat). The effluents collected were adjusted to a known volume V_2 by passing distilled water through the columns (V_2 was 50 ml for paraquat and $V_2 = 55$ ml for diquat). The effluent solutions were analyzed by reduction with alkaline sodium dithionite reagent. The results obtained for the efficiency have shown a successful removal of most of the paraquat and diquat from solution (Table XIV). Two other experiments conducted in the same way have indicated essentially the same result as the first one, thus confirming the reproducibility of the results (Table XIV). Another experiment, conducted this time with a large volume of pesticide

(1 liter of diquat at 16 ppm), showed that treated peat was again successful in removing diquat, although the efficiency has decreased slightly (92.32%), compared to the previous one found with small volumes (98.62%). The columns contained 1.5 g of treated peat this time, and the flowrate was adjusted to 1.60 ml/min.

Effect of the pH, Ionic Strength and Flowrate on Efficiency of Pesticide Removal

(a) Influence of pH

In order to study the effect of the pH on the efficiency, 16 ppm solution of paraquat and 16 ppm of diquat were each adjusted to pH = 2.0 and pH = 3.0 with HCl. A volume of each pesticide solution at the specified pH values was run through columns which were pre-treated by HCl to the appropriate pH's. The results of these experiments did not show a significant effect of pH on the efficiency (Table XV).

(b) Effect of the Ionic Strength

The ionic strength of 50% of the surface waters of the United States is less than 0.01M, and 97% of these waters have an ionic strength less than 0.05M. This statement is based upon surface quality data summarized by Rainwater (30). In 1964, the maximum ionic strength of the water supply of 100 large cities was calculated to be less than 0.07M (31).

However, the ionic strength of sea-water is approximately 0.7M (32) and estuarine water varies between these two limits.

Taking these data in account, experiments were conducted with the intention of showing the effect of sodium chloride (NaCl) on the efficiency of pesticide removal by treated peat. The solutions were made up in the following way:

(i) Sixteen mg of diquat (or paraquat) and 0.58 g of NaCl were mixed together and diluted up to one liter in a volumetric flask. This results in a solution which is 16 ppm in diquat (or paraquat) and 10^{-2} M in NaCl.

(ii) Sixteen mg of diquat (or paraquat) and 0.058 g of NaCl were mixed together and diluted up to one liter in a volumetric flask. This results in a solution which is 16 ppm in diquat (or paraquat) and 10^{-3} M in NaCl. A volume of each solution was passed through the columns. All the effluents were collected and adjusted to known volumes. Those solutions which were 10^{-2} M in NaCl were found to be slightly acidic (pH = 3.20 for diquat and pH = 3.25 for paraquat), due to displacement of hydrogen ions from the treated peat by the Na^+ ions. The pH's of those solutions which were 10^{-3} M NaCl were not significantly changed. The effluent solutions were analyzed by the same procedure outlined above (reduction by alkaline sodium dithionite). From the results, it appears that the efficiency was not greatly affected by these concentrations of sodium chloride (Tables (XV) and (XVI)).

(c) Effect of Flow Rate on Efficiency

Experiments were conducted to study the effect of the flowrate on the efficiency. The procedure was to run solutions of paraquat and diquat (16 ppm) at ambient pH and at various flowrates through the columns of the treated peat. The flowrate was determined by measuring the volume of effluent which passed through the column in a known time period.

The results from these experiments indicated that the efficiency of pesticide removal decreased very slightly with increase of flowrate (Tables XVIII and XIX).

(d) Elution of Pesticides from the Treated Peat

Having a cationic nature, paraquat and diquat are retained on a cation exchanger. It should also be possible to displace bound diquat and paraquat from the cation exchanger by using high concentrations of other cations, e.g. Na^+ or NH_4^+ . An examination of the literature showed that NH_4^+ ion was superior to Na^+ ions for the removal of paraquat from a synthetic sulfonic acid cation exchanger (Zeo-Karb 225) (28). The columns of treated peat containing bound pesticide were washed with 45 ml of 5.5 M NaCl. The effluents were adjusted to 50 ml with distilled water and were analyzed using alkaline dithionate. The results of the analyses showed that only a portion of pesticide (19.44% for paraquat and 58% for diquat) were displaced by the above procedure. The columns were then successively washed with 45 ml aliquots of 5.5 M

NaCl solutions and the effluents analyzed in the same manner. The results of these experiments are presented in Tables V and VI. After four washings of treated peat in the above manner, 91.28% of the diquat ion was displaced from the column, whereas only 41.15% of the paraquat was removed after seven washings.

Since the literature (28) indicated that NH_4Cl was a better eluting agent for paraquat than NaCl, in the case of synthetic resins, the above experiment for the elution of paraquat from the treated peat was repeated using 5.5 M NH_4Cl . The data are presented in Table VII. In this case, 82.57% of the bound paraquat was removed by nine washings, each with 45 ml of the 5.5 m NH_4Cl solution.

Paraquat was also eluted from the treated peat by means of saturated BaCl_2 (1.7M). However, determination of the eluted pesticide was foiled by the precipitation of barium dithionite when sodium dithionite was added to the eluted pesticide solution.

Basic Pesticides

Having a basic amine structure, amitrole differs from paraquat and diquat because it is a neutral species. A colorimetric analytical procedure, based on the reaction of amitrole with sodium nitroprusside reagent, was found applicable to this study.

Colorimetric Determination of Amitrole

Marston (33) found that guanidine gives a red color with a sodium nitroprusside reagent and used this test for the estimation of the compound. He discovered that small amounts of amitrole, which has chemical similarities to guanidine, give a grassy green color with the same reagent.

In order to use the sodium nitroprusside reagent, the following four solutions were prepared separately (34):

Sodium nitroprusside, $\text{Na}_2\text{Fe}(\text{CN})_5 \cdot \text{NO} \cdot 2\text{H}_2\text{O}$, 59.6 g/l

Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, 84.4 g/l

Sodium hydroxide, 10% NaOH (W/V)

Hydrogen peroxide, 3% H_2O_2 (V/V)

These solutions were mixed together with constant stirring in the proportions of 2:2:1:5, respectively, by volume, about 15 minutes before the reagent was used. A 1.2 ml aliquot of acetic acid was added per 100 ml of the mixed solution bringing the pH to 11.0, since the greatest color development is between pH 10.8 and pH 11.2 (34). The maximum absorbance for the product of reaction between the modified nitroprusside reagent and amitrole occurs at 625 nm (see figure 9).

Standard Solutions of Amitrole

In the preparation of a standard curve, 0.1 g of pure amitrole was dissolved in distilled water and diluted up to

