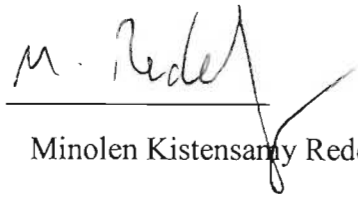
Sorption and Desorption of Pyridine by Pahokee Peat From Hexadecane in the Presence of Organic Co-solvents

M.K. Reddy

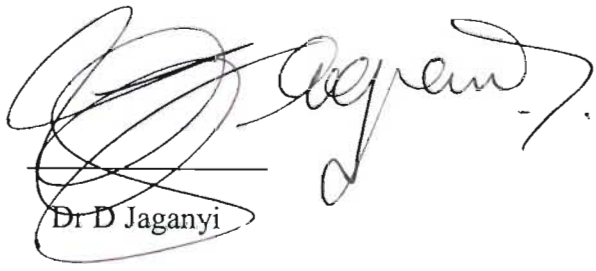
Submitted in partial fulfillment of the requirements for the degree of
Master of Science in the School of Chemical and Physical Sciences
University of Natal (Pietermaritzburg) 2002

Declaration

I hereby certify that this dissertation is my own work, except where specifically acknowledged in the text. Neither the present dissertation, nor any part thereof, has been submitted to any other University for a degree.

Author: 

Minolen Kistensamy Reddy

Supervisor : 

Dr D Jaganyi

Preface

The experimental work in this thesis was carried out under the supervision of Dr M Borisover of the Institute of Physical and Chemical Sciences, Volcani Institute, Ministry of Science and Agriculture, Bet Dagan, Israel. The experimental write up was carried out under the supervision of Dr D Jaganyi of the School of Chemical and Physical Sciences, University of Natal (Pietermaritzburg). This is the author's original work and has not been submitted in any other form to another University. Where use was made of the work of others, it was acknowledged in the text.

Acknowledgements

The author wishes to express his gratitude to the following people for their help during this study:

Dr M Borisover and Dr E Graber, my supervisors in Israel, for their guidance and expertise during the study.

The Moshe Greidinger Scholarship Fund for the financial assistance during the experimental part of the study in Israel.

The Rishon Le Zion, Haifa, and Jerusalem Rotary Clubs for their warm hospitality during my stay in Israel.

My flatmates Ozgur Batuman (Turkey), Rajiv Sharma (India), Ceasare Accinile (Italy), and Lu Jia (China) for their support and friendship during the course of my stay in Israel.

The staff of the Physical and Chemical Sciences Laboratory at the Volcani Institute for all their help.

Dr D Jaganyi for all his assistance and guidance in compiling the thesis.

My parents for all their support, and my girlfriend Chantal for all her support during the study period.

ABSTRACT

A study of the interactions of the specifically interacting organic compound pyridine with a model soil organic matter sorbent (Pahokee peat) was carried out from different non-aqueous organic liquid media, including neat n-hexadecane, acetonitrile, acetone and n-hexadecane mixtures with either acetone or acetonitrile. Kinetic and equilibrium studies using an activity-based comparison of the organic compounds in solution was used to study the interactions of soil organic matter (SOM) and pyridine sorption capability in the various non-aqueous organic liquid media. Quantification and qualification of pyridine and the other co-solvents were done using Gas Chromatography (GC).

Sorption of pyridine from neat organic solvents was not masked by sorption of the organic solvent. The apparent sorbed amount calculated from the change in solute concentration and reported on a dry weight basis was considered to represent the true sorbed concentration of pyridine in the sorbent phase. Pyridine sorption was found to be non-linear and distribution coefficients decreased with solute concentration, by approximately three times in n-hexadecane, more than five times in acetonitrile, and by ten times in acetone over the experimental concentration range. Pyridine sorption from n-hexadecane was also found to be comparable with sorbed amounts from acetone, but much lower in comparison to sorption from acetonitrile.

Sorption of pyridine from n-hexadecane mixtures with acetonitrile or acetone demonstrated the solvent assisted effect of pyridine sorption. Sorption uptake of pyridine increased as initial acetonitrile concentration increased, this acetonitrile assisted trend for pyridine sorption was found in the presence of a large excess of n-hexadecane. Sorbed concentrations of pyridine measured in the presence of high concentrations of acetonitrile (close to it's solubility limit) were found to be very similar to pyridine sorption from neat acetonitrile. Sorption behaviour of pyridine in n-hexadecane-acetone mixtures showed that increasing acetone concentrations had no effect on pyridine sorption.

Pyridine sorbed from n-hexadecane, n-hexadecane-acetonitrile, and n-hexadecane-acetone mixtures showed a hysteretic desorption to n-hexadecane. After a series of

repeated solvent extractions with solvents of increasing solvating power(1,4-dioxane, ethanol, dimethylsulfoxide), a fraction of pyridine remained bound to the peat. This non-recoverable fraction was approximately the same for the different organic media (0.45± 0.09 in n-hexadecane suspensions, 0.57±0.12 in n-hexadecane-acetonitrile mixtures, and 0.46±0.07 in n-hexadecane-acetone mixtures). Acetonitrile sorption by peat from n-hexadecane was found to be very non-linear and hysteretic. The acetonitrile sorbed was almost fully recoverable, around 90%, for the initial acetonitrile concentration range varying from 0.14-0.7% by volume. However in the presence of pyridine a significant portion of acetonitrile was not recovered even after multiple extractions of polar organic solvents. Pyridine irreversible binding was not induced by acetonitrile additions and was found to occur to the same extent in both neat n-hexadecane and n-hexadecane-acetone mixtures.

The solubilities of acetonitrile and acetone were determined by the flask method at 25°C using GC analysis. Solubility in volume percent for acetonitrile in n-hexadecane, 0.9±0.07, 0.57±0.02 for n-hexadecane in acetonitrile, 24.0±0.4 for acetone in n-hexadecane, and 13.4±0.2 for n-hexadecane in acetone, were found. Log Ostwald coefficient (1.63±0.02) for acetonitrile in n-hexadecane was measured at 25°C using head space analysis and was found to be constant in the acetonitrile concentration range 0.1-0.8% by volume. Log Ostwald coefficient for pyridine in hexadecane used was 3.02, for the pyridine concentration range 50 mg/L-500 mg/L, this value was constant even with 0.5% by volume additions of acetonitrile. Analyses of sorption isotherms were reported on an activity basis to eliminate the effect of differential solute interactions in the solvent, calculated using the solute equilibrium concentration, the concentration of saturated vapour, and the Ostwald coefficient.

Dissolution of peat components into n-hexadecane are known to be negligible. Peat components extracted after 12 hours and 3,5 months acetonitrile and acetone treatment (solid liquid ratio 1:10) showed 15 to 20 times less visible absorbance respectively (λ 465, 620, and 665, E4:E6 ratios using UV-Visible Spectroscopy), than the 12 hours aqueous peat extract. Quantification of the dissolved humic materials in the aqueous

extract was followed using a Total Organic Carbon analyser. The study found the degree of humification to be much lower in non-aqueous organic solvent extracts (2.5 for acetone extracts, and 3 for acetonitrile extracts) than in aqueous solution extracts (8.2)

Table of Contents

List of Reaction Schemes and Figures

List of Tables

Abbreviations and Acronyms

COD	Chemical Oxygen Demand
COOH	Carboxyl
DDT	Dichlorodiphenyltrichloroethane
DDW	Double Deionised Water
DMSO	Dimethylsulfuoxide
DNOC	Dinitrooctylcarbamate
ESR	Electronic Spin Resonance
FA	Fulvic Acid
FID	Flame Ionization Detector
f_{oc}	Fraction of organic carbon
GC	Gas Chromatography
HA	Humic Acid
HOC	Hydrophobic Organic Compound
HS	Humic Substances
IC	Inorganic Carbon
IR	Infra Red
K_d	Distribution coefficient
K_{oc}	Sorption coefficient
K_p	Partition coefficient
mg/L	Milligram per liter
mL/g	Milliliters per gram

OC	Ostwald coefficient
OM	Organic Matter
PAH	Polynuclear Aromatic Hydrocarbon
PCP	Pentachloropheno
ppm	Parts per Million
SOM	Soil Organic Matter
TBA	Trichlorobenzoic Acid
TC	Total Carbon
TCA	Trichloroacetate
TCE	Tetrachloroethane
TOC	Total Organic Carbon
TOC's	Toxic Organic Chemicals

CHAPTER 1

INTRODUCTION

1.1 Soil Organic Matter

Soil Organic Matter (SOM) is defined as the non-living portion of the soil organic fraction and it is a heterogeneous mixture of products resulting from microbial and chemical transformation of organic residues. Although the soil organic matter is, in most cases, only a small part of the total soil solid phase, it is of major importance in defining the physical, chemical and surface properties of the soil material.[1]

The major components of the soil organic matter and their definitions are summarized and presented in Table 1.1[2] The natural degredation products of the fresh organic debris are generally called humus, but, in reality, they may be composed of humic and non-humic substances. Humic substances could be amorphous or polymeric. The brown coloured humic substances are differentiated on the basis of their solubility properties. These are humic acids, fulvic acids, humins, and recognizable classes such as polysaccharides, polypeptides, and altered lignins to mention a few. These are usually synthesized by micro-organisms or arise from modifications of similar compounds[3].

The SOM can be extracted from the soils by fractionation on the basis of their solubility characteristics. The fractions commonly obtained include humic acid, fulvic acid, hymatomelamic acid, and humin. During extraction dark-coloured pigments are produced due to multiple reactions. The major pathway being condensation reactions involving polyphenols and quinones. The polyphenols derived from lignin are catabolized by micro-organisms and enzymatically converted to quinones, which undergo self condensation or combine with amino compounds to form N-containing polymers. The number of molecules involved in the process, as well as the number of ways in which they combine is unlimited. This explains the heterogeneity of the humic material in any given soil. The structural precursors of humic substances in soils are illustrated in Fig. 1.1

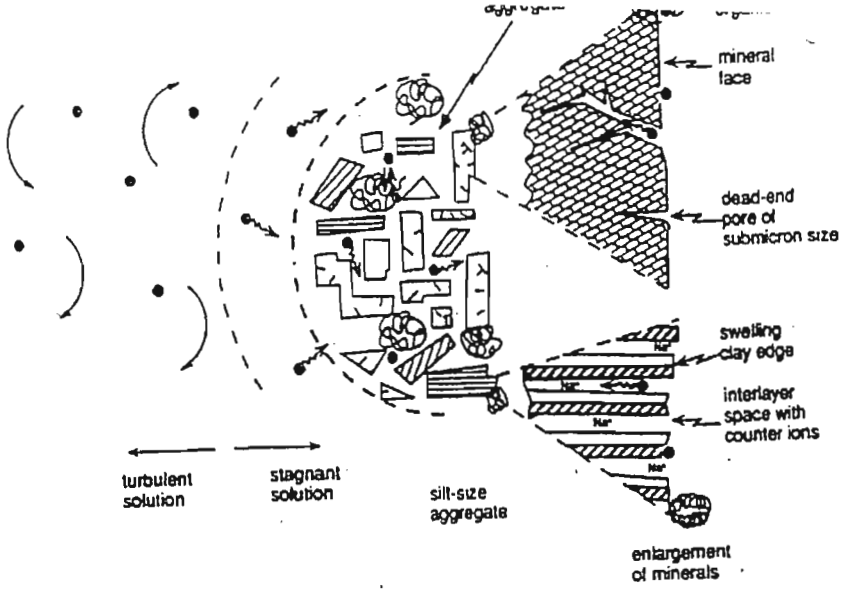


Fig.1.1 Schematic representation of humic substances in soils and their main components and origins.[3]

The major elements in the humic materials are carbon (50-60% by mass) and oxygen (30-35%). Fulvic acid has the lower carbon but higher oxygen content. The percentages of hydrogen and nitrogen vary between 2 – 6 % and that of sulfur from 0-2 %. The various fractions of the humic substances obtained on a basis of solubility characteristics are part of a heterogeneous mixture of organic molecules which, in different soils and locations, might range in molecular weight from hundred to several hundred thousands daltons. The average molecular weight range for humic acid is in the order of 10 000 - 50 000 daltons and a typical fulvic acid will have a molecular weight in the range of 500 – 7000 daltons.[4]

The humic fraction of the soil represents a colloidal complex including long-chain molecules or two or three dimensional cross linked molecules whose size and shape in solution are controlled by the pH and the presence of neutral salts such as a neutral sulfate complex ($MnSO_4$) with a bivalent metal cation as the central group. Under neutral or slightly alkaline conditions, the molecules are in an expanded state as a result of the repulsion of the charged acidic groups, whereas at low pH and high salt concentration, contraction and molecular aggregation occur, due to the charge reduction. These large organic molecules may exhibit hydrophobic properties which govern their interactions with non-ionic solutes.[5]

Components	Definition
Organic residues	Undecayed plant and animal tissues and their partial decomposition products.
Soil biomass	Organic matter present as live microbial tissue.
Humus	Total of the organic compounds in the soil exclusive of undecayed plant and animal tissues, their "partial decomposition" products, and the soil biomass.
Soil organic matter	Same as humus.
Humic substances	A series of relatively high-molecular-weight brown to black coloured substances formed by one of the following processes, chemical polymerisation, cell autolysis, and microbial synthesis. The term humic is used as a generic name to describe the coloured material or its fractions obtained on the basis of their solubility characteristics. These materials are distinctive to the soil (or sediment) environment in that they are dissimilar to the biopolymers of micro-organisms and higher plant (including lignin)
Non-humic substances	These are compounds belonging to known classes of biochemistry, such as amino acids, carbohydrates, fats, waxes, resins, and organic acids, to mention a few. Humus probably contains most, if not all, of the biochemical compounds synthesised from plant and animal residues by living organisms.
Humin	The alkali insoluble fraction of soil organic matter or humus.
Humic acid	The dark-coloured organic material which can be extracted from the soil by various reagents such as NaOH (0.1 or 0.5 M) and NaF (1%). This organic material is insoluble in dilute solutions of HCl-HF (0.5 ml conc. HCL + 0.5 ml of 48 % HF + 99 ml of H_2O).
Fulvic acid	The brown coloured material which remains in solution after the removal of humic acid by acidification.
Hymatomelanic acid	Alcohol soluble portion of humic acid.