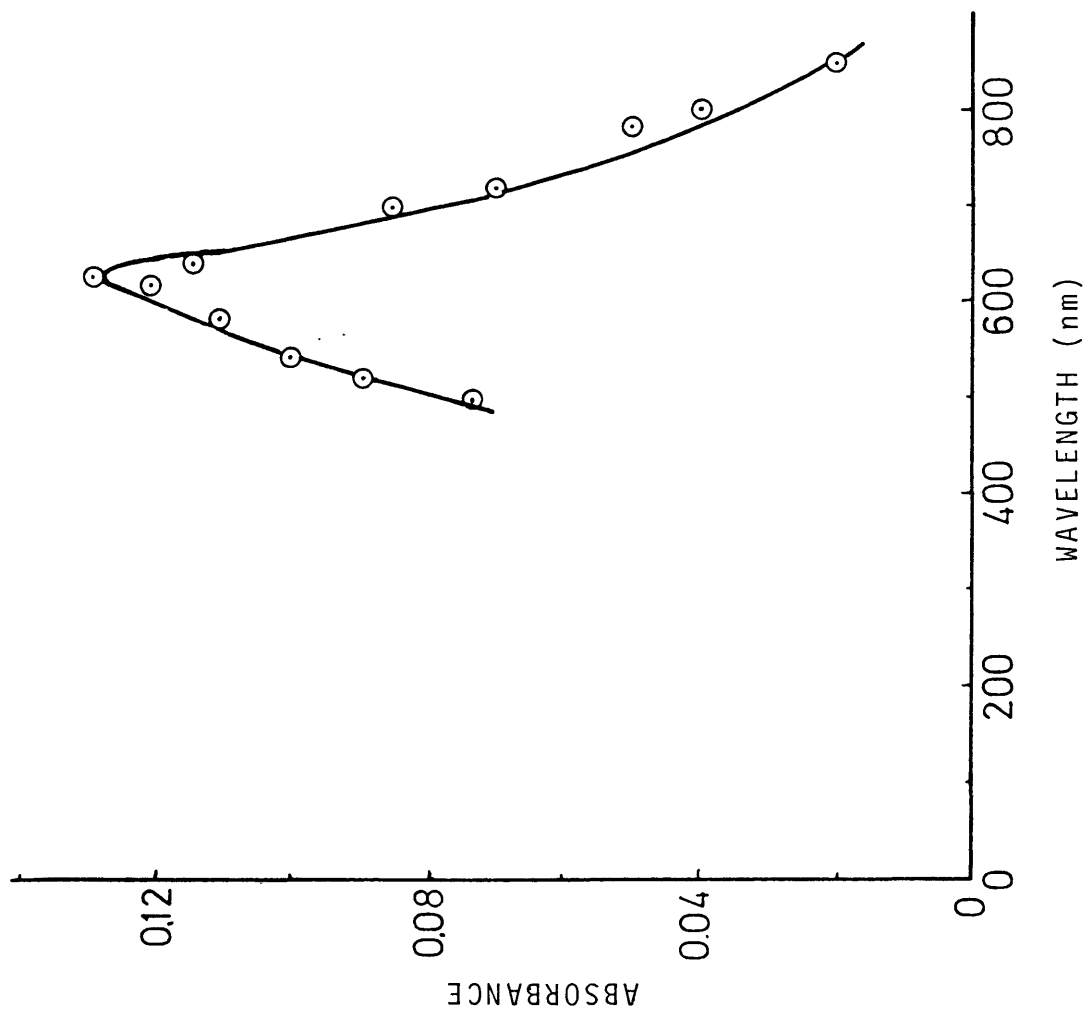


FIG. 9 VISIBLE SPECTRUM OF AMITROLE COMPLEX

1 liter. Thus 1 ml contained 0.1 mg of the compound. Amounts of solutions containing from 0.1 to 4.0 mg were delivered into 100 ml volumetric flasks and diluted to about 70 ml with distilled water. Next, 3 drops of 10% sodium hydroxide and 10 ml of the nitroprusside reagent were added. After being diluted to 100 ml, the solutions were allowed to stand for one hour, and at the end of this period, the absorbances were measured on a Beckman DU-2 spectrophotometer. The data are presented in Table VIII. However, a longer time is necessary for completion of the color producing reaction if the concentration of amitrole is greater than 1.6 mg/100 ml. The time limit suggested was two hours (34). The calibration curve conformed to Beer's Law (see figure 10). It should be noted that the concentration on the Beer's Law plot for amitrole refers to the final diluted solution. This is somewhat different than in the case of diquat and paraquat, and facilitates the direct determination of the concentration of unknown solutions from the Beer's Law plot.

Removal of Amitrole from Aqueous Solution by Treated Peat

As with diquat and paraquat, 45 ml of 0.1 g/l amitrole solution were run through columns containing a fixed amount of treated peat (0.7 g) in the H^+ form. The effluent was

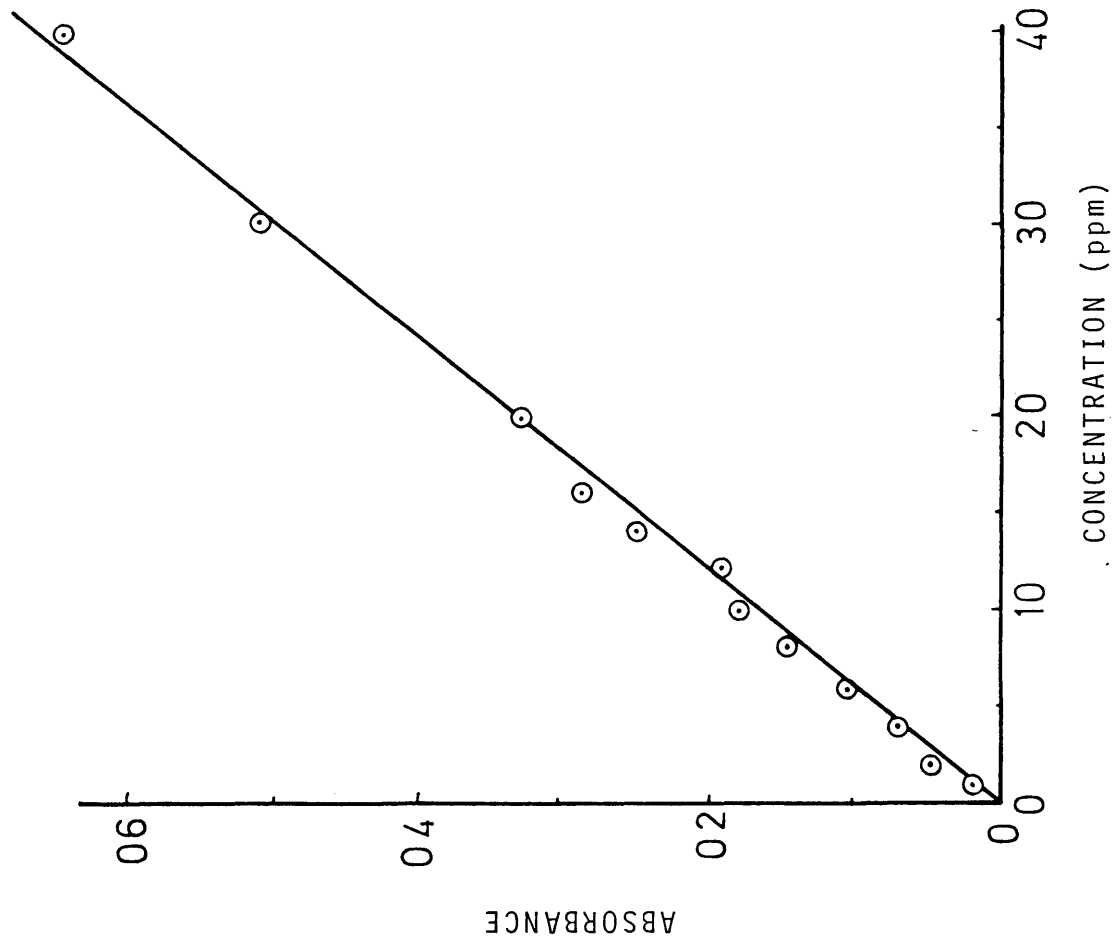


FIG. 10 BEER'S LAW PLOT FOR AMITROLE COMPLEX
AT 725 nm

collected and the amitrole was determined using the nitroprusside reagent as described above (in a 100 ml volumetric flask). The absorbance of the effluent solution, measured on a Beckman DU-2 spectrophotometer, was low, indicating a high efficiency for the removal of amitrole. Two other experiments conducted in the same way indicated the reproducibility of the results (Table XIV).

Effect of pH, Flowrate and Ionic Strength on Efficiency of Amitrole Removal

The experiments conducted for the study of these effects on the efficiency were similar to those conducted with paraquat and diquat. However, the analytical procedure remains based on the reaction of the pesticide in the effluents with sodium nitroprusside reagent.

Effect of pH

Amitrole solutions (0.1 g/l) were adjusted to pH 2 and pH 3 with HCl. The efficiency of removal at pH = 2.0 and pH 3.0 did not differ greatly from the efficiency at ambient pH (5.50) (Table XVII). Another experiment involved passing a solution of amitrole at pH = 7.0 through a column of treated peat preconditioned at pH = 7.0. At this pH, most of the amitrole molecules should be in the unprotonated form (pK_b of amitrole = 9.83). The column was preconditioned by washing with 3 M NaCl followed by extensive washing with

water adjusted to pH = 7.0 by addition of a small amount of sodium hydroxide. Washing was continued until the pH of the effluent remained constant at pH = 7.0. After that, 45 ml of amitrole solution at 0.10 g/l and adjusted to pH = 7.0 was passed through a column at slow flow rate (1.20 ml/min). The efficiency was found to be 72.22% in this case. (see Table XVII).

Effect of Flowrate

As with the diquat and paraquat, a set of experiments was conducted in order to study the effect of flowrate on the efficiency of amitrole removal by the treated peat. The results of these experiments did not show a marked decrease of the efficiency as a function of flowrate (Table XX).

Effect of Ionic Strength

The experiments carried out in this section have shown that the effect of NaCl on the efficiency of amitrole removal was not marked (Table XVII). The analytical procedure was based on the reaction of amitrole with sodium nitroprusside reagent and the experimental procedure was the same as used with diquat and paraquat (i.e. 10^{-2} M NaCl and 0.1 g/l of amitrole and 10^{-3} M NaCl and 0.1 g/l of amitrole).

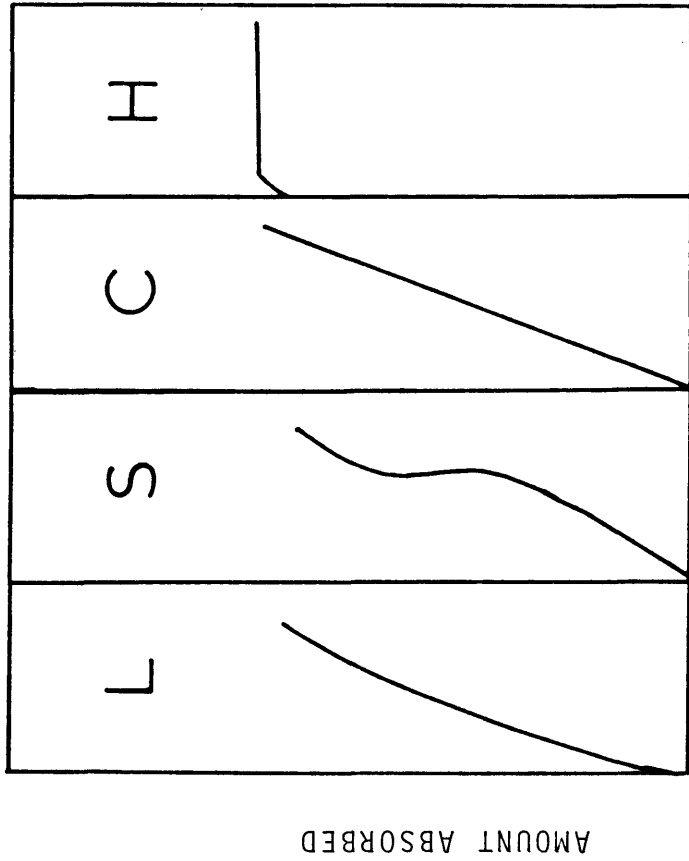
Elution of Amitrole by 3M NaCl

The elution of amitrole by 3M NaCl was carried out in

several steps, as with diquat and paraquat. In each step, a volume of 45 ml of the eluant (3M NaCl) was used. All the effluents were adjusted to a known volume and analyzed by the same analytical procedure used for the determination of the standard curve of the amitrole. Five elutions resulted in complete removal of the amitrole from the treated peat. The results are presented in Table IX.

Capacity of the Chemically Modified Peat for Various Cationic Pesticides

The determination of cation exchange capacities of the treated peat by displacing hydrogen ions with Na^+ and Ba^{2+} has already been described. It was decided to establish the capacity of the treated peat for binding pesticides (paraquat, diquat and amitrole) by determining the respective isotherms. Construction of adsorption isotherms was employed by numerous workers to describe the reaction of pesticides with soils. As pointed out by Weber (35) adsorption of a pesticide from solution onto a solid is not the two-phase system for which the Freundlich and Langmuir equations were intended. Water is always present and competes for the surface sites as do any other solute molecules in the system. Giles et al. (36) developed an empirical classification of adsorption isotherms in which four basic types were recognized (see figure 11):



EQUILIBRIUM CONCENTRATION

FIG. 11 CLASSIFICATION OF ADSORPTION ISOTHERMS ACCORDING TO GILES (36)

L-type, which represents a relatively high affinity between the solid and the solute;

S-type, which indicates an increase of the adsorption as the concentration of the solute increases;

C-type, which represents constant partition between solution and surface. The adsorption is always directly proportional to solution concentration; and

H-type, which represents very high affinity between solute and solid.

Experiments were conducted in order to study the capacity of the treated peat for binding all three pesticides (two cationic and one basic). Stock solutions of the three pesticides were obtained by separately dissolving 0.3 g of pure paraquat, 0.5 g of pure diquat and 0.1 g of pure amitrole in deionized water and diluting up to 1 liter, giving the following molarities:

$$\text{Paraquat } \frac{0.3}{257} = 1.16 \times 10^{-3} \text{ M}$$

$$\text{Diquat } \frac{0.5}{361.80} = 1.38 \times 10^{-3} \text{ M}$$

$$\text{Amitrole } \frac{0.1}{84.1} = 1.18 \times 10^{-3} \text{ M}$$

Determining Isotherms for Binding of Paraquat and Diquat by Treated Peat

The experimental procedure was first to derive from these

stock solutions a number of pesticide solutions of same volume and known concentration.

Amounts varying from .3 to 6.6 mg for paraquat and .50 to 11.0 mg for diquat were delivered into volumetric flasks of 100 ml capacity, and diluted to 100 ml. The next step was to add a given weight of treated peat, here 0.1 g, to each batch of pesticide solution with constant stirring in stoppered polyethylene bottles. All experiments were carried out at room temperature ($25^{\circ}\text{C} \pm 3^{\circ}\text{C}$). The final step to equilibrium of the reaction mixture was monitored by measuring absorbances of solution samples over a period of days using the same analytical procedure described previously (following reduction with alkaline dithionite). After 6 days for paraquat and 14 days for diquat (the solutions were shaken occasionally during this period), the rate of change in solution concentrations were slow, indicating close approach to equilibrium. After the above information was obtained the experiments were repeated allowing the paraquat systems to stand for 6 days and the diquat systems to stand for 14 days before measuring the isotherm data. The results are quoted in Table X for paraquat and Table XI for diquat. From the measured concentrations of the pesticides in solution, the amounts of pesticides bound to the treated peat were derived by mass balance, and adsorption isotherms

were drawn. The limiting values for the bound pesticides indicate the effective capacity of the treated peat for the respective pesticides under these conditions. (see figure 12 for paraquat and figure 13 for diquat).

Determining Capacity of the Treated Peat for Binding Diquat by the Column Method

The capacity of the treated peat for binding of diquat was also determined by passing an excess of the pesticide through a column of the exchanger. A 50 ml aliquot of 0.11 M diquat was slowly passed through a column containing 0.15 g of treated peat. The column was then washed with 10 ml of water and the total effluent was titrated to a phenolphthalein end-point with standard hydroxide as was previously done when using Na^+ or Ba^{2+} as the displacing cation. It required 16.0 ml of 10^{-2}N NaOH to reach the end-point, giving a capacity of 1.06 meq/g for binding of diquat to sulfuric acid-treated peat.