1.2 The Structure of Soil Organic Matter

Sediment organic matter is viewed as a polymer structure of various organic matter constituents (humic and fulvic material, polysaccharides, partially decomposed cellular material, and humins). It is thought to be formed by depolymerization of macromolecular plant constituents, followed by oxidation reactions, in which carboxyl groups are formed.[7] This process results in the formation of amphiphilic molecules, with their polar sites at the aqueous exterior and their hydrophobic sites at the interior.[7] Sediment organic matter is the most hydrophobic sediment constituent and therefore it is probably the most important determinant in studying the sorption and desorption behavior of toxic organic chemicals. Based on what is known from structural fragments studied by pyrolysis Gas Chromatography-Mass Spectroscopy as well as Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy, the structure proposed is shown in Fig. 1.2.[6]

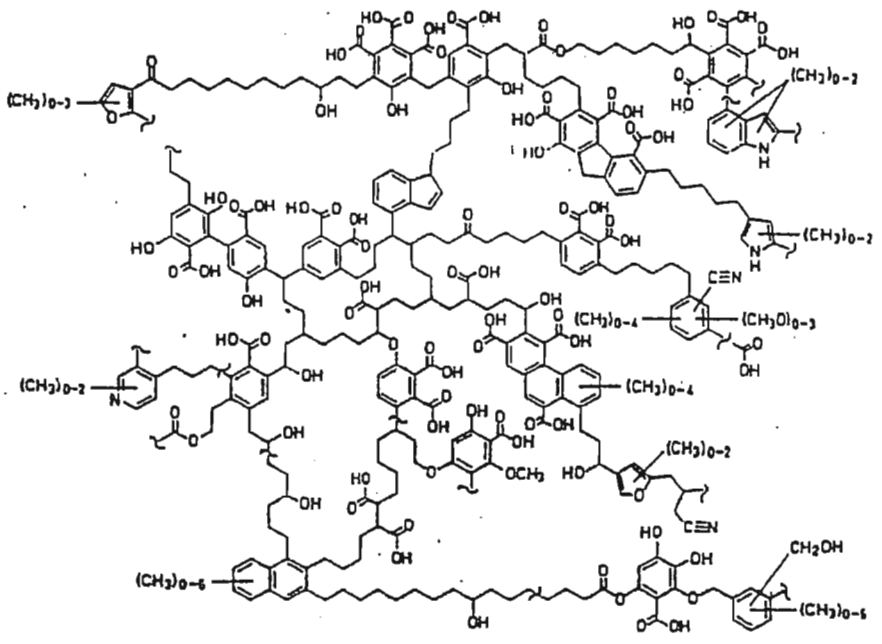


Fig. 1.2. The proposed structure of soil organic matter [7]

Both humic and fulvic substances have many functional groups, such as hydroxyl, amino, carboxyl and carbonyl groups. The molecular weights of fulvic and humic acids can vary from hundreds to many thousands of daltons. Heterogeneity also exists in organic matter (OM) at the microscopic level. Regions of various densities, polarities, hydrophobicity and water contents coexist. Due to the high oxygen and nitrogen content, sediment organic matter is more polar than hydrocarbons or chlorobenzenes.[8]

The structures of humic and fulvic acids are probably punctuated by voids (holes) that may trap organic solutes[9,10]. The glassy parts of humic materials are assumed to contain such voids[10-12], similar to glassy polymers.[13] Through computational chemistry on structural fragments, determined by several mass spectrometry methods[10], it has been shown that a compound like atrazine can be trapped in such voids. Humic and fulvic acids are polyelectrolytes in which there is a variable degree of rotational freedom around the numerous linkages.[9] The linkages are influenced by pH, resulting in aggregation at low pH where many H-bridges can be formed and dispersion at high pH where H-bridges dissociate and electrostatic repulsion occurs.[9]

1.3 Interactive Properties of Humic Substances

Humic substances are polydisperse materials exhibiting polyelectrolytic behaviour, whereby some of the functional groups exhibit electric charges in aqueous solution. The size of the charge, as well as its sign, is controlled by the properties of the surface to which the functional groups are bound, and by the composition of the surrounding liquid phase. Electron microscopy, viscosity and ultracentrifuge measurements have been used to obtain information on these properties.[14-16] Soil, aqueous solutions, and sedimentary aquatic forms of Humic acid (HA) and Fulvic acid (FA) have been shown to be surface-active,[17,18] i.e. the development of anionic character on the macromolecular framework, with the resultant effects on functional group reactivity and molecular confirmation. This is an important property of Humic Substances (HS) since it makes them interactive toward hydrophobic compounds in the soil and aquatic environments, affecting the structure and solubilization of some of the HS. It has also been shown that the surface tension of soil FA and HA solutions is concentration and pH dependant due to the ionisation of the acidic functional groups.[19] The amphiprotic

character, i.e the capability of exhibiting both acidic and basic properties. The surface activity of HA and FA will therefore increase at high pH values, when acid COOH and phenolic OH groups form more hydrophilic sites. Increasing pH and concentration of both HA and FA lower the surface tension of water, thus increasing soil wettability and affecting the interaction phenomena of HS with both hydrophobic and hydrophilic organic chemicals in solution. Surface active properties such as surface acidity (the ability of the surface to act as either a Lewis or a Bronsted acid) of HS assume higher importance in interaction phenomena occurring in aquatic environments. This is due to the greater ease of dissociation of adsorbed water molecules as compared to free water molecules. Comparing the aquatic and terrestrial FA and HA, it is found that aquatic species are more surface active than their terrestrial correspondents.[18]

It has also been reported that HS exhibit high concentrations of stable free radicals, probably of the semiquinone type. These are considerably reactive especially in the binding of organic molecules. It was also shown that the free radical content of HA, FA, and FA fractions were pH and visible-light irradiation dependent.[19,20] Also found, was that the higher the pH, the greater was the spin content. Solid samples show small increases in free radical concentrations, while HS in solution exhibited much higher increases.[20] It was also shown[21] that the pH dependence and photo-induced radical production might be the basis for many photo-degradation reactions in soils and surface waters.

1.4 Reactions of Soil Organic Matter With Toxic Organic Molecules

Approximately one half of the industrially-produced organic chemicals reach the global environment via direct and indirect ways, such as through agriculture, municipal and industrial wastes plus landfill effluents. These products include a variety of pesticides and their metabolites, aliphatic and aromatic organic derivatives of petrol and plastics, organic solvents, and surfactants and detergents.[22] When these substances reach the natural environment, various degradation and transfer processes are initiated. Chemical properties of each specific organic compound, such as molecular structure, volatility, ionic charge and ionizability, polarizability and water solubility will determine which processes predominate. The known interaction

processes, leading to activation-inactivation, physical sorption onto soil, and chemical binding or partitioning into SOM, are most important phenomena that Toxic Organic Chemicals (TOC's) are subjected to in the global environment.

The fate and behaviour of TOC's in the environment are affected by many different processes. These include degradation, persistence, mobility, bioactivity, phytotoxicity, volatility and leachability. All these have a direct relationship to the nature and content of HS in the environment. Many physical, chemical and biochemical properties, climatic factors and geochemical effects influence the behaviour of TOC in the environment. The highest correlations and general dependence has been found with concentrations of HS.[15,16]

1.4.1 Pesticides

Organic pesticides that are presently used belong to different families of organic chemicals and may be grouped in various ways. The classification used is based on the interactive properties towards HS.[23] These are cationic, basic, acidic, anionic, and non-ionic. Selected pesticides of various applications such as herbicides, insecticides, fungicides, and germicides and their interactions with HS are discussed (see 1.4.1.1 – 1.4.1.4). Among various TOC's, pesticides represent the group of compounds which are most commonly found in soils and have an interaction with the soil humus. Comparative studies have suggested that most pesticides have a greater affinity for organic surfaces than for mineral surfaces, thus organic matter, and in particular humin fractions, play a major role in the performance of soil-applied pesticides.[16] Nevertheless, in most soils HS are partly associated with clay minerals, thus firmly clay-bound fractions of HS (e.g. humin) do not behave as a separate entity in the interaction of soil constituents with pesticides.[16]

1.4.1.1 Cationic Compounds

Bipyridilium herbicides such as diquat and paraquat are the only important compounds of this group that have been investigated thoroughly in relation to interactions with aquatic and soil HS. These are available commercially as dibromide and dichloride salts, respectively, they are used as herbicides and desiccants.[24-26]

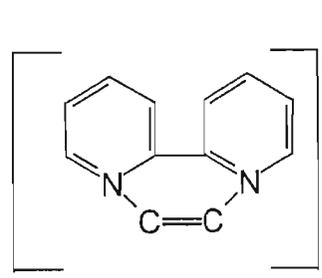


Fig. 1.3 Diquat ion

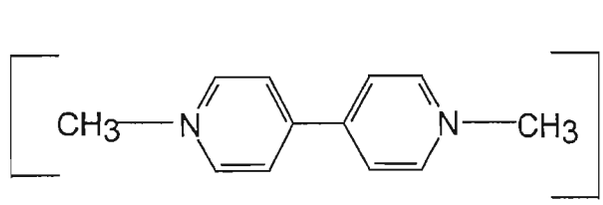


Fig. 1.4 Paraquat ion

The solubility of cationic pesticides is generally high in aqueous solutions, where they dissociate readily to form divalent cations. Diquat (Fig. 1.3) and paraquat (Fig. 1.4) are non-volatile compounds and do not escape as vapours from aquatic and soil systems. They are known to readily photo-decompose when exposed to sun or UV-light, but are not photo-decomposed when adsorbed onto particulate matter.[24] These compounds are able to form well-defined charge-transfer complexes with phenols and many other donor chemicals.[27]

Diquat and paraquat become partly inactivated in highly organic soils.[28,29] The phytotoxicity to plants grown in media containing organic matter is reduced.[30] Sorption, i.e. uptake of a solute by a soil (or by a constituent of the soil) without reference to a specific mechanism, of diquat and paraquat on soil organic matter has been proposed to be the major factor responsible for the decrease in herbicide activity, although the chemicals are still biologically active towards plants and micro-organisms.[31,32] Diquat and paraquat, being divalent, have the potential for reacting

with more than one negatively charged site on soil humic colloids, such as through two carboxylic ions. It has been suggested that paraquat and diquat in a muck soil are present in "tightly" bound fractions, not available to plants, and a "loosely" bound fraction which can potentially become available.[33]

The fungicide phenacridane chloride, the germicide thiamine, and the plant growth regulator phosphon have also been studied somewhat for their interaction with soil organic matter.[23] Phenacridane chloride and thiamine are cationic compounds that have been found to adsorb strongly on soil organic matter. These two compounds have the highest level of adsorption followed by phosphon, diquat, and paraquat.[31] This is due to the number of protonatable functional groups such as NH_2, COOH, and NH. As an example the, C=O group in the phenylcarbamate and substituted urea pesticides can form a hydrogen bond with the NH in soil organic matter.

1.4.1.2 Basic Compounds

The most important and studied pesticides of this group are amitrole and several members of the family of s-triazines (Fig.1.5). Amitrole had been widely used as a herbicide, but its use as a registered product for application on food crops was cancelled starting in 1971 because it was suspected of inducing thyroid tumours in rats [33]. Amitrole is soluble in water, showing a weak basic character (pK_b = 10) and behaves chemically as a typical aromatic amine.[23,24]

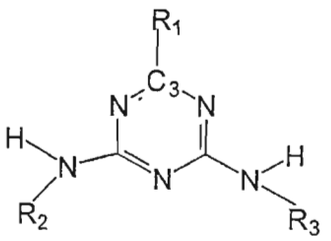
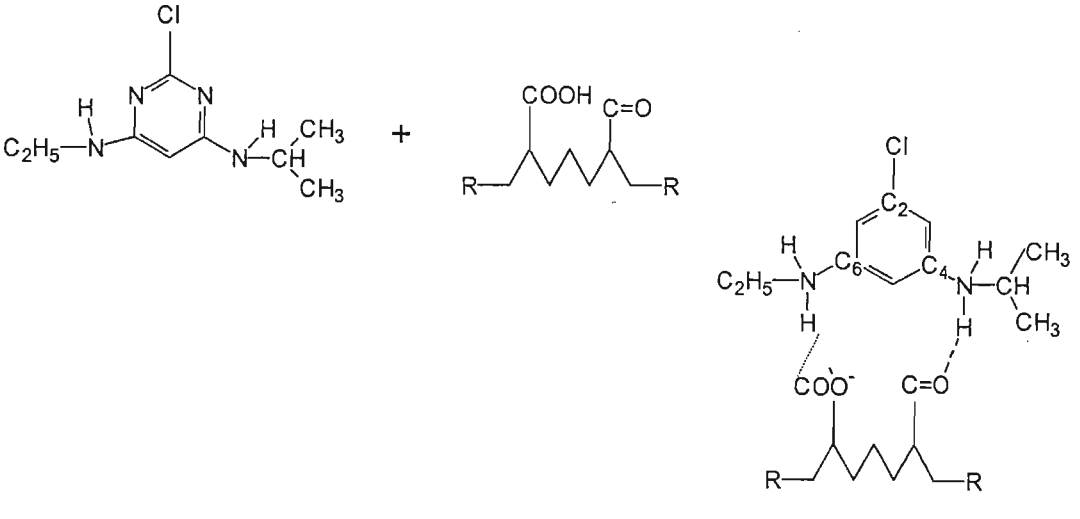


Fig. 1.5 S-Triazine

S-Triazines that are currently used as selective or general herbicides are substituted diamino-s-triazines which have a chlorine, methoxy, methylthio, or azido group attached to carbon-3 ring atom. The substituent at R_1 position determines the ending of the common name of the compound. R_2 and R_3 representing alkyl substituent

groups. The solubility in water of the compound is also determined by the R_1 substituent, with the $-OCH_3$ substitution resulting in the highest solubility. Symmetric triazines have low mutual solubilities in water, the 2-chloro-s-triazines being less soluble than the 2-methylthio and 2-methoxy analogues. Water solubility increases at pH values where strong protonation occurs, e.g. between pH 5.0 and 3.0 for 2-methoxy- and 2-methylthio-s-triazines, and at pH 2.0 or lower for 2-chloro-s-triazines.

Structural modifications of the substituents significantly affect solubility at all pH levels. Increasing solubility (Scheme 1.1) is associated with increasing electron-donating capability of the substituents at carbon-2-and increasing size and branching of the N-alkyl groups at the 4- and 6-positions.

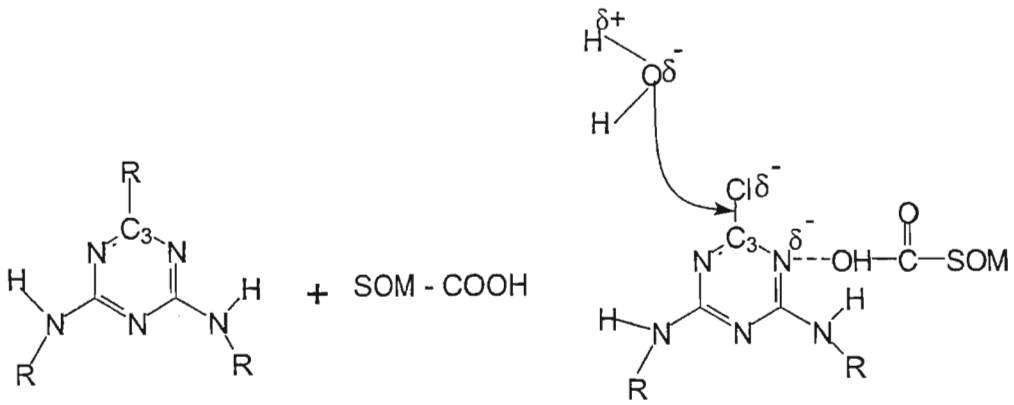


Atrazine–Humic Acid complex

Scheme 1.1 Interaction of Atrazine and Humic Acid.