Determining Isotherm for Binding Amitrole by Treated Peat

Amounts of the stock amitrole solution (0.1g/l) containing from 0.6 to 1.8 mg pesticide were added to a series of capped polyethylene bottles. A 0.1 g quantity of treated peat was added to each of these bottles and the samples were left standing for 24 hours with occasional shaking. Each of

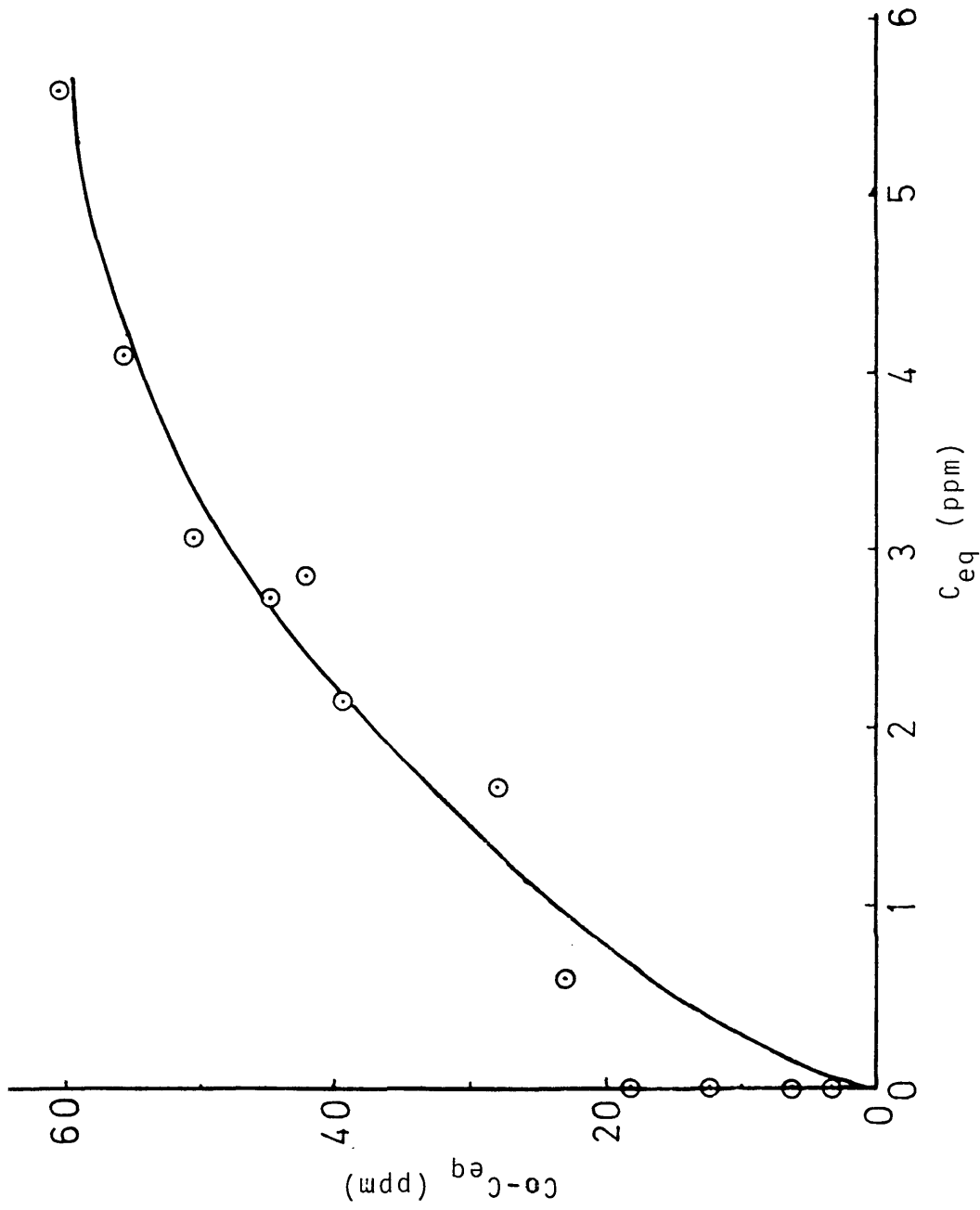


FIG. 12 ADSORPTION ISOTHERM FOR PARAQUAT BINDING TO TREATED PEAT

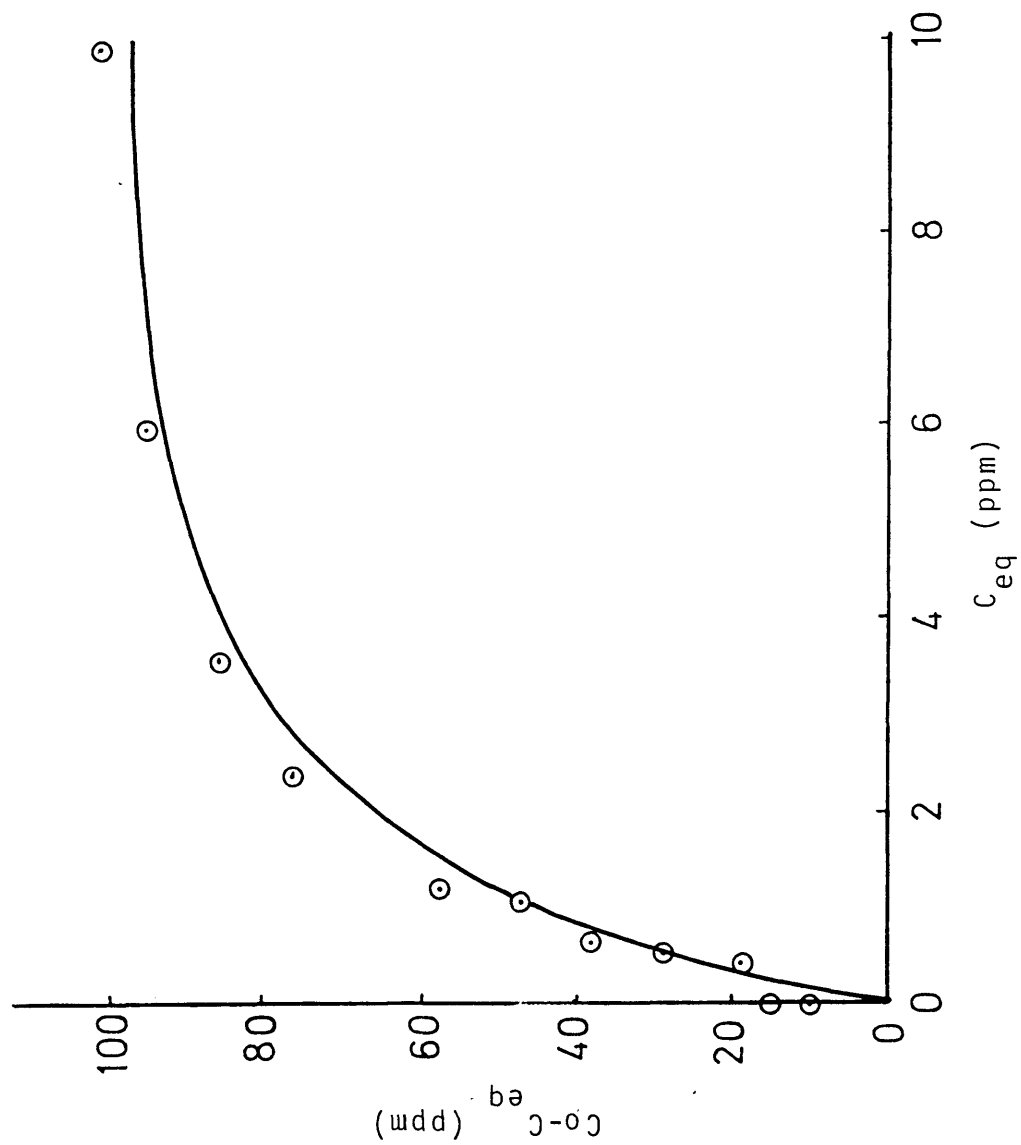


FIG. 13 ADSORPTION ISOTHERM FOR DIQUAT BINDING TO TREATED PEAT

these bottles contained a different volume of amitrole at the same original concentration. This, of course, cannot be a source of problem since we are interested in plotting $C_0 - C_{eq}$ versus C_{eq} , these quantities being independent of the volume. After 24 hours the solutions were filtered (Whatman No. 1 filter paper) into 100 ml volumetric flasks. The amitrole in these solutions was determined by the method outlined previously (i.e. addition of nitroprusside reagent, followed by dilution to 100 ml). The complete procedure was repeated twice more with identical fresh batches of treated peat and amitrole, and the mixtures were allowed to stand for 48 and 72 hours, prior to determining the concentrations of amitrole in solution. There was little difference between the concentration of amitrole in the solution phase after 48 and 72 hours (see Table XII and Table XIII). The limiting value for the bound pesticide indicates the capacity of the treated peat for amitrole (see figure 14) under these conditions.