The s-triazines, and especially the chloro-s-triazines are chemically hydrolysed in aqueous systems. Chloro- and methlythio-s-triazines are partly photo-decomposed in aqueous systems by UV and IR radiation, including sunlight, while methoxy-substituted compounds are not photodegradable, most s-triazines are relatively volatile, so that they can be lost from aquatic and soil systems by volatization processes [23].

Adsorption of S-Triazine to SOM was postulated[34] to take place between a ring nitrogen atom and a protonated carboxyl (COOH) group as shown in Scheme 1.2. Hydrogen bonding of the ring nitrogen is believed to cause the withdrawal of electrons from the electron deficient carbon atom bonded to the chlorine atom, thereby enabling water to replace the chloride atom. The presence of electron-rich nitrogen atoms confers on s-triazines electron donor ability, i.e. weak basicity, and the capacity to interact with electron acceptor molecules, giving rise to electron donor-acceptor (charge-transfer) complexes.



Scheme 1.2 Postulated interaction between S-Triazine and SOM

1.4.1.3 Acidic Compounds

This group of pesticides comprises different families of chemicals with herbicidal action. These include substituted phenols, chlorinated aliphatic acids, chlorophenoxyalkanoic acids, and substituted benzoic acids. These compounds possess carboxyl or phenolic functional groups capable of ionising in aqueous media to yield anionic species. These compounds range in acid strength from strong acid to relatively weak acids. Chlorinated aliphatic acids show the highest water solubility and the strongest acidity among this group of chemicals. This is because of the strong electronegative inductive effect of the chlorine atoms replacing the hydrogens in the aliphatic chain of these acids The water solubilities of the phenoxyalkanoic acids are low as they have a considerable lipophilic content. Most commercial formulations of these herbicides, however contain the compound in the soluble salt form, thus the anionic species predominate in neutral aqueous systems, while at low pH levels they are present in

the molecular rather than the anionic form. These herbicides may undergo reactions of alkylcarboxylic acids, aromatic compounds and esters. Dinitrophenols and pentachlorophenol (PCP) are generally of intermediate solubility in water, while they are highly water soluble as alkali salts which represent most of their common commercial formulations. With the exception of picloram and phenols, acidic pesticides are considered non-volatile from aqueous and soil systems [23]. Some ester formulations of these compounds also behave as herbicides. They do not ionise in solution and are less water soluble than the acid or salt forms. They are eventually hydrolyzed to acid anions in aqueous and soil systems, but in the ester form are non-ionic and relatively volatile. The most widely known and used phenoxyalkanoic acids are 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid. The most extensively used halogenated benzoic acid herbicides are chloramben, dicamba, and 2,3,6-trichlorobenzoic acid (TBA). Phenols most used as herbicides are Dinoseb and dinitrooctylcarbamate (DNOC), while ioxynil, and bromoxynil, pentachlorophenol (PCP), trichloroacetate (TCA) and Dalapon are the major chlorinated aliphatic acids used as insecticides. Picloram is the only prominent member of pyridine derivatives that has been extensively studied and commercially developed as a herbicide.[23]

Bioactivity and transport of acidic pesticides and their substitute esters were found to correlate with the organic matter content of the soil, even though the adsorption level of these herbicides is much lower than that of cationic or basic pesticides.[29,32] This is due to the fact that chemical hydrolysis and sunlight photodecomposition are more pronounced for basic pesticides.[29] Persistence of these pesticides, measured in terms of biological activity, as well as residual toxicity, is the highest in soils containing high levels of organic matter.[32,35] leachability of picloram, amiben, and PCP was negatively correlated with the percentage of organic matter.[32,36] The usefulness of PCP as a pesticide decreases due to adsorption into the organic matter matrix.

1.4.1.4 Non-Ionic Pesticides

Pesticides of this category do not ionise significantly in aqueous systems and vary widely in their chemical composition and properties. The properties include their solubility, polarity, tendency to volatilization and molecular volume in water. Chlorinated hydrocarbon insecticides are among the most widely known and studied non-ionic pesticides. The most studied being dichlorodiphenyltrichloroethane (DDT), which is about ten times more insoluble than the other compounds of this family. Therefore it is considered to be immobile in soil systems. This is also true with respect to toxaphene, chlordane, and heptachlor which are insoluble in water as well.[23] Endrin, dieldrin, lindane, and aldrin show higher water solubility and are therefore slightly mobile in soils. The vapour pressure of chlorinated hydrocarbons varies from low (DDT, endrin and dieldrin), to moderate (toxaphene and aldrin), to high (chlordane and lindane), and to very high (heptachlor). Volatilization of DDT from soils and other surfaces is, therefore, almost insignificant.[24]

The other group of non-ionic pesticides are organophosphates which are more toxic than chlorinated hydrocarbons, in particular to humans. These exhibit lower persistence in soils and do not accumulate in soil fauna.[33] This is because the compounds are highly water soluble and have a higher vapour pressure. Malathion and parathion insecticides are known to be chemically hydrolysed and biodegraded by micro-organisms in soil systems. The most used organophosphates herbicide is glyfosate.[37]

Insecticidal activity of organophosphates and their adsorption in soils is strongly influenced by the organic matter content of soils.[38] Functionalities situated on the ends of the organic matter provide the opportunity for organophosphates to react, bind, and form stable persistence species.[39] This relationship is observed with diazinon and parathion in moist soils, but not in dry soils.[39] Water is a good solvent for ionic pesticides. The activity (and therefore the chemical potential) of a solute in solution depends in part upon the solubility of the solute in the solvent. Changes in solute activity in the bulk solution are important because the difference between the activity of the solute in solution and the activity of adsorbed solute contributes to the

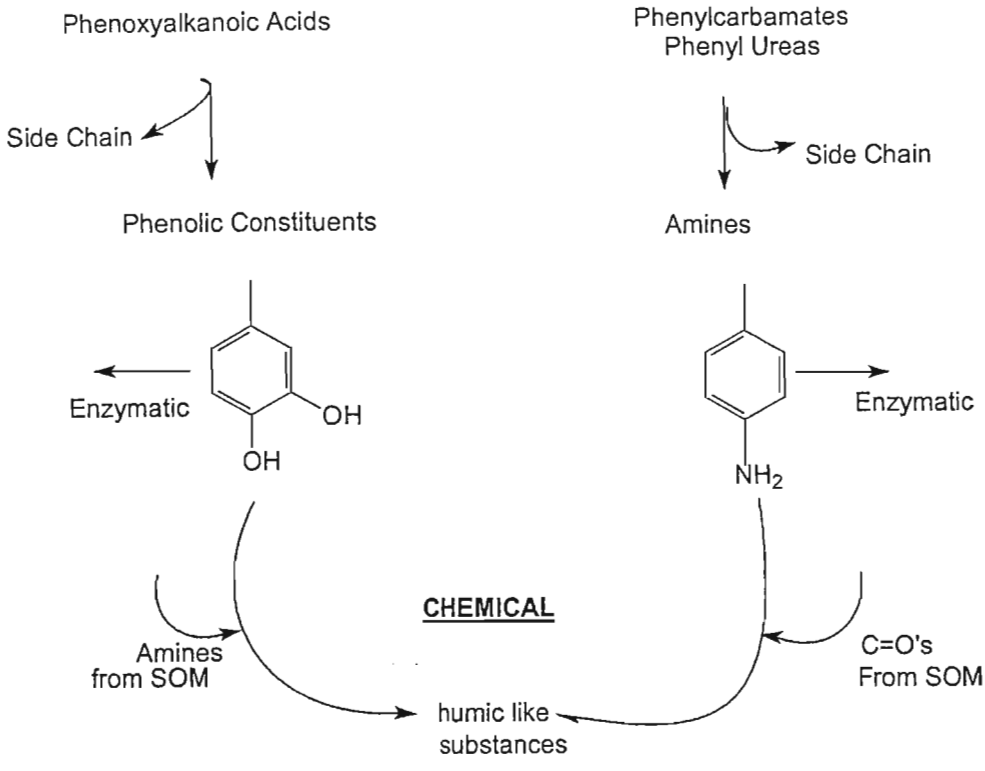
difference in partial molal free energies. This is the driving force for the adsorption process.[40] The pesticide fonofos has a persistence of
more than two years in organic soils. This is partly due to it's adsorption on HS which also controls the compounds mobility in soils.[40,41]

Phenylcarbamates, and carbanilates, generally exhibit low water solubilities, thus they are almost immobile in soil systems. Chlorpropham and propham are readily volatised from soil systems, but tebutol and carbaryl are not. Among chemical reactions carbamates may undergo, there are ester and amide-hydrolysis, N-dealkylation and hydroxylation. N-methylcarbamate insectides commonly used in soils are carbaryl, methiocarb, aldicarb, and carbofuran.[42,43]

Phenylcarbamate herbicides show a lower herbicide activity in fine textured soils than in coarse ones. This is because of the higher organic matter content of the former soils.[32] The phenolic and carboxylic functionalities positioned on the surface of the organic matter matrix can form chemical linkages with pesticides and hence reduce their activity[4] as illustrated in Reaction Scheme 1.3. The increase in soil organic matter content reduces the phytotoxicity of the pesticide chlorpropham. Similaraly the loss of propham and chlorpropham from moist soils through evaporation decreases as the organic matter content increases.[35]

Substituted urea herbicides also belong to the non-ionic group with more than twenty five different compounds available commercially. The most important are phenylureas (fenuron, monuron, diuron, fluometuron, and chlortoluron) and cycluron which has the aromatic nucleus replaced by a saturated hydrocarbon moiety. Benzthizuron and methabenzthiazuron are more recent selective herbicides of the class, with the aromatic moiety replaced by a hetrocyclic ring system. With the exception of fenuron, substituted ureas exhibit low water solubilities, which decrease with increasing molecular volume of the compound. The majority of phenlyureas have relatively low vapour pressures, and are therefore not very volatile. These compounds show electron donor properties and thus they are able to form charge transfer complexes by interaction with suitable electron acceptor molecules as illustrated in Reaction Scheme

1.3. Hydrolysis, acylation and alkylation reactions are also possible with these compounds.[43,44]



Reaction Scheme1.3 Postulated chemical reactions between herbicides and constituents of soil organic matter.[4]

The herbicidal activity, adsorption , and transport of several phenylureas, including monuron, linuron, neburon, fluometuron and diuron in soil decreases as the organic matter content of soil increases.[35,45-47] The addition of organic matter to sandy soil has been shown to significantly reduce the herbicidal activity of fluometuron and fenuron in a growth chamber study and in field experiments.[32] Other important herbicides known to be relatively mobile and volatile in soil are substituted anilide, thiocarbamate, and carbithioate herbicides.[48] Substituted dinitroanilines and benzonitrile herbicides on the other hand are known to be relatively immobile in soil systems.[44,48]

Insectide activity, degradation, inactivation, leaching and volatilisation of several chlorinated hydrocarbons, including aldrin, dieldrin, endrin, endosulfan, lindane, heptachlor, DDT, toxaphene, and chlordane decreases as the organic matter content of soil increases.[49] For nitrogen containing compounds, ammonia is absorbs by the

reactive humic surfaces. The humic acid of the organic matter polymerises as it absorbes the ammonia and hetrocyclic rings are formed.[50,51] In the case of the reaction of "protein-like" materials with the phenoxy groups of soil organic matter, the phenoxy groups are converted to quinines to which the polypeptides become attached, and this combination resists acid hydrolysis.[52] This effect is most prominent in moist soils.[32,53,54] Higher levels of organic matter is known to incease the persistence of DDT, lindane, and aldrin. These are found to be in a larger quantity in muck-soil than in mineral soil.[55] The reason being that peat muck has a higher organic matter content than the mineral soil. Transport of DDT in forest soils is associated with soil humic acids (HA) and fulvic acids (FA) fractions.[56,57]

The leaching of DDT decreases as the percentage of humic acids and fulvic acid increases.[55] It has been determined through a bioassay technique that soil organic matter is the principal means of deactivation of DDT.[57] The increase in organic matter content results in the concentration of stable free radicals of the semiquinone type, these are considerably reactive for the binding of certain organic compound like DDT.

1.4.2 Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons (PAH) are in general a hazardous class of widespread contaminants produced in large quantities from the combustion of fossil fuels, in chemical manufacturing, petroleum manufacturing, metallurgical processes, and in some coal, oil-shale and tar sand conversion systems. PAH are present in waste streams from these processes and through various environmental pathways.[58]

PAH are neutral, non-polar organic molecules consisting of two or more benzene rings arranged in various configurations with hydrophobicity increasing with molecular weight. Many members of this class of chemicals have been identified to exhibit toxic and hazardous properties. Some materials have been demonstrated to cause mutations and certain types of cancer.[49,58]

Although there is evidence that the environmental sources of PAH also include natural inputs such as combustion (e.g. forest fires[51])sediment diagenesis,[59] geological phenomena (such as volcanoes) and seepage from rock formation,[60] and biological

conversion of biogenic precursors,[61] most of the PAH contamination of aquifers, soils, sediments and water bodies comes from anthropogenic sources.[52] These compounds are hydrophobic in nature. Therefore adsorption is very important in determining their fate in surface and subsurface water-soil or water-sediment systems.

The interaction of PAH with HS is through hydrophobic adsorption, with the retention of nonpolar PAH, or PAH having a predominance of nonpolar over polar regions, by hydrophobic surfaces of HS. This kind of adsorption originates from a weak solute–solvent interaction, i.e. the low solubility, or hydrophobic nature of the solute. Water molecules are not good competitors with nonpolar molecules for adsorption on HS hydrophobic surfaces.[59] Hydrophobic active sites of HS include aliphatic side chains or lipid portions and lignin-derived moieties with high carbon content and a small number of polar groups.[9] Adsorption by this mechanism is independent of pH[59] but increases with methylation of the HS that blocks the hydrophilic groups.[62]

1.5 Sorption coefficients

For the purpose of comparing the adsorption into SOM of numerous pesticides without showing the individual isotherms, one can obtain from the isotherms the amount of each pesticide adsorbed at a given concentration. The other alternative is to determine a distribution coefficient (K_d) for a known solution concentration. K_d is expressed as a ratio of amount adsorbed to that in solution as shown in equation 1.1

$$K_d = \frac{\text{Pesticide adsorbed (moles/kg)}}{\text{Pesticide in solution (moles/liter)}} \qquad (1.1)$$

The distribution coefficient is also refered to as a partition coefficient (K_p) when comparing the ratio between the concentration of pesticide adsorbed into SOM to that in aqueous solution.[63,64]. When studying the sorption behaviour of different soils, the organic carbon content determines the pesticide sorption. To compensate for this and ensure that the correct K_d or K_p is obtained, the K_d and K_p are normalized against the organic carbon content. A sorption coefficient (K_{oc}), normalized for organic carbon content is obtained, as shown in equation 1.2

$$K_{oc} = \frac{K_p \text{ or } K_d}{f_{oc}} \qquad (1.2)$$

where f_{oc} is the fraction of organic carbon.

Correlations of pesticide sorptive behavior with systems components such as fraction of organic matter and initial solute concentration, have traditionally been made under assumed equilibrium conditions. Usually the period necessary to attain equilibrium is determined in preliminary experiments where uptake is followed until it appears to level off. This period is reported to range from minutes to a few hours.[63-69]

An ideal system at true equilibrium will yield distribution coefficients (K_d) that are identical whether equilibrium is approached from an adsorptive or desorptive direction. Ideal sorption isotherms would give superimposable curves. This is known as singularity. However in many studies[63-69], hysterisis, or nonsingularity has been observed, giving rise to sorption isotherms that follow different paths from the adsorptive and desorptive directions.

1.6 Aims of the study

Sorption of environmentally hazardous organic molecules in soil or porous media is arguably the most important factor governing the fate of such pollutants in the environment. The hysteretic desorption of these compounds will have important practical implications concerning the nature of bound organic compound residues in soil and aquifer remediation. Sorption of organic compounds by SOM from organic solvents may be used to probe the structure of SOM. This will help to gain more insight into the structure of the SOM macromolecular phase, deduced from the experimental SOM/organic compound/solvent compatibility. Replacing water with organic solvents in the sorption of pyridine affects both the SOM structure and the SOM-sorbate interactions. This is because of change of ionisation status of SOM functional groups, SOM swelling, competitive solvent-sorbate interactions in the sorbed phase. Hence, by altering a medium, it is possible to examine the role of water

in sorption of organic compounds by SOM. The interactions of soils with non-aqueous phases formed from petroleum (and solvent) spills which are composed of numerous organic compounds make it important to evaluate the sorption of organic compounds by SOM in the presence of organic solvents. The other reason is that these solvents and their mixtures are also normally used in the extraction of humic substances form soils, a similarity exists between the sorption of organic compounds by SOM from organic solvents and the extractability potential of organic media.

A literature survey carried out showed that only three studies since 1969 have looked at the sorption of organic compounds onto dry soil organic matter based sorbents from non-aqueous organic media.[31,35,70] However these results are not comparable since they were not reported on an activity basis, but rather on a solution concentration basis. Activity basis expresses the sorbed amount of organic compounds against the activity of the compound in solution rather than against its solution concentration. Activity basis calculations include the effect of differential solute interactions in the solvent, whereas expressing as solution concentrations excludes this important factor[12,72]. Also a recent study has looked at the sorption of pyridine onto SOM from aqueous solution, and was found to be linear.[72]

It is clear that information of sorption of organic compounds by SOM in non-aqueous solvents is missing. The purpose of this research was therefore to study organic compound solvent assisted cooperative binding in SOM. This was done using an activity based comparison of sorption and desorption data, to examine the soil organic matter pyridine sorption capability in various non-aqueous organic liquid media. The results obtained were used to derive the implications concerning the hydration effect on sorption of specifically interacting organic compounds by soil humic material. The study also aimed to investigate the effect of slow desorption and hysteretic behaviour of organic compounds.

CHAPTER 2

THEORY

2.1 Mechanisms of Adsorption

Adsorption is defined as the condensation of vapours or solutes (both referred to as sorbates) on surfaces or interior pores of a solid (adsorbate) by physical or chemical bonding forces.[9] Several types of mechanism often operate simultaneously in the absorptive interaction between Humic Substances (HS) and Toxic Organic Chemicals (TOC's). The following mechanisms have been proposed: ionic bonding (ion exchange), hydrogen bonding, Van der Waals attractions, ligand exchange, charge transfer (electron donor acceptor process), covalent binding (chemical or enzyme-mediated) and hydrophobic bonding.[73] Most of these mechanisms show very specific adsoption isotherms.

2.1.1 Sorption Isotherms

Construction and use of sorption isotherms from equilibrium sorption data has been employed to describe the adsorption of TOC's on solid matrix. An isotherm represents a relationship between the amount of solute adsorbed per unit weight of solid adsorbent and the solute concentration in solution at equilibrium. The relationship between solute sorption mechanism on solid surfaces and the shapes of the sorption isotherms has been investigated.[74] This has resulted in an empirical classification which recognises four main types of adsorption isotherms as shown in Fig. 2.1

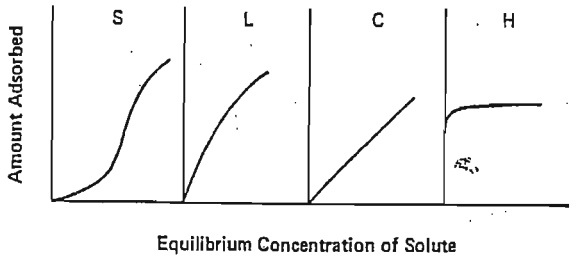


Fig.2.1 Classification of adsorption isotherms

The L-type also known as the Langmuir isotherm, is the most common and occurs when the adsorbent has a moderately high affinity for the solute in the initial stages of the isotherm. As adsorption sites are filled, the solute molecules have increasing difficulty in finding vacant sites and the slope of the curve decreases. The S-type is also known as 'Co-operative adsorption'. In this case initial sorption is low compared with the solvent or other solutes, and increases as the number of solute molecules on the surface increase. The C-type or 'Constant partition' isotherms are obtained by solutes which penetrate into the solid more readily than does the solvent. A C-type isotherm can also be a combination of L + H type at low solute concentrations. These curves are characterized by a constant partition of solute between the solution and the substrate, and therefore the adsorption is always directly proportional to the solute concentration. The H-type well known as ''high affinity'' isotherms represent very high affinity between the solute and the solid.

Generally two mathematical equations are used to quantitatively describe adsorption of TOC's to organic matter adsorbent:

(i) Freundlich equation which is an empirical equation

$$\frac{x}{m} = K_{oc} \times C^{1/n} \qquad (2.1)$$

where x is the moles of adsorbate and m the mass of organic matter. The adsorbate concentration in solution at the equilibrium is represented by C while K_{oc} and n are constants. Normally within a reasonable range of adsorbate concentrations, the logarithmic form of Eq. 2.1 is linear with 1/n being the slope. The K_{oc} value is used as an index of the degree of adsorption of various adsorbates by different organic surfaces, made at the same concentration range. Adsorption of many pesticides on soil organic matter fit the linear equation with an exponent 1/n =1. [1, 9, 75]

(ii) The Langmuir equation expressed in terms of concentration

$$\frac{x}{m} = \frac{K_1K_2C}{1+K_1C} \qquad (2.2)$$

where K_1 is a constant of the system dependent on the temperature and K_2 is a monolayer capacity of adsorbate. The reciprocal of Eq.2.2 provides a straight line with intercept $\frac{1}{K_2}$. The adsorption of a number of pesticides on organic surfaces have also been found to fit the Langmuir model equation. Therefore carefully controlled adsorption measurements of TOC's to HS and the shapes of the relationships to the isotherms may provide information on the type of adsorption mechanism involved.

2.1.2 Ionic Bonding (Ion Exchange)

Adsorption of toxic organic chemicals (TOC's) to humic substances by this mechanism applies only to the relatively small number of TOC's which are cations in solution or can accept a proton, i.e. protonate, to become cationic. Adsorption via cation exchange or ionic bonding operates through ionised carboxylic and phenolic hydroxyl functional groups of the HS.[7] Diquat and paraquat, being divalent cationic pesticides can react with more than one negatively charged site on HS (e.g. two COO^- groups or a COO^- plus a phenolate ion). Infrared[76,77] and potentiometric titrations data[78,79] were used to demonstrate that the predominant mechanism for adsorption of bipyridilium herbicides by HS is ion exchange. Similar results were obtained from IR studies on the interaction between cationic pesticide chlorodimeform and HA.[80] Adsorption of other cationic pesticides, such as phosphon and phenacridane chloride through ionic bonds onto OM have also been reported.[23] HA and FA are known[79] to retain paraquat and diquat at levels that are considerably lower than the exchange capacity of the HS. This implies that not all the negative sites of the HS seem to be positionally available to large cations, due to steric hindrance. It has also been noted that the higher reactivity of simazine with respect to atrazine and prometryn is related to the smaller steric hindrance of the reactive N-H group of this herbicide.[81]

2.1.3 Hydrogen Bonding

This is a special kind of dipole-dipole interaction in which the hydrogen atom serves as a bridge between two electronegative atoms, one being held by a covalent bond and the other by electrostatic forces.

The presence of oxygen and nitrogen containing functional groups as well as hydroxylated and amino groups on HS strongly suggests that H-bonding represents an important adsorption process for TOC's containing similar groups. However, the organic compounds are in competition with water molecules for such adsorption sites.[82] H-bonding mechanism plays a part in the interaction of s-triazine with OM.[82] Multiple sites are available on both HS and herbicide molecules for this type of bonding, in particular through C=O groups of HS and secondary amino groups of s-triazines.[83] Heat of formation of the HA-atrazine complex has shown that there exists one or more H-bonds in the formation of the complex.[83,84] Hydrogen-bonding also plays an important role as an adsorption mechanism for substituted ureas and phenylcarbamates[85,86] as well as non-ionic polar TOC's which possess functional groups that can form H-bonding with HS sites. Acidic or anionic pesticides, such as chlorophenoxyalkanoaic acids and esters, asulam and dicamba can be adsorbed by H-bonding onto HS at pH values below their pKa in non-ionized forms through their COOH and COOR groups and other analogous groups.[78,86,87]

2.1.4 Van der Waals Attractions

Van der Waals forces, although very weak, operate in all adsorbent-adsorbate interactions. These result from short range dipole-dipole or dipole-induced dipole or induced dipole-induced dipole attractions of several types. Although Van der Waals interactions are universally acting forces, they assume particular importance in the adsorption of non-ionic and non-polar molecules or portion of molecules on similar sites, of the adsorbent humic molecule.[75] These forces are additive, thus their contribution increases with the size of the molecule and with its capacity to adapt to the adsorbent surface. Van der Waals forces are considered to be involved in the physical adsorption of

carbonyl and parathion on soil SOM[88] and alachlor and cycloate.[89] They are the principal adsorption mechanism for picloram and 2,4-D by HS.[90,91] Van der Waals forces have also been claimed to be involved in the interactions of HS with polychlorobiphenyls,[92] thiocarbamates, carbothioates, acetanilides,[93] benzonitrile and DDT.[94]

2.1.5 Electron Donor-Acceptor Interaction (Charge –Transfer)

In this process charge transfer complexes are formed, electrostatic attraction takes place when electrons are transferred from an electron rich donor to an electron deficient acceptor. Charge transfer interactions take place only within short distances of separation between the interacting species.[95]

The presence of groups possessing an electron deficient acceptor (e.g. the quinone mphasiz) and electron- rich donor (nitrogen or activated aromatic rings) in HS and the existence of TOCs possessing the same ability, renders the interaction based on the formation of electron donor-acceptor or charge transfer systems between suitable TOC and HS moieties possible.[96]

Infra Red (IR) analysis has provided evidence[77,78] for the charge-transfer process between bipyridilium herbicides and humic substances. Electron Spin Resonance (ESR) studies have shown that electron deficient quinone–like structures in humic substances are able to remove electrons from electron rich herbicides.[96-98] It has also been shown that the lower the capacity of humic substances to form ionic and hydrogen bonds, the higher is their tendency to give rise to electron donor-acceptor systems in their interaction with s-triazines.[96] Suggestions have been made that phenylurea herbicides could be bound by their deactivating ring to activated sites of soil organic matter through charge transfer bonding.[99] This is in contrast with the well known electron donor nature of these compounds. Substituted ureas are in fact expected to act as electron donors from the nitrogen or oxygen atoms to electron acceptor sites on quinone or similar or similar units in humic acid molecules.

The importance of charge-transfer interactions in HA chemistry is its importance in understanding the conditions prevailing in soil and water systems.[95] The charge-transfer acceptor and donor properties of HA in aqueous solutions have been established by UV-Visible spectrophotometric studies involving interactions with donor dihydroxy benzene and acceptor p-benzoquinone at varying pH levels. In addition the capability of electron donation of HS to chloranil which is a known electron electron acceptor was confirmed[73,100] by direct measurement of binding constants using UV-Visible spectroscopy.

2.1.6 Covalent Binding

This mechanism involves the formation of covalent bonds which lead to stable, mostly irreversible incorporation of TOC's into HS, or their toxic degraded intermediates or products (e.g. anilines and phenols). The degradation is normally mediated by chemical, photochemical or enzymatic catalysts. Acylanilides, phenylcarbamates, phenylamide, phenylureas and analogous herbicides are known to be biodegraded in soil with the release of free chloroaniline residues. These are prevalently immobilized by chemical binding to the soil OM without the intervention of microbial activity.[101] The chemical attachment of chloroanilines to HS is postulated[102] to occur by two mechanisms involving carbonyl, quinone and carboxyl groups of HS and leading to hydrolyzable (probably anil, a Schiff base, and anilinquinone) and to non-hydrolyzable (probably hetrocyclic rings or ether) bound forms. In the case of ring-substituted anilines, the interaction with HS is through the amines.

Pesticides that do not originally contain aromatic amines may be bound to HS in a similar fashion if they can be microbially transformed to aromatic amines. This has been demonstrated for organophosphate insecticides such as parathion and methylparathion [23,25], dinitroaniline herbicides, and nitoaniline fungicides.[74,103] Recently[96-98] ESR spectroscopic studies looking at the binding mechanisms of herbicides suggest that homolytic cross-coupling reactions lead to the formation of strong covalent bonds between free radicals and highly reactive phenoxy and aryloxy radicals from the herbicide.

The average order of reactivity of HA to herbicides according to origin is: synthetic > peat > soil > coal > compost.[96] This is because synthetic SOM has the largest carboxyl content and the largest ratio of COOH to phenolic OH, whereas compost has the smallest. In addition, the reactivity of HA towards chlorophenoxy herbicides is inversely proportional to the carboxyl content and to the ratio of COOH to phenolic OH, of HA.[96,98] This is because the chlorine atoms on the phenoxy ring of chlorophenoxyl inteferes with the crosslinking to humic macromolecules.[96]

2.2 Mechanisms of Desorption

Desorption is defined as a change in the physio-chemical characteristics of the fluid phase surrounding the solid phase retaining the organic compound (pollutant). This is classically obtained by lowering the pollutant concentration in the solution previously brought in equilibrium with the solid phase. Theoretically, the adsorption-desorption process should be expressed by isotherm singularity. In many cases, however, the release isotherms do not coincide with the retention isotherms. In this cases the phenomenon of hysteresis or non-singularity is encountered. This means that not all retained molecules can be transferred back into the solution phase.[32,75,87,100]

Desorption isotherms differ from adsorption isotherms in two situations. The first corresponds to systems which are not at equilibrium because the desorption rate is smaller than the adsorption rate. The second situation occurs when the adsorbed molecules undergo some modification of their physio-chemical state, due to chemical and/or biochemical reactions with the solid phase.[75,87]

Irreversible retention of TOC's is not fully understood. Several mechanisms have been put forward to explain the formation and properties of bound residues, but they have not been completely verified. These are discussed as organic matter diffusion, site entrapment, chemical non-equilibrium, interaggregate dispersion, and micropore diffusion.