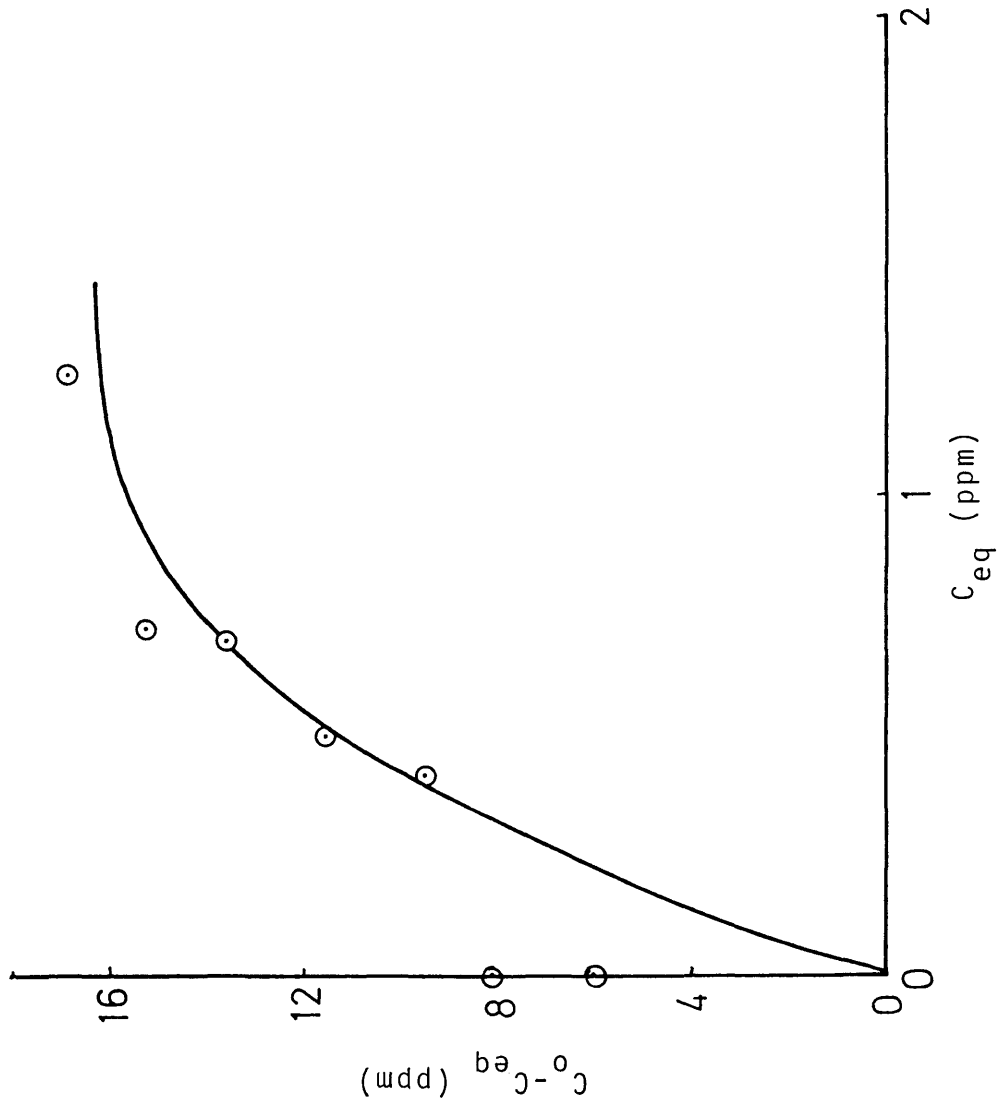


FIG. 14 ADSORPTION ISOTHERM FOR AMITROLE BINDING TO TREATED PEAT

RESULTS AND DISCUSSION

Preparation of the Treated Peat

The treated peat was prepared according to a published procedure (14) and no further modifications in that regard were introduced during this work. The resulting product has similar properties to that previously reported (14) in terms of cation exchange capacities and resistance (or susceptibility) to leaching as a function of pH. Furthermore, the treated peat, unlike the raw peat, was suitable for column use. The choice of particle size range was based on a previous report (14) in terms of its suitability for column use.

Most of this research was carried out using treated Irish peat, since this type of material had been studied in some detail in the past (14). Peat from Colorado was also studied in these investigations. All experiments, except determination of isotherms for the binding of pesticides, and studies of the influence of pH, ionic strength and flow-rate on pesticide removal, were carried out with the Colorado peat in addition to the Irish peat. The Irish peat was used for all types of investigation. However, in general, no major differences in properties were observed between the Colorado peat and the Irish peat.

Cation Exchange Capacity of Chemically Treated Peat

The cation exchange capacities determined by displacement of hydrogen ions using Na^+ and Ba^{2+} ions from both Irish and Colorado peats are given in Table I. These data show that the capacity obtained using Ba^{2+} is higher than the capacity obtained using Na^+ for both types of peat. It is known that Ba^{2+} , a divalent cation, has a higher charge density than the univalent cation, Na^+ . Since peat has functional groups of different acidity (i.e. groups of strong acidity and groups of weak acidity), we can conclude that there are some sites where the acidity is so weak that the proton cannot be displaced by Na^+ while it can be displaced by Ba^{2+} . Thus, the exchange capacity with divalent cations is higher than the exchange capacity with univalent cation. The results obtained in this research were somewhat less than the results reported by Smith et al. (14).

Efficiency of Pesticide Removal by the Treated Peat

Two methods were considered for the determination of the efficiency of pesticide removal on a column of treated peat. In the first method, the efficiency of removal was defined as the percent of pesticide removed from aqueous solution when it is passed through a column containing a fixed mass of adsorbent. It was determined by knowing the original concentration of the influent solution, and

measuring the concentration of the effluent. The efficiency can then be expressed by the following equation:

$$\text{Efficiency} = \frac{C_1V_1 - C_2V_2}{C_1V_1} \quad (7)$$

(C_1V_1) represents concentration and volume of the influent solution; (C_2V_2) represents concentration and volume of the effluent solution.

In the second method, the efficiency of removal can be estimated through an elution process which consists of displacing the retained cationic species by a concentrated solution of salt, for example sodium chloride or ammonium chloride. In this case the efficiency can be expressed by another equation:

$$\text{Efficiency} = \frac{C_3V_3}{C_1V_1} \quad (8)$$

where C_3V_3 represents the concentration and volume of the solution after elution. Of course, in order to use equation (8) it is necessary to be able to elute the bound pesticide from the column with 100% efficiency. In fact, as will be discussed later, this was not possible in general and thus the less restricted equation (7) is used in these studies.

As pointed out in the experimental section, the initial experiments were carried out with cationic dyes for safety reasons. The absorbances of all effluents of the malachite green, of the acridine orange, and the toluidine blue,

measured on a Beckman DU-2 spectrophotometer, were essentially zero. By using equation (7), the efficiency of removal was found to be 100% for all three cationic dyes.

Efficiency of Paraquat, Diquat and Amitrole Removal from Aqueous Solution

The plot of absorbances versus paraquat concentrations, diquat concentrations and amitrole concentration in solution are shown in Figures 6,7,8 and 10. The concentration of each effluent during the efficiency determinations was deduced by using these plots. The evaluation of the efficiency was performed on the basis of relation (7) for the reasons mentioned above.

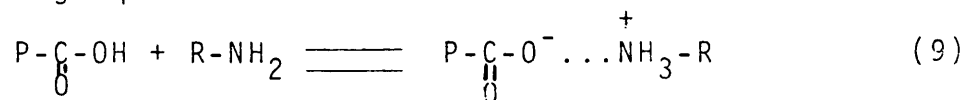
The results, presented in Table XIV show that both the Irish peat and Colorado peat were very effective in removing the three pesticides of interest from aqueous solution. The Irish peat and the Colorado peat were almost of the same quality as adsorbents for cationic pesticides when treated in the same manner. Treated peat has been used on a number of occasions in the past for removing metal ions from water (37,38,39). However, to the author's knowledge, this is the first study in which treated peat has been used for the removal of cationic and basic pesticides from water. These initial results were encouraging, showing the treated peat to be very effective in removing these pesticides from aqueous

solution. This approach may have potential as a cheap method for large scale application in the removal of cationic and basic pesticides from contaminated water prior to its discharge into the environment.

It should be pointed out that in the experiments with paraquat 45 ml of 16 ppm solution was passed through a column containing 0.7 g of treated peat. This corresponds to 5.58×10^{-3} meq of paraquat passing through 0.637 meq of treated peat showing that the treated peat was present in excess by a factor of about 114 over the pesticide (based on the capacity obtained with Ba^{2+} (Table(I))). Similarly, the treated peat was present in excess by a factor of 150 over the diquat concentration. This excess of treated peat ensures a high degree of removal of the pesticides.

Mechanism of Pesticide Removal by Treated Peat

Exchange may occur through a displacement of protons since these two pesticides are cationic by nature. This causes a decrease of pH as described previously. However, amitrole, having no charge, can become positively charged by a transfer of proton from the exchanger and thus becoming bound to the treated peat. This can be best illustrated by the following equation:



Effect of pH, Ionic Strength and Flowrate on the Efficiency of Pesticide Removal from Aqueous Solution by Treated Peat

The experiments in the following section were carried out only with the Irish peat.

Influence of pH and Ionic Strength

The results quoted in Tables (XV) (XVI) and (XVII) show that the efficiency decreases slightly for all three cationic pesticides, as the pH decreases from 3.0 to 2.0, and as the concentration of sodium chloride increases from 10^{-3} to 10^{-2} M. These effects can be explained by the competition of hydrogen ions or sodium ions with pesticides, for the exchange sites.

As shown in Table XVII, 72.22% of the amitrole was removed from solution by the treated peat at pH 7.0. This lower efficiency of removal is to be expected since amitrole is a basic pesticide with a pK_b of 9.83. At pH 7.0, amitrole should be essentially in the unprotonated form.

Influence of Flow Rate

As shown by the data in Tables (XVIII) and (XX), flowrate did not have a significant effect on the efficiency of pesticide removal by the treated peat, over the range of flow rates which was studied in this work. There was a slight decrease in efficiency with increased flow rates, in all cases, as would be expected.

Elution of Paraquat, Diquat and Amitrole from Treated Peat by Concentrated Salt Solutions (5.5M NaCl and 5.5M NH₄Cl)

Again, the experiments in this section were carried out only with Irish peat.

By looking at the data in Table (V) it appears that sodium chloride (5.5M) is not a very effective eluting reagent for paraquat, whereas it is reasonably effective as an eluting reagent for diquat as indicated in Table (VI). However, ammonium chloride (5.5M) was more effective than sodium chloride in removing paraquat from the treated peat (Table VII). This is consistent with a previous report (28) showing that NH₄Cl is more effective than NaCl in eluting bound paraquat from a synthetic sulphonic acid cation exchanger (Zeo-Karb-225). By comparing the results of the first elution for each pesticide (i.e. paraquat and diquat) it appears that paraquat interacts more strongly with treated peat than diquat or that more exchange sites are available to paraquat.

The elution of amitrole by 3M NaCl (see Table IX) was very effective (the efficiency was found to be 100.83%)

Capacity of the Chemically Modified Peat for Various Pesticides

Isotherms were measured for adsorption of various .

pesticides in order to evaluate the capacity of the exchanger. The isotherms consist of plots of $(C_0 - C_{eq})$ versus C_{eq} , where,

C_0 = initial concentration of the pesticide in solution;

C_{eq} = equilibrium concentration of the pesticide in solution,

which was found by spectrophotometric determination of pesticide in the equilibrated solutions, in conjunction with the appropriate Beer's Law plot. For paraquat, the standard curve used was that constructed at $\lambda = 596$ nm, rather than 390 nm, since at the former wavelength the absorbance was less intense (see Figure 5). This facilitated all measurements since we were dealing with more highly concentrated solutions of paraquat than during the column experiments involving dilute solutions of paraquat where the 390 nm absorption band was used. The isotherms are reported in Figure (12) for paraquat, in Figure (13) for diquat, and in Figure (14) for amitrole. The evaluation of the capacity of the treated peat was deduced graphically from the limiting value of $(C_0 - C_{eq})$. The capacity (B) is given by the following equation:

$$B = \frac{(C_{lim})(V) \times 10^{-3}}{E.m} \text{ eq/gr or } B = \frac{(C_{lim})(V)}{E.m} \text{ meq/gr (10)}$$

where: C_{lim} is the limiting value of $C_0 - C_{eq}$ in mg/l

V is the volume (ml) of pesticide solution equilibrated with the treated peat.

E, is the equivalent weight of each pesticide (i.e. molecular weight/n, where n is charge of ion)

m, is the mass of treated peat.

The capacities calculated according to the above relation (10) are given in Table (XXI). The capacity of the treated peat for diquat was also determined by the column method giving a value of .1.06 meq/g

The capacity of the treated peat for diquat, as determined by the column method, was somewhat greater than that for Ba^{2+} but the values were still comparable. The capacity of the treated peat for diquat and paraquat, as estimated from the limiting values of the isotherms were considerably smaller (Table XXI). This is due, presumably, to the fact that in the isotherm experiments the limiting value may not necessarily correspond to the maximum binding capacity. On the other hand, in the column experiments the exchange reaction is driven to completion by passing a large excess of the displacing cation through the column of treated peat and simultaneously removing the displaced hydrogen ions from the system.

Consideration of Pesticide Toxicity Hazard

The main goal of this research was the development of methods for removing toxic substances, like pesticides, from water. The laboratory work involved extensive handling

of pesticides. Precautions were taken in disposing of experimental solutions and other items in order to avoid contamination of the environment:

(i) Experiments were conducted with only one pesticide at any given time.

(ii) After each set of experiments, all solutions containing pesticides were transferred to storage bottles for subsequent disposal.

(iii) All solid material contaminated by pesticides was stored in plastic bags for subsequent disposal. This material included litmus paper, cloth towels, paper tissues, etc.

(iv) At the completion of this research all of the residual material (solid and dissolved) was assigned to the care of a commercial disposal company.

Chemicals Used

Dyes: Acridine orange, malachite green, toluidine blue, Gallard Schlesinger Chemical Mfg. Corp. Carle Place, LI, N.Y.

Pesticides: Paraquat, diquat, amitrole, Chem Service, West Chester, PA, 19380 (solid form).

Other Chemicals

Sulfuric Acid: Baker analyzed reagent, 36.0N

Hydrochloric Acid: MCB Reagents, 11.3N

Sodium Dithionite: J.T. Baker Chemical Co., Phillipsburg, N.J. 08865

Sodium hydroxide reagent, solid form

Sodium chloride reagent, solid form

Sodium nitroprusside reagent practical solid form

Potassium ferrocyanide: crystal form, Baker analyzed reagent

Hydrogen peroxide 30% solution

Ammonium chloride: analytical reagent

Buffer solutions: 0.1M KH_2PO_4 , 0.1M NaOH, 0.1M KCl, 0.1M H_3BO_3 . All these were reagent grade.

Equipment

The apparatus for ion-exchange experiments is illustrated in Figure 3.