2.2.1 Organic Matter Diffusion

This is a movement of sorbed solutes over a concentration gradient established within the SOM matrix. The diffusion gradient in SOM matrix is established due to a difference in the diffusion path lengths. The slowly sorbing solutes are present in remote parts of the SOM matrix for which the diffusion path lengths are long. The rapidly sorbed solutes are present at the exterior, or exposed parts of the SOM[104]. Because of slow intra-SOM diffusion, a concentration gradient within the SOM is established during sorption and desorption. This usually occurs from the interactions between the solute and polymer chains, due to the similarity in hydropobicity.

It has been suggested[15,16] that organic matter diffusion occurs in small micro particles inside the large macroscopic sediment particles. This implies that the diffusional distances within SOM are short. Humic acids are thought to be smaller than SOM unities in soil and sediments and can therefore be expected to show shorter diffusional distances.

Research has proved that this mechanism is rate limiting in soils[105-108] , by showing that the desorption rate constants $K_{d\ slow}$ are higher for humic acids than in soils, this due to the relatively low diffusional distances within humic acids. The high K_d, slow desorption indicates that distance through organic matter plays a role in non-equilibrium.

A study showed that addition of alkyl groups to benzene resulted in a higher degree of non-equilibrium in sediments and soils[106]. This was explained to be due to the entrapment of these bulky groups between the organic matter groups. In the same study, calcium ions were observed to show a much lower extent of non-equilibrium than HOCs. According to the authors, this effect can only be explained by internal organic matter diffusion, because their pore diffusion model predicted a much lower $K_{d\ slow}$ value as expected based on the log K_p - log $K_{d\ slow}$ correlation obtained for HOCs. However protonated quinoline (at low pH) had a much larger $K_{d\ slow}$. This could only be explained by internal organic matter diffusion and not by retarded pore diffusion.

2.2.2 Site Entrapment

This is an additional form of retention of pollutants in soils and occurs in the case of water immiscible fluid compounds or of pollutants adsorbed on suspended particles. The water-immiscible fluids hinder each other's transport in the soil pore space until a maximum degree of saturation is reached. However, it is also possible that soil pore geometry permits the flow of the nonwetting fluid at a level greater than saturation, leaving behind an enclave of water immiscible liquid. The trapped immiscible liquids will remain in the unsaturated zone for an indefinite time, serving as a source of contamination. This will decrease in magnitude as a result of abiotic processes such as volatilization or dissolution in the water phase.[32,100]

Various research groups have their own versions of this mechanism. One proposal was that these pores are similar to the voids that are present in the glassy polymers.[109] The analogy was that in these internal pores slow desorption could take place. A molecular mechanics study[10] showed that it is probably energetically beneficial to accommodate a solute molecule in an SOM void, because of favourable interactions between the hydrophobic solute and the hydrophobic wall structures of a void in rigid SOM. The release of the chemical from the void is then slow because the favourable interactions have to be disrupted before it can be released. Another possibility is that slowly desorbing chemical is sorbed in voids in rigid parts of the SOM. However the actual rate limitation in its desorption is not the release from the void, but the subsequent diffusion from the void to the sediment-water interface, or to the exterior rigid parts of the SOM.

2.2.3 Chemical Non-Equilibrium

Chemical non-equilibrium is defined as the retardation a toxic organic chemical-SOM system experiences due to specific chemical interactions between the toxic organic chemical and the SOM surfaces.[100] These interactions may involve slowly reversible or irreversible chemical bonding, resulting in prolonged equilibration times. The specific interactions involved in this mechanism are only expected for solutes possessing some reactive functional groups in combination with reactive groups on the surface or in the

inside of the SOM i.e. the sorbent. An example is the adsorptive bonding of salicylate to small aluminum hydroxide particles.[8] Chemical non-equilibrium can be ruled out beforehand as being the general mechanism of HOC non-equilibrium phenomena, because the specific and electrostatic interactions involved are not expected for most non-reactive HOCs, merely for polar and ionic substances, like metal ions or organics with polar or reactive functional groups.

Experimental confirmation was given by the fact that the clay mineral montmorillonite (with a high surface area and a lot of active surface groups) shows hardly any slow desorption of tetrachloroethane (TCE).[110] In some non-general cases involving reactive sorbates chemical non-equilibrium can be the mechanism of slow desorption, like that proposed for salisylic acid on silica.[111]

2.2.4 Interaggregate Dispersion

Interaggregate dispersion is defined as the dispersion of solutes through the macropores of SOM between the different particles of SOM. It occurs as a result of the differences in flow pathways within the SOM macromolecular structure.[105] It affects both sorbing and non-sorbing solutes, whereas in intra-aggregate porosity only sorbing solutes that encounter a net extra retardation relative to water are affected.

Intra-aggregate flow takes place on a relatively short time scale because of the turbidity of the water flow. Inter-aggregate non-equilibrium can be ruled out as a possibility of solute dispersion through the macropores because the residence time for dispersion in the turbid water flow is much lower than that in the immobile intra-aggregate regions of SOM.[75]

2.2.5 Micropore diffusion

Micropore diffusion is diffusion of toxic organic chemicals to SOM, in the stagnant aqueous regions of SOM (the intra-aggregate structure) where advection of water is negligible. In this mechanism the slowly desorbing toxic organic chemical is present in micropores only slightly wider than the diameter of the solute. Slow diffusion along the pore walls becomes a transport limiting factor.[86] Diffusional limitations in the water of the micropores include entrapment in dead-end pores or sterical hindrance in micropores as a result of the pores being restricted and tortous,(i.e. cul-de-sac's having one opening into the continuous interconnecting passages through the solid while the other end is blocked.)

Also, part of the toxic organic chemical may be retarded by sorption onto the solids, or immobile in solution as lipid units such as fat globules or lipoidal organelles. In addition to the steric effect of narrow pores, the ratio (pore wall surface / pore volume) increases with decreasing pore diameter. This results in enhanced retardation by pore wall sorption, since the walls are made hydrophobic due to SOM coatings.[110] The aqueous phase in combination with the SOM sorption effects can also affect the transport of toxic organic chemicals. This occurs on a microscale for interactions with the hydrophobic pore walls.[70] Especially in combination with high tortuosity of porus structures and steric hinderance in micropores[111], adsorption to pore walls may delay desorption. In this mechanism, the slowly desorbing solute is supposed to be present in micropores only slighter wider than solute diameters.

CHAPTER 3

EXPERIMENTAL

3.1 Experimental Procedures

3.1.1 Materials

Model soil organic matter sorbent Pahokee peat obtained from the International Humic Substances Society consisted of 83% organic matter (OM). Elemental analysis on a dry weight basis showed that the sample was made up of 3.3% nitrogen, 4.3% hydrogen, and 0.5-1.2% sulfur. Final moisture content of the peat samples was between 2-3% (w/w) this was determined by oven drying at 105°C. All the solvents used in the study were of analytical grade; chromatographic grade pyridine from Fluka (Buchs, Switzerland), n-hexadecane from Aldrich, acetonitrile, dimethylsulfoxide, ethanol, dioxane, hexane and acetone from Bio-Lab. The mininert valves, glass vials, and micro-pore filters were all from Supelco.

3.1.2 Determination of Humic Material Released into Organic Media

3.1.2.1 Degree of Humification

This study focused on the sorption of pyridine by soil organic matter (SOM). Any significant release of humic material from the peat organic matter into the solvent media would not allow reflection of the true interaction between pyridine and SOM. It was therefore important to investigate the release of these substances into the solvent. Dissolution of humic substances into aqueous media is well documented, and the soluble fraction is obtained as a dark coloured brown solution. So far researchers have concentrated on the sorption of organic compounds from aqueous media by different soils, and in many cases not on highly rich organic matter sorbents. These studies have shown that many other constituents of the soil composition contribute to the sorption of organic compounds, hence a comparison cannot be drawn between the studies involving

organic matter rich sorbents. The dissolution of organic material into n-hexadecane has been reported to be negligible[111]. One of the prerequisites of this study was therefore to determine the release of organic material into acetonitrile, and acetone since these solvents were used as co-solvents in this study. The reason was to find out if acetone and acetonitrile were acceptable solvents for sorption experiments with regards to dissolution of organic matter into organic solvents. The dissolution of peat components into aqueous solvent and double deionised water (DDW) was also determined. This was to check in which media was the release of peat humic materials the greatest, into organic solvents or aqueous media.[107] To determine the degree of humification, the E4/E6 ratios were determined by measuring absorbance of organic carbon at two different wavelengths namely 465 and 665 nm. This is because the absorption of radiation in the UV-Visible range by organic carbon is at a maximum at these two wavelengths. The instrument used was a HACH DR 2000 Direct Reading spectrophotometer. This is a qualitative measurement of the peat organic matter released into the solvents. Quantification of the organic matter released into a solvent is obtained by determining the total organic carbon (TOC) content.

The degree of humification involved measuring 1.5 g of fresh peat extract accurately weighed into three 25 ml screw cap vials. To these 15 ml of deionised water, acetonitrile, and acetone were pipetted into each container. Triplicate samples for each solvent-peat system were prepared. The vials were shaken horizontally using a Barnstead Thermolyne Labquake Shaker for 24 hours set at 25 $\pm 1^{\circ}C$. The acetonitrile and acetone treatment was allowed to continue shaking for a period of 3.5 months, this was done so as to show the effect of microbial degradation in the peat-aqueous extracts as opposed to no anticipated microbial degradation for the organic media. Should there be microbial degradation the solvent would appear as a dark brown solution having a maximum UV absorbance at 465, 620, and 665 nm. The shaking of the vials containing the aqueous extract was stopped after 24 hours. The vials were centrifuged using a Kubota Centrifuge KS-5200 C for 15 minutes. A 2.5 ml volume was then pipetted out for the degree of humification anaylsis. All the extracts were filtered through 0.45μm Teflon filters. Reference solutions comprising double deionised water (DDW), 10% acetone in DDW, and 10% acetonitrile

in DDW were prepared for the determination of the interference caused by the carbon structure of the organic solvents at the the chosen wavelengths. The pH of the aqueous extracts was between 7 and 8 which is the recommended range for the determination of the degree of humification[107]. The extracts from acetonitrile and acetone solutions needed pH adjustment, this was done by drop wise addition of 0.05 M sodium hydrogen carbonate ($NaHCO_3$, Bio-Lab 99%+).[107] The absorbance readings were recorded in triplicate at 15 second intervals so as to obtain the most stable reading. The degree of humification was then calculated by taking ratio of the absorbances at 465 nm and 665 nm.

To confirm the results obtained for the degree of humification, the same extract samples were used to determine the organic matter. Two methods exist for quantifying the amount of organic matter in solvents. These can be expressed as Chemical Oxygen Demand (COD) or as Total Organic Carbon. Due to the environmental protection legislation the analytical method involved in determining the Chemical Oxygen Demand is not favoured. This is because the COD determination takes into account all chemical species capable of being oxidized, whereas the Total Organic Carbon gives a more accurate indication of the carbon containing species in solution. Hence the Total Organic Carbon method is mostly used and as such was selected for this study. The Total Organic Carbon analysis of the extracts was done using a Lumitron TOC Analyser (Formacs). The aqueous extract was diluted twice while the samples from the acetonitrile and acetone extract were diluted five times before being analysed. All these analyses were carried out in triplicate.

3.1.3 Preparation of Solvents

3.1.3.1 Determination of The Solubility of Solvents In One Another

According to the literature survey there is no mention of an organic co-solvent such as acetone and acetonitrile having been used to study the sorption or desorption of organic compounds by SOM. It was thus important to determine the solubility of acetonitrile and acetone in hexadecane, and also the solubility of hexadecane in acetone and acetonitrile,

so that the solutions of pyridine in acetonitrile/acetone – hexadecane mixtures, represent these solvents at their unit activity. An activity of one therefore represents the maximum solubility in volume percentage for the solvent combinations. Hexadecane was chosen as the solvent medium since it is inert to SOM[111], and the dissolution of SOM in hexadecane is negligible. The solubility of acetone in acetonitrile and vice versa was not needed since this solvent combination was not used in this study. Hexadecane thus provided the ideal nonaqueous inert medium in which to study the sorption of pyridine and organic co-solvent interactions with SOM. This was achieved by using the Macro Technique flask method[112] at 25°C. The procedure involved pipetting 2 mls of acetonitrile (HPLC grade, Bio-Lab, 99.999%) into a 4 ml Teflon screw cap vial, to which 2 mls of hexadecane was added. The samples were left to equilibrate in a Velp Scientifica Fridgotheimostato set at 25°C). A homogeneous mixture was maintained by shaking the samples for 24 hours using a Barnstead – Thermolyne Labquake Shaker. The same procedure was followed for the other two solvent combinations namely acetone in hexadecane and hexadecane in acetonitrile/acetone mixture. Acetonitrile having the higher density constituted the bottom phase in all its combinations with hexadecane. Therefore 1 ml of the top phase was pipetted out to determine the solubility of acetonitrile in hexadecane. However, for the determination of hexadecane in acetonitrile, the top phase or hexadecane rich phase was completely removed using a Pasteur pipette, thereafter 1 ml was pipetted out. In the case of acetone-hexadecane mixture, acetone formed the bottom phase for these mixture combinations. The 1 ml aliquots were diluted ten times with hexadecane for the determination of acetonitrile or acetone solubility in hexadecane. A ten times dilution was also used for the determination of hexadecane solubility in acetone or acetonitrile before analysis was carried out. Triplicate 1 µl. injections of each sample were made using a Varian 8200 autosampler connected to a gas chromatograph (Varian CP3800) fitted with a flame ionization detector. The solubility was determined in volume percent, measured against a set of external standards for the specific solvent combinations.

3.1.3.2 Determination of Ostwald Coefficients

According to the literature most of the studies involving sorption of organic compounds to soil organic matter rich sorbents express the final solution concentration of the sorption or desorption systems as milligram of organic compound per liter of solvent (mg/L). Expressing the final organic compound solution concentration in this way excludes the effect of differential solute interactions in the solvent[12,72]. To account for these differential solute interaction effects, the final solution concentration should be expressed on an activity basis. The log Ostwald coefficient (L) is defined as the ratio between solute concentration in the solution phase to the solute concentration in the gas phase. No literature data exists for Ostwald coefficients of pyridine in acetonitrile and acetone, therefore these values were determined using headspace analysis according to the previously published method[113], at solute concentrations not exceeding 1% v/v. Acetonitrile in n-hexadecane was measured at 25°C using the GC-Headspace technique using a Varian Gas Chromatograph CP3800 series with an 8200 series autosampler. This was done for the 0.1 – 0.8% volume by volume (v/v) concentration range. A 0.8% v/v solution of acetonitrile in hexadecane was prepared and serial diluted down to 0.6, 0.3, and 0.1%. 0.5 mls of each solution was pipetted into a 4 ml GC vial and closed with a Teflon septum cap. This ensured that a sufficient headspace was allowed to form above the solution in each vial. This also ensured that the needle of the gas tight syringe from the autosampler was able to penetrate the septum and enter the vial without touching the solution itself, while removing a sample of the equilibrium vapour. The log Ostwald coefficient obtained was compared to that obtained by Abraham et. al.[113] for the experimental solubility of acetonitrile in n-hexadecane. The solubility was calculated using the experimentally determined Ostwald coefficient and compared to the calculated value obtained using the Abraham et. al. Log Ostwald coefficient. For the pyridine in hexadecane solutions a log Ostwald coefficient of 3.02 was used.[114] This was after the Ostwald coefficient was found to be constant when 0.5% v/v acetonitrile was added and when the pyridine concentration was increased from 50 mg/L to 500 mg/L. Since there was no significant change in the value of the Ostwald coefficient, this meant that no correction for concentration dependence of the Ostwald coefficient was needed for

pyridine in n-hexadecane. The Ostwald coefficient value 3.02 was used for pyridine in different acetonitrile-n-hexadecane mixtures. The linearity of the GC method was determined by the correlation obtained between the peak areas and the solution concentrations.