Spectrophotometers: Beckman DU-2 and Beckman DK-2 spectrophotometers were used.

pH meter: Sargent-Welch model IP

Conclusion and Summary

This research was aimed at considering the feasibility of using chemically treated peat for the removal of cationic species from water (i.e. cationic pesticides and cationic dyes). The peat itself is a natural substance which can be cheaply obtained directly from the land in many areas of the world. Its utilization without any chemical modification was not practical, since the raw peat is prone to leach substances which are a source of pollution in themselves.

Furthermore, the raw peat is impervious to the flow of water. However, the sulfuric acid treatment leads to a product having an increased cation exchange capacity and good physical characteristics. The product is capable of being used up to approximately pH = 8.0 and is very suitable for column operation since it is of a granular form, and possesses good capacities for cations.

This research was primarily intended to remove cationic pesticides from water. From the data obtained, the treated peat was found to be very effective for removing these toxic substances. Factors which can influence the efficiency of the treated peat for pesticide removal were examined (i.e. pH, ionic strength, and flowrate). It has been concluded that all of these factors had no significant effect on efficiency of pesticide removal over the range of variations studied.

Another aspect of this research was to study the adsorption isotherm for the binding of the various pesticides on the treated peat. The experiments conducted in this case were different from the previous ones which were based on column operation. The batch method for determination of isotherms was adopted.

With this simple procedure, these cation exchangers might find use in municipal water treatment and industrial

waste water handling. The treated peat may have the potential of being a cheap substitute for some of the synthetic resins currently used for water treatment.

TABLE I. Cation Exchange Capacities of Treated Peat (Irish and Colorado Peat) for Na^+ and Ba^{2+}

<u>Irish Peat</u>		<u>Colorado Peat</u>	
<u>Na^+</u>	<u>Ba^{2+}</u>	<u>Na^+</u>	<u>Ba^{2+}</u>
0.68 meq/g	0.91 meq/g	0.76 meq/g	0.96 meq/g

TABLE II. Absorbances of Standard Solutions of Reduced Paraquat at 390 nm

<u>Concentration (mg/l)</u>	<u>Absorbance</u>
0.5	0.050
1	0.075
2	0.133
3	0.260
4	0.355
6	0.530
8	0.715
10	0.900

TABLE III. Absorbances of Standard Solution of Reduced Paraquat at 596 nm

<u>Concentrations (mg/l)</u>	<u>Absorbance</u>
1	0.024
2	0.070
4	0.135
6	0.194
8	0.263
10	0.325
12	0.392
14	0.440
16	0.510

TABLE IV. Absorbances of Standard Solutions of Reduced Diquat at 380 nm

<u>Concentrations (mg/l)</u>	<u>Absorbance</u>
2	0.105
4	0.207
6	0.332
8	0.420
10	0.570
12	0.682
14	0.712
16	0.900

TABLE V. Results of Elution of Paraquat
by 5.5M NaCl

<u>Elution Number</u>	<u>% Removal</u>
1	19.44
2	11.59
3	3.81
4	2.98
5	2.29
6	1.04
7	0.0

TABLE VI. Results of Elution of Diquat by
5.5M NaCl

<u>Elution Number</u>	<u>% Removal</u>
1	58
2	26
3	5.55
4	1.73
5	0.0

TABLE VII. Results of Elution of Paraquat
by 5.5M NH₄Cl

<u>Elution Number</u>	<u>% Removal</u>
1	35.41
2	15.27
3	9.72
4	6.66
5	4.86
6	4.02
7	3.78
8	2.85
9	0.0

TABLE VIII. Absorbance of Standard Solution
of Amitrole Complex at 625 nm

<u>Concentration (mg/l)</u>	<u>Absorbance</u>
1	0.020
2	0.048
4	0.075
6	0.107
8	0.148
10	0.180
12	0.194
14	0.255
16	0.290
20	0.330
30	0.510
40	0.650

TABLE IX. Results of Elution of Amitrole
by 3M NaCl

<u>Elution Number</u>	<u>% Removal</u>
1	77
2	11.90
3	5
4	4.13
5	2.80
6	0.0

TABLE X. Data Related to the Adsorption
Isotherm of Paraquat

<u>C_o (mg/l)</u>	<u>C_{eq}</u>	<u>C_o - C_{eq} (mg/l)</u>
3	0	3
6	0	6
12	0	12
18	0	18
24	0.61	23.39
30	1.58	28.42
36	2.82	39.38
42	2.17	39.83
48	2.75	45.25
54	3.09	50.91
60	4.10	55.90
66	5.60	60.40

TABLE XI. Data Related to the Adsorption Isotherm of Diquat

<u>c_o (mg/l)</u>	<u>c_{eq} (mg/l)</u>	<u>$c_o - c_{eq}$ (mg/l)</u>
5	0.0	5
10	0.0	10
15	0.0	15
20	0.49	19.51
30	0.51	29.49
40	0.68	39.32
50	1.01	48.99
60	1.20	58.80
80	2.35	77.65
90	3.52	86.48
100	5.98	94.02
110	9.90	100.10

TABLE XII. Data Related to the Adsorption Isotherm for Amitrole After Standing for 48 Hours

<u>c_o (mg/l)</u>	<u>c_{eq} (mg/l)</u>	<u>$c_o - c_{eq}$ (mg/l)</u>
6	0.40	5.6
8	0.42	7.58
10	0.65	9.35
12	0.85	11.15
14	0.86	13.13
16	1.0	15.0
18	1.50	16.50

TABLE XIII. Data Related to the Adsorption Isotherm of Amitrole After Standing for 72 Hours

<u>C_o (mg/l)</u>	<u>C_{eq} (mg/l)</u>	<u>C_o - C_{eq} (mg/l)</u>
6	0.00	6
8	0.00	8
10	0.420	9.58
12	0.50	11.50
14	0.70	13.30
16	0.72	15.28
18	1.25	16.75

TABLE XIV. Efficiency of Removal of Pesticides by Irish Peat and Colorado Peat

	Irish Peat (0.7g)			Colorado Peat (0.7g)		
<u>Pesticides</u>	<u>Paraquat</u>	<u>Diquat</u>	<u>Amitrole</u>	<u>Paraquat</u>	<u>Diquat</u>	<u>Amitrole</u>
pH	5.85	6.15	5.50	5.85	6.15	5.50
Flowrate	1.10	1.0	1.15	1.07	1.18	1.20
	ml/min	ml/min	ml/min	ml/min	ml/min	ml/min
Efficiency (%)	99.30	98.16	99.33	99.65	97.22	98.66
	99.0	98.69	99.55			
	99.51	98.54	98.88			

TABLE XV. Influence of pH and Ionic Strength on Removal of Paraquat from Solution by Treated Irish Peat

<u>pH</u>	<u>Efficiency</u>
pH = 2.0	97.98%
pH = 3.0	98.0 %
Ionic Strength	
10^{-2} M NaCl	98.61%
10^{-3} M NaCl	98.90%

TABLE XVI. Influence of pH and Ionic Strength On Removal of Diquat from Aqueous Solution by Treated Irish Peat

<u>pH</u>	<u>Efficiency</u>
pH = 2.0	92.64%
pH = 3.0	93.35%
Ionic Strength	
10^{-2} M NaCl	94.5 %
10^{-3} M NaCl	96.48%

TABLE XVII. Influence of pH and Ionic Strength on Removal of Amitrole from Solution by Treated Irish Peat

<u>pH</u>	<u>Efficiency</u>
pH = 2.0	98.13%
pH = 3.0	98.48%
pH = 7.0	72.22%
Ionic Strength	
10^{-2} M NaCl	96.44%
10^{-3} M NaCl	97.77%

TABLE XVIII. Effect of Flowrate on Removal of Paraquat from Solution by Treated Irish Peat

<u>Flowrate (cm³/min)</u>	<u>Efficiency (%)</u>
1.0	99.30
2.5	96.50
10.5	95.86
23.0	95.13

TABLE XIX. Effect of Flowrate on Removal of
Diquat from Solution by Treated
Irish Peat