3.1.4 Sorption Kinetics and Equilibrium Studies

Kinetic studies had to be done to determine how much time would be required before pyridine in acetone/acetonitrile, and the combination systems (pyridine-acetonitrile-hexadecane, pyridine-acetone-hexadecane) would reach equilibrium due to the sorption by peat. The kinetic study for the pyridine in acetone system was followed using a 2100 mg/L solution. One gram of peat was accurately weighed into a 5 ml glass vial. Three millilitres of 2100 mg/L pyridine in acetone solution was pipetted into the vial closed by a Teflon Mininert valve (see Fig. 3.1). This procedure was followed to prepare peat suspensions for the following concentrations of pyridine in acetone in triplicate; 5600, 4900, 3840, 3233.33, 2600, 2100, 938.69, 400, and 68mg/L.

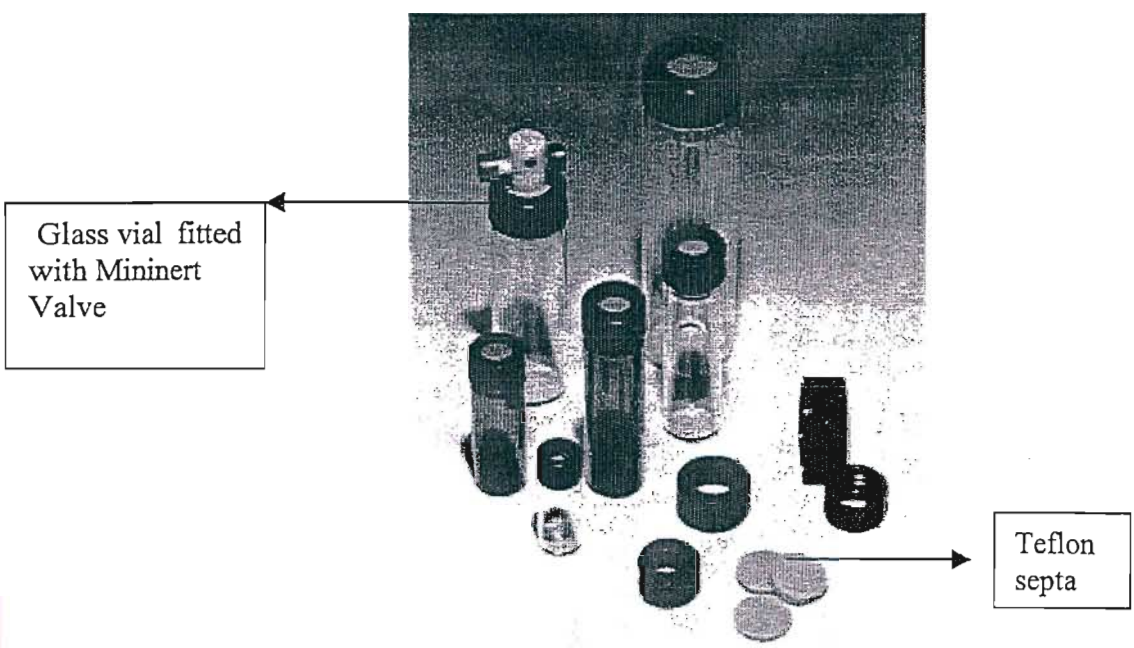


Fig. 3.1 Vials, septa, and Mininert valves used.

For each solution concentration two vials containing the solution only were monitored. This was used as control solutions to monitor any losses during the experiment for each

solution concentration. The vials were shaken continuously at 25°C. Sorption kinetics were tested for the 2100 mg/L system only. The remaining vials representing the equilibrium system were allowed to mix continuously and were stopped only when the 2100 mg/L kinetic system had reached equilibrium which was after approximately 1000 hours. The vials were centrifuged to ensure that all particulate matter was collected at the bottom of the vial, leaving a clear liquid phase. The mininert valve was then set to the open position and 1µl of sample was withdrawn using a 1µl syringe. The syringe was flushed three times after which 1µl was withdrawn and injected into the optimised GC.

A temperature program was used to separate pyridine and acetone. The final concentrations of pyridine in acetone at equilibrium were measured against a set of external standards and corrected for any losses calculated from the control solutions. The sorption at each solution concentration was done in duplicate.

Altogether sorption by peat was studied for six systems (Table 2.1), pyridine from acetone (I), pyridine from acetonitrile (II), pyridine from hexadecane (III), acetonitrile from hexadecane (IV), pyridine and acetonitrile from hexadecane (V), and pyridine from acetone-hexadecane mixtures (VI). Sorption isotherms expressed as sorbed amount (pyridine/acetonitrile) versus activity (pyridine/acetonitrile) were constructed from the sets of data obtained from the equilibrium studies for each peat-solvent system.

Table 3.1 Systems studied showing equilibrium time, solid-liquid ratio, solute range, and concentrations at which kinetics was followed.

Number	Solvent System	Maximum time allowed (hours)	Solid-Liquid ratio (g-mls)	Initial solute conc. Range [b]	Concentrations at which kinetics was followed	K_d Range (mL/g) [c]
I	Pyridine-Acetone	1000	1:3	68-5600 mg/L	2100 mg/L	0.3-3
II	Pyridine-Acetonitrile	940	1:10	50-7500 mg/L	230 mg/L	1.5-9
III	Pyridine-Hexadecane	900	1:30	27-207	-----	
IV	Acetonitrile-Hexadecane	2060	1:25	0.018-0.9 % v/v	0.14, 0.36, 0.72 (vol%)	10-50
V	Pyridine-Acetonitrile-Hexadecane	2300	1:30	58-600mg/L-pyridine 0.05-0.72% v/v –acetonitrile	58, 400, 600-pyridine (mg/L) 0.05, 0.2, 0.5-acetonitrile (vol%)	7-140 (pyridine) 10-70 (acetonitrile)
VI	Pyridine-Acetone-Hexadecane [a]	1600	1:6	100-600 mg/L	100, 600 (mg/L)	8-25

[a] Initial acetone concentrations were 5, 10, and 15 % v/v.
[b] Full concentration ranges are shown under the section Calibration Curves.
[c] Distribution coefficient is defined as ratio of sorbed concentration to solution concentration.

3.1.5 Desorption Kinetics and Extraction Studies

3.1.5.1 Desorption Kinetics

Desorption of pyridine and acetonitrile were studied to determine if the sorbed amounts of these compounds were bound reversibly or irreversibly to SOM and to further investigate the aspect of cooperative binding in SOM. The finite sink method was used to study the desorption kinetics.[8] In the finite sink method the vials at the end of the sorption studies upon attaining sorption equilibrium, are centrifuged, weighed and the masses of the vials recorded.

When equilibrium was reached for the pyridine in hexadecane system, the hexadecane solvent was removed. This was done using a Pasteur pipette, as much of the solvent as possible was removed without disturbing the settled peat. The vials were reweighed, the

difference in the masses of the vials containing only the dry peat, and the vials after the solvent removal, indicated the mass of hexadecane containing pyridine at equilibrium concentrations entrapped in the solid phase. This volume was taken into account when calculating the sorbed amounts of pyridine onto the peat phase. Three millilitres of fresh hexadecane solvent was then pipetted into the vials to follow the concentration of pyridine extracted. This was the second extraction step using hexadecane. This procedure was repeated for the pyridine and acetonitrile in hexadecane system, and acetonitrile in hexadecane system.

In the pyridine-acetone in hexadecane mixtures, the second extraction step replacement solvent ontained the initial acetone (5, 10, and 15% by volume) in hexadecane concentrations. In this part of the study only desorption of pyridine was checked due to the erratic behaviour of the acetone during the chromatographic determination of the final acetone equilibrium concentrations during the sorption studies. The vials were then shaken continuously at 25°C. After 24 hours the vials were centrifuged, thereafter 1µl sample volumes were withdrawn using a 1µl syringe. The syringe was flushed three times before injecting the sample into the GC. The equilibrium solution concentrations for the samples of pyridine in hexadecane system were measured against a set of pyridine in hexadecane standards. The results indicated that desorption equilibrium was reached after 200 hours in all the pyridine in hexadecane systems.

3.1.5.2 Solvent Extraction

After reaching the desorption equilibrium, it was noted that not all the sorbed pyridine and acetonitrile were recovered after two 3 ml washings with hexadecane solvent only. This was evident from the difference between the sorbed amounts calculated after sorption equilibrium had been reached compared to the amount recovered after the desorption equilibrium had been reached. A significant sorbed amount of pyridine and acetonitrile was still bound to the peat for all the systems that were to be investigated. Solvent extraction was thus employed to recover the remaining sorbed fractions.

Extraction solvents used were dioxane, ethanol, and dimethylsulfoxide (DMSO) used in that order so as to gradually change the polarity of the peat phase through the extraction process. Dioxane being the least polar and DMSO the most polar of the three extracting solvents. After the solvent systems (III-VI, Table 3.1) reached desorption equilibrium the vials were weighed and the masses recorded. A Pasteur pipette was then used to carefully remove as much of the hexadecane solvent as possible without disrupting the solid phase. The vials were reweighed and the masses recorded, these vials still contained a small volume of the hexadecane solvent with pyridine and acetonitrile at the desorption equilibrium concentrations. Then 3 ml of dioxane was pipetted into each of the vials and the masses recorded. The vials were then shaken continuously at 25°C for 72 hours and then centrifuged. Thereafter 1µl sample volumes were withdrawn as in the previous cases and analysed using a GC. The equilibrium concentrations for the samples of the pyridine in dioxane system were measured using the external standard method. The same procedure was followed to determine the extractable amounts of pyridine and acetonitrile in all the other systems. The exception was the pyridine-acetone-hexadecane system where only extractable pyridine was determined. The shaking time allowed for DMSO extraction was 144 hours. This procedue was repeated with ethanol and DMSO as the extracting solvents. DMSO is capable of significantly disrupting humic materials[71], thus any sorbed pyridine and acetonitrile still bound to the peat phase after solvent extraction with dioxane and ethanol, should be released into the solution phase. It was also mentioned[71] in the literature that the disrupted components of humic materials in solution after treatment with DMSO may interfere with the GC analysis of pyridine and acetonitrile. In this study no interference was observed. Fig.3.16 shows a chromatogram for the extraction of pyridine with dioxane. Pyridine elutes at 4.098 minutes. The large off-scale peak is dioxane (3.857 minutes), while the other smaller peaks are extractable material from peat sorbent.

3.1.6 Data Analysis

3.1.6.1 Solvent Sorption and Its Effect on Calculation of Sorbate Distribution Coefficients.

Sorption was determined by change in solution phase concentration and is given on a dry weight basis. Because a change in solution concentration may result from sorption of either or both the solute and solvent, it may be important to account for sorption of the different solvents and solvent mixtures when computing sorbate distribution coefficient (K_d). It can be shown that the measured K_d (in mL/g) of a sorbate differs from the true K_d by the value of solvent sorption (in mL/g of sorbent)[115]. This correction will account for any masking effect of solvent sorption on K_d. The need to apply such a correction is as follows:

(a) Volumetric swelling of peat samples demonstrated a significant size-exclusion effect in solvents with molar volumes greater than 93 cm^3/mol,[116] such that n-hexadecane solubility in peat is not expected to exceed solubility of *n*-hexane in peat. Using *n*-hexane solubility of 0.046 mL/g in dry peat[117], the maximum masking effect of *n*-hexadecane sorption on sorbate K_d would be less than 5% for a measured K_d of 1 mL/g, and negligible for K_d values above unity (Systems III, IV-VI, Table 3.1). This is because the Kd values obtained for these systems were all much greater than 1mL/g.

(b) The sorption isotherm of acetonitrile on peat was determined from *n*-hexadecane (System IV). It was expected that sorption of acetonitrile would be the same from both neat acetonitrile and acetonitrile-saturated with *n*-hexadecane. This is because acetonitrile saturated with *n*-hexadecane corresponds to unit acetonitrile activity. From the Freundlich model fitting to the sorption isotherm in Fig. 4.4 ($S=0.086a^{0.59}$). S represents the mL/g of acetonitrile taken up by peat at its solubility point in *n*-hexadecane. This is 0.086 ± 0.005 mL/g. This indicates that the maximum masking effect due to acetonitrile

This indicates that the maximum masking effect due to acetonitrile sorption on pyridine K_d would thus be around 9% for a measured pyridine K_d value of unity. This would then be negligible in Systems II and V (Table 3.1) because the K_d values obtained were greater than 1 mL/g.

(c) Acetone sorption could not be accurately determined, but an approximate level is estimated to be 0.1 mL/g[118] at around 20% of acetone solubility in *n*-hexadecane. This would result in a 25% underestimation of the actual K_d for pyridine when the measured K_d is 0.3 (System I, K_d varies from 0.3 to 3; Table 3.1) and as such is negligible for system VI (Table 3.1). This is because for an initial pyridine concentration of 5600 mg/L the measured Kd was around 3. For system VI the maximum initial pyridine concentration was 600 mg/L and the Kd was less than 1 mL/g, thus a 25% underestimation for a pyridine Kd less than 1mL/g would not affect the pyridine sorption trend.

The amount of pyridine and acetonitrile sorbed to peat after desorption equilibrium, and after each solvent extraction step was calculated using equation 3.1.

$$S_{AD} = \frac{[(S_{AS} \times M_S) + (E_{FAS} \times V_{RS}) - E_{FAD} \times (V_S + V_{RS})]}{M_S} \qquad (3.1)$$

Where;

S_{AD} = Amount sorbed on peat after desorption/solvent extraction

S_{AS} = Amount sorbed on peat after sorption equilibrium

M_S = Mass of sample

E_{FAS} = Equilibrium concentration of solvent remaining after sorption/desorption/extraction

V_{RS} =Volume of solvent remaining after sorption(volume= mass/density)

E_{FAD} = Equilibrium concentration after desorption/extraction

V_S = Volume of solvent added for desorption/extraction

The distribution coefficient (K_d) for each kinetic system was calculated as follows:

$$K_d = \frac{\frac{V_S}{M_S} \; X \; \left[1 - \frac{C_{OBS})}{C_{INT.}}\right]}{\frac{C_{OBS}}{C_{INT}}} \qquad (3.2)$$

Where;

V_S = Volume of solution

M_S = Mass of peat

C_{OBS} = Observed solution concentration

C_{INT} = Initial solution concentration

Equation 3.3 was used to calculate the sorbed amount (S_{amt}) after sorption equilibrium:

$$S_{amt} = K_d \text{ x } C_{OBS} \qquad (3.3)$$

The sorbed volume would therefore calculated as :

$$S_{vol} = \frac{S_{amt}}{\text{Density of sorbate}} \qquad (3.4)$$

3.1.6.2 Activity Based Comparison of Pyridine Sorption Isotherms

Comparison of the sorption isotherms for pyridine in different media was done using pyridine activities obtained for the pure pyridine liquid state. Activity is defined as

$$a = \frac{C_e H}{C_{sat}^{vap}} \qquad (3.5)$$

where a is activity, C_e is pyridine equilibrium concentration in solution (mg/L), C_{sat}^{vap} is concentration of saturated pyridine vapor over pure pyridine liquid (reported valve is 87.7 mg/L, calculated from saturated vapor pressure[117]), and H is the dimensionless pyridine Henry's constant. A log Henry's constant for pyridine in *n*-hexadecane of –3.02[113] was

used for calculation of pyridine activities in *n*-hexadecane and *n*-hexadecane-acetonitrile mixtures. Henry's constants for pyridine in acetonitrile and acetone were determined by head space analysis according to the technique described in the literature.[119,120] The Henry's constants were found to be -4.21 and -4.26 respectively (log values), at solute concentrations not exceeding 1% v/v.

3.1.6.3 Volumetric swelling

Sorption data are presented on a dry peat weight basis. Sorption data could also be presented per volume of swollen sorbent. The volume of the swollen peat phase can be calculated from the sorbed amount of solvent (assuming volume additivity) and dry peat particle density (1.3 g/mL being the reported literature value).[121]

Expressing the dry peat density of 1.3 g/mL as volume gives a value of 0.769 ml/g (1/1.3 g/mL). To obtain the total volume the volume of acetone, acetonitrile, or hexadecane taken up by peat is added. From literature[121] it is reported that 0.1 ml/g of acetone or acetonitrile and 0.046 ml/g as a maximum for hexadecane is taken up by peat. This means that the swollen peat volume per gram for acetone or acetonitrile will be 0.869 ml (0.769 ml + 0.1 ml), and for hexadecane 0.815 ml. Normalization for pyridine sorption in the acetone/acetonitrile swollen peat phase is 1.15 or 15% (1/0.869), and for the hexadecane swollen phase is 1.23 (1/0.815) or 23%. However it is clear from Fig. 4.3 that normalization of pyridine sorption data per volume of the sorbed phase cannot account for the significant differences of pyridine uptake in the acetonitrile and hexadecane solvent systems. As such all the pyridine sorbed amounts in this study were related to the dry peat phase and no corrections to the data for peat swelling were made.

3.2 Analysis of E_4 / E_6 Ratios

3.2.1 Introduction

Humic substances yield uncharacteristic spectra in the UV and visible regions.[122] Absorption spectra of alkaline and neutral aqueous solutions of humic acids (HA's) and fulvic acids (FA's) and of acidic aqueous FA solutions are featureless. The optical

density usually decreases showing no maxima or minima as the wavelength increases.[9] The light absorption of humic substances appears to increase with increase in:

(a) the degree of condensation of aromatic rings that these substances contain.[122]

(b) the ratio of carbon in aromatic "nuclei" to carbon in aliphatic side chains.[123]

(c) total carbon content and the molecular weight.

The ratio of optical densities or absorbance's of dilute aqueous HA and FA solutions at 465 and 665 nm are widely used by soil scientists for the characterization of these materials. This ratio is usually referred to as E_4/E_6, and is independent of concentrations of humic materials, but vary for humic materials extracted from different soil types[9,112] Analytically, the determination of E_4/E_6 ratios of HA's and FA's [9] is a rapid and convenient procedure that does not require complex equipment and advanced technical skills. Nonetheless this method can provide potentially valuable information, such as the degree of condensation of the aromatic carbon network, about these type of materials. Since the method cannot quantify the total organic carbon, the total organic carbon analyser was chosen for the quantification of total organic carbon released.

3.2.2 Principles of UV-Visible Spectroscopy

The basic parts of any type of spectroscopic equipment are the radiation source, the sample container, the monochromator, the detector, and the detector output measuring instrument. In the simplest spectrometer, a single beam of light is taken from the source through the various optical components of the detector. A typical single beam spectrometer is shown in Fig. 3.2

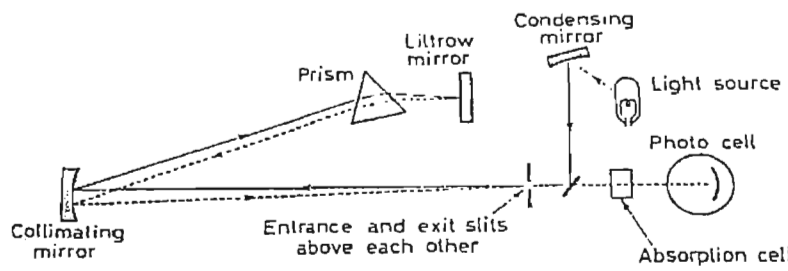


Fig. 3.2 Optical system in a simple photoelectric spectrophotometer.[124]

3.2.3 Experimental Results for UV-Visible Spectroscopy

A HACH DR 2000 Direct Reading Spectrophotometer was used to obtain the absorbance readings of the aqueous and non aqueous solutions at 465 and 665 nm.

Table 3.2 Absorbance readings for the aqueous peat extracts

Solution	Initial pH	Absorbance at initial pH		Adjusted pH	Absorbance at. Adjusted pH		E4:E6 ratio
		465nm	665nm		465nm	665nm	
Blank DDW	7.1	0	0				
Peat-Water ext.10X dil.	7.3	0.191	0.023				
		0.192	0.023				
		0.192	0.024				
Average		**0.19**	**0.02**				**8.21**

Table 3.3 Absorbance readings for the acetonitrile extracts

Solution	Initial pH	Absorbance at initial pH		Adjusted pH	Absorbance at adjusted pH		E4:E6 ratio
		465nm	665nm		465nm	665nm	
Blank 10%Acetonitrile	7.0	0	0				
Peat-Acetonitrile not dil.	5.85	0.012	0	7.58	0.027	0.009	
		0.012	0		0.027	0.009	
		0.013	0		0.027	0.009	
Average		0.012	0		**0.027**	**0.009**	**3.0**

Table 3.4 Absorbance readings for the acetone extracts.

Solution	Initial pH	Absorbance at initial pH		Adjusted pH	Absorbance at adjusted pH		E4:E6 ratio
		465nm	665nm		465nm	665nm	
Blank 10%Acetone	7.0	0	0				
Peat-Acetone not dil.	4.4	0.067	0.03	7.3	0.120	0.048	
		0.068	0.03		0.120	0.048	
		0.068	0.03		0.119	0.048	
Average		0.068	0.03		**0.12**	**0.048**	**2.49**

3.3 Analysis of Total Organic Carbon

3.3.1 Introduction

Total carbon (TC) is represented as the total mass of carbon per amount of sample made up of total organic carbon (TOC) and inorganic carbon (IC). TOC is a measure of the organic carbon that is converted into carbon dioxide after oxidation. Direct TOC measurement is done after acidification of the sample. TOC in water samples should ideally include carbon in volatile materials, although most laboratories report TOC samples where the volatiles have already been removed before analysis. The results are still generally accepted as TOC. inorganic carbon (IC) is the inorganic carbon in a sample that after acidification, turns into carbon dioxide. IC includes all carbonates, bicarbonate, and dissolved carbon dioxide. IC=TC - TOC

3.3.2 Principles of Total Organic Carbon Analyzer

TC and IC Analysis

The sample is injected by means of the integrated Auto Sampler into the high temperature reactor. In the reactor, at high temperature of 950°C using cobalt oxide catalyst or 680°C using a platinum catalyst, all organic and inorganic carbon is oxidized into the gaseous carbon dioxide. The catalyst present helps the oxidation to go to completion. A flow of air or oxygen transports the carbon dioxide to the infrared detector. The oxygen required for the reaction is taken from the airflow or in the case of nitrogen flow it is taken from the sample. The carbon dioxide is then measured at 4.2 μm.[125]

After the TC analysis a second injection of the sample is made into the low temperature liquid reactor. In an acid medium and at room temperature, all inorganic carbon is converted to the gaseous carbon dioxide, which is analysed like TC. The air /oxygen transports the carbon dioxide to the IR detector to be measured. In this way the concentration of the total organic carbon can be calculated by subtracting the result of the low temperature measurement(IC) from the high temperature(TC). TOC = TC - IC

Materials
Anhydrous Potassium Biphthalate,$C_8H_5KO_4$, 2.1254g.

Phosphoric acid 85%

3.3.3 Preparation of standards and calibration curves.

The stock solution was prepared by weighing 2.1254 g of anhydrous potassium biphthalate (Bio Lab 99%). This was dissolved in carbon free water and diluted to 800ml. The solution was then preserved by acidifying it with phosphoric acid and made up to 1000 ml using pH 2 acidified water, giving 1.00 ml = 1.0 mg carbon. The stock standard had a shelf life of 4 weeks at 4°C in a well closed bottle. The concentration of the working solutions that were prepared were 10, 20, 50, 100, and 250 mg/L. The results are shown in Table 3.5 and the graph in Figure 3.3.

The concentrations for peat aqueous extracts are shown in Table 3.6, the values reported are average values of two readings.

Table 3.5 Peak areas for TOC standards

Standard (mg/L)	Average peak areas
10	589472
20	901269
50	2085353
100	3853230
250	9179105

Table 3.6 Peak areas and observed concentrations for peat aqueous extracts.

Time	Average peak area	Concentration (mg/L)
Blank	8926210	245.4
12 hours	3798876	100.6
3.5 months	5923724	160.6

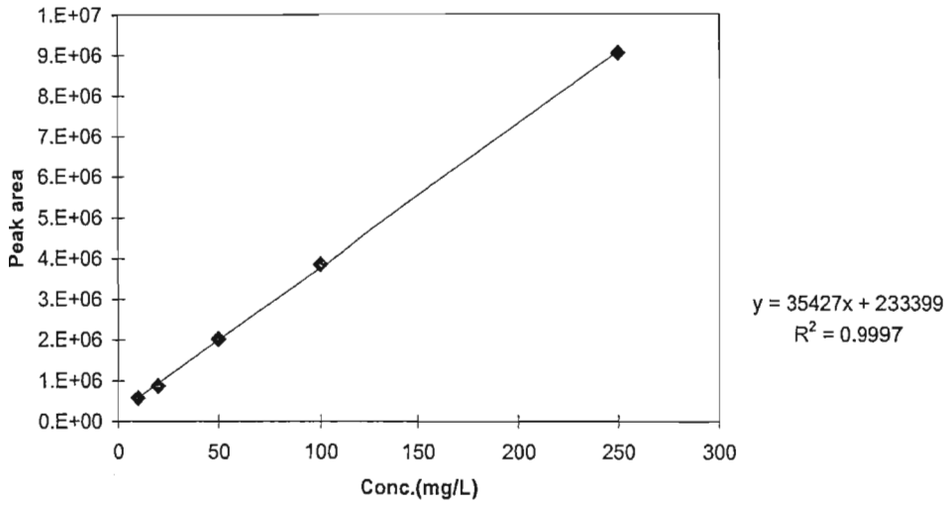


Fig. 3.3 Calibration curve for TOC.

3.4 Analysis of Activity Coefficients

3.4.1 Introduction

The gas chromatographic analysis of vapours which are in equilibrium with a liquid phase in a closed system requires a special experimental technique different from that used in ordinary gas analysis. Gas-liquid extraction is known by other names such as headspace analysis or vapour equilibrium analysis. This is a true equilibrium system whereby a known volume of an inert gas is equilibrated with a known volume of the sample solution.[126]

The instrumental parameters must maintain the sample container at a constant and reproducible temperature. This also applies to the handling of the specimen during its preparation and during the actual sampling from the headspace vessel, since condensation and fractionation of components can easily occur at this stage. This affects the integrity of the qualitative analysis and the accuracy of the quantitative determination.

The special advantage of this method is that it requires a small liquid sample of only 1ml. It is not necessary to wait for a state of equilibrium to be completely established, since partial pressure sampling method is employed. In this method the use of a reduced pressure enables a definite amount of material to be reproducibly removed from the headspace. A considerable amount of quantitative data can be obtained without causing significant changes in the concentrations in the liquid phase. This simple and ingenious technique makes the method particularly suitable for measurements of isothermal vapour-liquid equilibrium in multicomponent systems. Attention is paid to the following points when a headspace analysis vessel is selected :

(a) If a rubber septum is employed, the exposed surfaces must be as small as possible. This is to minimize effects due to dissolution and diffusion. In addition the internal surface of the septum can be covered with a metal foil.

(b) The volume of headspace should not be too large compared with that of the sample, since total evaporation into the gas phase of the component being determined for might take place.

3.4.2 Principles of Headspace Gas Chromatography

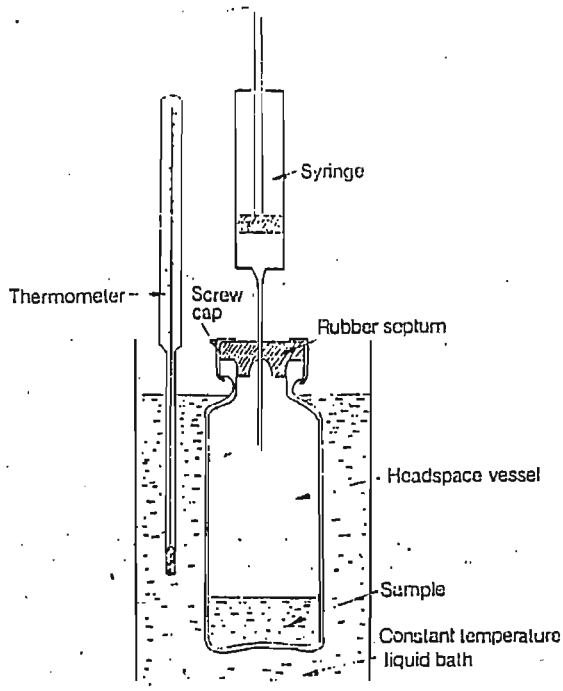


Fig. 3.4 Headspace analysis vessel.

This technique involves the equilibration of a known volume of a solution (mixture or pure) in a glass vial closed off with a rubber septum and cap. A gas tight syringe is then used to pierce the rubber septum and slowly withdraw a known volume of the vapour phase from the headspace above the liquid solution. This is then injected into the GC. This procedure is used to obtain the peak areas, obtained from the GC integrator, of the headspace above the pure solvent as well as the headspace of binary systems.[126]

The GC apparatus and specification are similar to that of automated injection mode (Table 3.12), the exception being the integrator software which is version 5.3. A typical GC chromatogram obtained for headspace analysis of acetonitrile in hexadecane is shown in Fig. 3.17. Acetonitrile elutes at 2.467 minutes.