<u>Flowrate</u>	<u>Efficiency (%)</u>
1.0	98.69
6.10	97.91
11.50	97.74
22.0	97.33

TABLE XX. Effect of Flowrate on Removal of
Amitrole from Solution by Treated
Irish Peat

<u>Flowrate</u>	<u>Efficiency (%)</u>
1.2	99.55
4.2	98.00
8.1	97.44
14.20	94.66
23.50	93.88

TABLE XXI. Capacity of the Treated Irish Peat for Amitrole, Paraquat, and Diquat as Determined from Isotherms

<u>Pesticides</u>	<u>Capacity in m_{eq}/g</u>
Amitrole	0.20
Paraquat	0.40
Diquat	0.47

TABLE XXII. Moisture Content for Irish Peat and Colorado Peat

<u>PEAT</u>	<u>M O I S T U R E</u>		<u>C O N T E N T (%)</u>	
Batch	Batch (I)	Batch (II)	Batch (III)	Batch (IV)
Irish Peat	86.70	85.60	87.0	85.70
Colorado Peat	75.10	78.60	75.30	78.88

REFERENCES

1. Gomaa, Hassan and Faust, Samuel D., 1974, "Pesticides in Soil and Water," Guenzi (Ed.) Soil Science Society of America, Madison, p 413.
2. Ginsburg, M. M., 1974, "Pesticides in Soil and Water," Guenzi (Ed). Soil Science Society of America, Madison, p 449.
3. Young, L. A., Nichelson, H. P., 1972, "Fate of Organic Pesticides in the Aquatic Environment," Advances in Chemistry Series, No. III. Amer. Chem. Soc., Washington, D. C. p. 56.
4. Robeck, G. G., Postal, K. A., Cohen, J. M., and Kressl, J. F., 1965, "Effectiveness of Water Treatment Processes in Pesticide Removal." J. Amer. Water Works Assoc, 57:181-199.
5. Gomaa, H. M. and Faust, S. D., 1971, Kinetics of Chemical Oxidation of Dipyriddylium Quaternary Salts." J. Agr. Food Chem. 19:302-307
6. Aly, O. M., and Faust, S. D., 1965, "Removal of 2,4-D Derivatives from Natural Waters," J. Amer. Water Works Assoc., 57:221-230.
7. Aly, O. M., and Faust, S. D., 1964, "Studies on the fate of 2,4-D and Ester Derivatives in Natural Surface Waters," J. Agr. Food Chem. 12:541-544.
8. Weber, J. B., 1972, "Fate of Organic Pesticides in the Aquatic Environment," Advances in Chemistry Series, No. III American Chemical Society, p. 65.
9. Leopold, A. C., Van Schaik, P., and Neal, M., 1960, "Molecular Structure and Herbicide Adsorption," Weeds 8:48-54.
10. Vinson, Joe A., 1972, "Improved Method for the Removal of Organic Pollutants from Water," Prep. Pap. Nath. Meet. Div. Water, Air Waste Chem., American Chemical Society 12(2):8-11
11. Moore, P. D. and Bellamy, D. J., 1974, "Peatlands," Springer Verlag, New York, N.Y. Chapter 8.

12. Rogozhkin, V. I., 1977, "Adsorption of Organic Compounds from Waste Waters of the Rubezhansk Chemical Plant," *Izv. Sev. Kavk, Nauch. Tsentra YySSH. ShK.*, ser Ser. Tekh Nauk 5(2):102-4, Chem. Abstr. V. 89 (1978) #645456.
13. Bazin, J. 1978, "Treatment of Urban Waste Waters Filtration on Peat," *Inf. Chim.* V. 184, pp 157-61.
14. Smith, E. F., MacCarthy, P., Yu, T. C.; Mark, Jr., H. B., 1977, "Sulfuric Acid Treatment of Peat for Cation Exchange," *J. Water Pollution Control Control Federation*, pp. 633-638.
15. Spencer, E. Y., 1968, "Guide to the Chemicals Used in Crop Protection," Canada, Dept. of Agriculture, London, Ontario, Canada.
16. Mortensen, J. L., and Himes, J. 1964., "Soil Organic Matter," pp 206-241, In F. E. Bear (Ed), *Chemistry of the Soil*, Reinhold, New York.
17. Stevenson, F. J., 1972, "Reviews and Analyses, Organic Matter Reactions Involving Herbicides in Soil," *Journal of Environmental Quality*, pp 333-343.
18. Martin, J. P., and Haider, K. 1971, "Microbial Activity in Relation to Soil Humus Formation," *Soil Sci.*, 111:54-63.
19. Wershaw, R. L., and Goldberg, M., 1972, Chapter 7, "In Fate of Organic Pesticides in Aquatic Environment," *Advances in Chemistry Series No. III*, American Chemical Society, Washington, D. C.
20. Best, J. A., Weber, J. B., and Weed, S. B., 1972 "Competitive Adsorption of Diquat 2^+ , Paraquat 2^+ , and Ca^{2+} on Organic Matter and Exchange Resins." *Soil Sci.* 114:444-450.
21. Weber, J. B., 1972, "Interaction of Organic Pesticides with Particulate Matter in Aquatic and Soils Systems," *Fate of Organic Pesticides in the Aquatic Environment. Advances in Chemistry Series No. III.*, American Chemical Society, Washington, D. C. pp 55-120.

22. Weber, J. B., Ward, T. M. Weed, S. B., 1969, "Adsorption of s-triazines by Soil Organic Matter," *Weed Sci.*, 17:417-421.
23. Bailey, G. W., White, J. L., and Rothberg, T., 1968, "Adsorption of Organic Herbicides by Montmorillonite: Role of pH and Chemical Character of the Absorbate," *Soil Sci. Soc. Amer. Proc.* 32:222-234.
24. Adamson, A. W., 1970, "Physical Chemistry of Surfaces," Interscience Publisher, New York.
25. Hayes, M. H. B., 1970, "Adsorption of Triazines Herbicides on Soil Organic Matter, Including a Short Review on Soil Organic Matter Chemistry," *Residue Rev.* 32:131-174.
26. Bower, V. E., and Bates, R. G., 1955, "pH Values of the Clark and Lubs Buffer Solutions at 25°C," *J. Res. Natl. Bur. Standards* 55, 197.
27. Gurr, E., 1958, *Encyclopedia of Microscopic Stains*, pp 13, 256, and 392.
28. Calderbank, A. and Yuen, S. H., 1965, "Ion Exchange Methods for Determining Residue in Food Crops," *Analyst*, 90, 99.
29. Calderbank, A., and Yeun, S. H., 1961, "Determination of Diquat Residues in Potato Tubers," *Analyst* 86, 569.
30. Rainwater, F. H., 1962, "Hydrologic Investigations," Atlas HA-61, U. S. Geological Survey.
31. Durfor, C. N. and Becker, E., 1964., *J. Amer. Water Works Assoc.* 56,237.
32. Chave, K. E., 1971, *J. Chem. Educ.* 48, 148.
33. Marston, H. R., 1924, *Australian Exptl. Biol. Med. Sci.*, 1, 99-103.
34. Sund, Kenneth A., 1956, "Residual Activity of 3-Amino-1-2-4-triazole in Soils." *J. Agr. Food. Chem.* 4, 57-60.
35. Weber, J. B. 1970, "Mechanisms of Adsorption of S-Triazines by Clay Colloids and Factors Affecting Plant Availability," *Residue Rev.* 32:93-130.

36. Giles, C. H., MacEwan, T. H., Nakhwa, S. N. and Smith, D., 1960. "Studies in Adsorption, Part XI. A System of Classification of Solution Adsorption Isotherms, and its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Areas of Solids, "J. Chem. Soc. pp. 2973-3993.
37. Brogan, J. C., 1964, Trans. Internatl. Soc. Soil Sci., Bucharest, pp. 227-234.
38. Ingle, R. M. and Martin, D. F., 1971, Environ. Letts. 1, 69.
39. Szalay, A. and Sailagyi, M. 1961, Acta Phys. Hung., 13, 421.