3.4.2.1 Data Analysis

The distribution coefficient (Kd) and the Ostwald coefficient for the headspace analysis was calculated as follows:

$$K_d = \frac{\text{(Average peak area liquid phase) X (Split flow ratio)}}{\text{(Average peak area gas phase)}}$$

$$\text{Split flow ratio} = \frac{\text{(Volume gas sample) / (split flow gas)}}{\text{(Volume liquid sample) / (split flow liquid)}}$$

3.4.3 Experimental Conditions

3.4.3.1 Acetonitrile in Hexadecane and Pyridine in Acetonitrile/Acetone – Hexadecane Mixture

GC Varian CP 3800 was used. The oven program was initially 40°C, held for 2 min, ramped at 50°C/min until final temperature of 280°C, and held for 1 min. Injector temperature 150°C held for 2 min, ramped at 150°C/min to the final temperature of 300°C and held for 1 minute. The detector temperature was 300°C and range was 12. The injection volume was 1 μL for liquid samples and 50 μL for gas samples.

3.4.4 Preparation of Solutions to Determine Ostwald Coefficients

The following solutions were prepared to determine the Ostwald Coefficients for acetonitrile in hexadecane, pyridine in hexadecane, and pyridine in acetone/acetonitrile-hexadecane.

3.4.4.1 Acetonitrile in Hexadecane

A 0.8% by volume solution of acetonitrile (Biolab-analytical grade) in hexadecane (Aldrich-analytical grade) was prepared. This solution was serial diluted with hexadecane to obtain solutions with concentrations of 0.6, 0.3, 0.1 % by volume acetonitrile in hexadecane. The values reported in Table 3.8 are an average of two readings. The

distribution coefficient is obtained by dividing the area for solution phase by that of the vapour or headspace phase. The Ostwald coefficient is then obtained as the Log of the distribution coefficient The Ostwald coefficient is then substituted into equation 3.4 to determine the activity of acetonitrile for this mixture, and in the case of the pyridine mixtures, the activity of pyridine. The calibration graph for acetonitrile in hexadecane in solution phase is shown as Fig. 3.5. The linearity of the method is shown in Fig. 3.6 using the vapour phase concentrations in the headspace over the acetonitrile – hexadecane solutions. Split flow used was 50 ml/min liquid samples and 1 ml/min gas samples.

Table 3.8 Determination of Ostwald Coefficients for Acetonitrile in Hexadecane.

Solution – volume % acetonitrile in hexadecane	Peak area solution phase	Peak area headspace	Distribution coefficient (K_d)	Ostwald Coefficient (Log K_d)
0.1	3542	82	42.9	1.63
0.3	10693	245	43.6	1.64
0.6	18620	423	44.01	1.64
0.8	21945	509	43.1	1.63

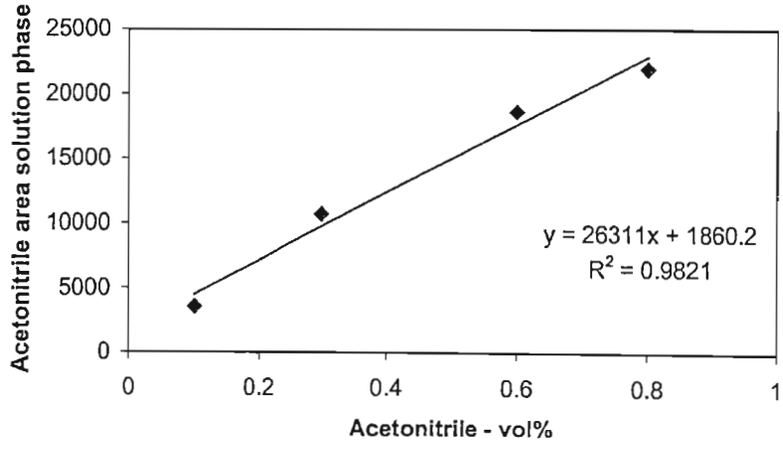


Fig. 3.5 Acetonitrile in Hexadecane calibration graph

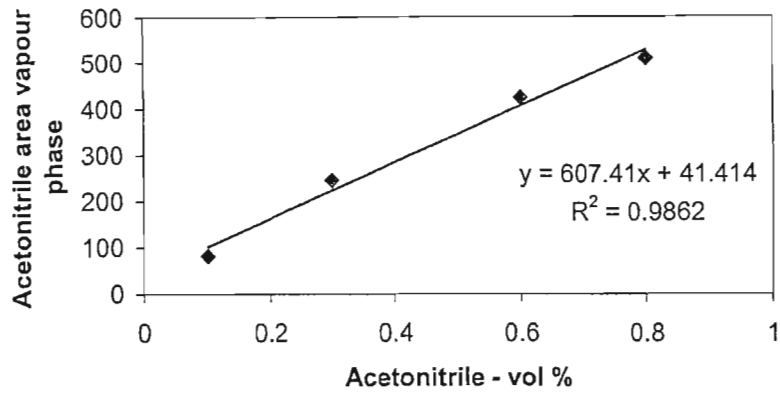


Fig. 3.6 Linearity of Headspace analysis method

3.4.4.2 Pyridine in Hexadecane With additions of Acetone

All the solutions were made separately, no serial dilution was employed. A 6000 ppm pyridine solution containing 15 % acetone (Biolab, analytical grade) was required . The acetone concentration was 15 % by volume. To achieve this 0.15 ml of pyridine was pipetted into a 25 ml flask, containing the 15 % by volume acetone and made up to the mark with hexadecane. Similarly the following pyridine in hexadecane solutions with acetone additions were prepared, 6000 ppm pyridine-10 % acetone, 6000 ppm pyridine-15 % acetone, 50 ppm pyridine-5 % acetone, 50 ppm pyridine-10 % acetone, and 50 ppm pyridine-15 % acetone. The intention of this part of the study was to determine what effect the various acetone concentrations would have on the Ostwald Coefficient for pyridine. Should there be a significant difference in the Ostwald coefficient for the different solution concentrations, then the activities for pyridine according to equation 3.4 would be dependent on solute and co-solvent concentration, and this would need to considered when constructing the isotherms. Split flow used was 50 ml/min liquid samples and 1 ml/min gas samples. The data presented in table 3.9 indicate that the Ostwald Coefficient was constant over the concentration range for pyridine and acetone additions and as such is independent of the solute and co-solvent concentrations.

Table 3.9 Determination of Ostwald Coefficient for Pyridine in hexadecane with acetone additions.

Solution	Peak area solution phase	Peak area headspace	Distribution coefficient (K_d)	Ostwald Coefficient (Log K_d)
50 ppm pyridine-5 % acetone in hexadecane	1784	0.11	16218	4.21
50 ppm pyridine-10 % acetone in hexadecane	1239	0.08	15488	4.19
50 ppm pyridine-15 % acetone in hexadecane	830	0.05	16596	4.22
6000 ppm pyridine-5 % acetone in hexadecane	38379	2.26	16982	4.23
6000 ppm pyridine-10 % acetone in hexadecane	30047	1.94	15488	4.19
6000 ppm pyridine-15 % acetone in hexadecane	23460	1.35	17378	4.24

3.4.4.3 Pyridine in Hexadecane

Three working solutions were prepared. A 500 ppm pyridine (Sigma chemicals – analytical grade) in hexadecane, this was diluted with hexadecane to obtain a 50 ppm solution of pyridine in hexadecane. The third solution prepared was a pyridine-acetonitrile hexadecane mixture comprising of 500 ppm pyridine and 0.5% acetonitrile in hexadecane. This was done to study the effect on the Ostwald coefficient for pyridine in hexadecane in the presence of a large amount of acetonitrile, and at the same time increasing the pyridine concentration ten fold from 50 ppm to 500 ppm. Split flow used was 14.76 ml/min liquid samples and 2.38 ml/min gas samples The data are presented in table 3.10.

Table 3.10 Determination of Ostwald Coefficient for Pyridine in hexadecane with acetonitrile addition

Solution	Peak area solution phase	Peak area headspace	Distribution coefficient (K_d)	Ostwald Coefficient (Log K_d)
50 ppm pyridine in hexadecane	28	4.21	2062	3.31
500 ppm pyridine in hexadecane	306	44.7	2118.	3.33
500 ppm pyridine-0.5 % acetonitrile in hexadecane	298	45.7	2021	3.31

3.4.4.4 Pyridine in Acetonitrile

A 6000 ppm pyridine in acetonitrile solution was prepared. The volume of pyridine used to make a 6000 ppm solution in a 25 ml volumetric flask was 0.15 ml. The 6000 ppm solution was then serially diluted with acetonitrile to obtain solutions of 500 ppm and 50 ppm pyridine in acetonitrile. Split flow used was 50 ml/min liquid samples and 1 ml/min gas samples The injection volume was 1 μL for liquid samples and 50 μL for gas samples.The data are presented in table 3.11

Table 3.11 Determination of Ostwald Coefficient for pyridine in acetonitrile.

Solution	Area solution phase	Area headspace	Distribution coefficient (K_d)	Ostwald Coefficient (Log K_d)
50 ppm pyridine in acetonitrile	931	0.05	18621	4.27
500 ppm pyridine in acetonitrile	3275	0.18	18197	4.26
6000 ppm pyridine in acetonitrile	9826	0.54	18197	4.26

3.5 Analysis of Organic Compounds

3.5.1 Introduction

Gas chromatography (GC) is a very versatile technique and can be used for the direct separation and analysis of gaseous samples, liquid solutions, and volatile solids. In addition to analysis, GC may be used as a physical research technique to study the structure of chemical compounds, determine the mechanisms and kinetics of chemical reactions, and measure isotherms, heats of solutions, heats of adsorption, free energy of solution and/or adsorption, activity coefficients, and diffusion constants.[8,112,127]

GC can be applied to the solution of many problems in various fields. In the field of environmental studies GC has made the detection and measurement of pesticides and their residues relatively simple. One of the advantages of GC is it's analysis time. The separation of all the components in a sample may take from several seconds up to 30 minutes. The sensitivity and separating power of GC largely account for it's extensive use. The level of sensitivity is more impressive when one considers that the sample size used is of the order of 1μL or less. The costs compared with many analytical instruments available today represent GC as excellent value.[8]

3.5.2 Principle of Gas Chromatography

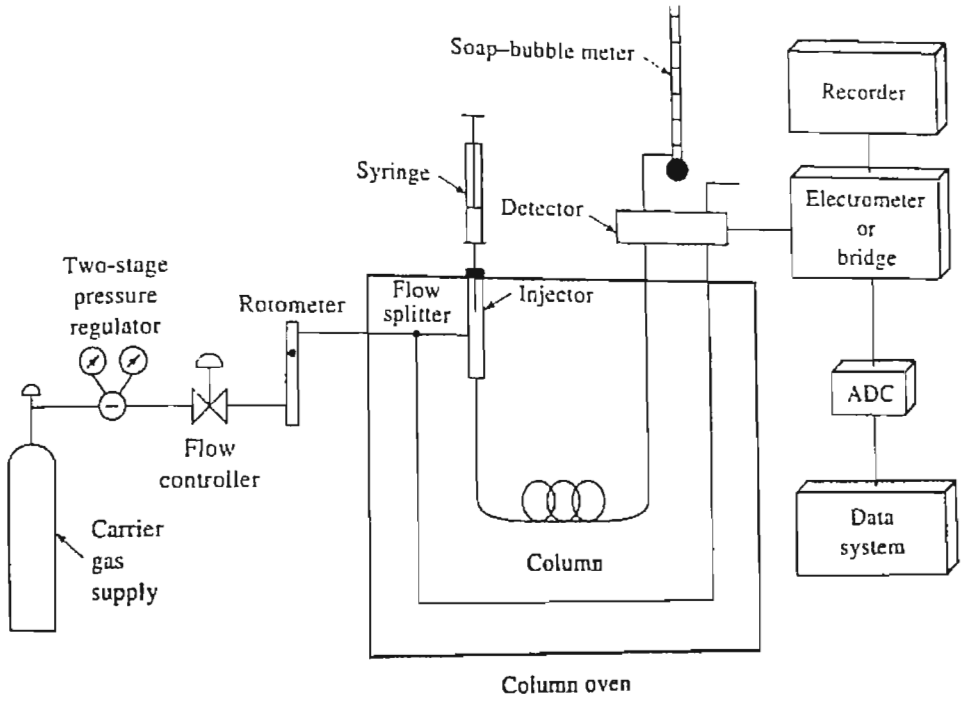


Fig. 3.7 Schematic of a Gas Chromatograph

The fundamental parts of a GC shown in Fig. 3.7 are, the carrier gas supply, the injector, the column, the detector, and finally the data system (integrator or software package). The sample is injected by means of a syringe, for multiple analyses and sample integrity, automated injection system is used. The injector is maintained at a high temperature, usually to ensure sample is vapourised into the column. An inert carrier gas serves as the medium to transport the sample through the column. The column is the heart of the GC, separation of the sample components take place. An equilibrium develops between the components and the packing material of the column. This ensures that components travel through the column at different rates. The components leave the column into a detector. Many types of detectors exist, the Flame Ionization Detector (FID) was used for this study. An electrical signal is generated and converted by the data system into a chromatogram. Figures 3.16 to 3.19 are typical GC chromatograms.

3.5.2.1 Carrier Gas Supply

These must be chemically inert, include helium, nitrogen, and hydrogen. The type of carrier gas is usually dictated by the type of detector used. Associated with the gas supply are pressure regulators, gauges, and flow meters. In addition, the carrier gas system often contains a molecular sieve to remove water or other impurities. Flow rates are normally controlled by a two-stage pressure regulator, inlet pressures normally range from 10 – 50 psi (above room pressure), which leads to flow rates of 25 to 150 mL/min with packed columns and 1 to 25 mL/min for open tublar capillary columns. Generally, it is assumed that flow rates will remain constant if the inlet pressure remains constant. Many modern commercial gas chromatographs are equipped with electronic flow meters that are computer controlled to maintain the flow rate at any desired level.[8]

3.5.2.2 Sample Injection System

The sample injection system is made up of a self-sealing, silicone-rubber diaphragm or septum and a flash vaporizer port located at the head of the column.The sample port is ordinarily held about 50°C above the boiling point of the least volatile component of the sample to prevent condensation and hence sample loss. The most common method of sample injection involves the use of a microsyringe to inject a liquid or gaseous sample through the septum For ordinary analytical columns, sample sizes vary from a few tenths of a microliter to 20 microliters. Capillary columns require much smaller samples ($\sim 10^{-3}$ μL); here, a sample splitter system is employed to deliver only a small fraction of the injected sample to the column head, with the remainder going to waste. Column efficiency requires that the sample be of a suitable size and be introduced as a "plug" of vapour; slow injection of oversized samples causes band spreading and poor resolution. For the purposes of this study automated injection was employed for the headspace analysis and manual injection for the rest of the study.[8]

3.5.2.3 Column Configurations and Column Ovens

Generally two types of columns are encountered in GC, packed and open tubular, or capillary. Most of the GC work in the past has been carried out on packed columns, however this situation is changing rapidly. Majority of the work is done on the more efficient and faster open tubular columns.

The lengths of the open tubular columns vary in length from less than 2 m to 50 m or more. They are constructed of stainless steel, glass fused silica, or Teflon. In order to fit into an oven for thermostating, they are usually formed as coils having diameters of 10 to 30 cm.

Column temperature is an important variable that must be controlled for precise work. The column is usually housed in a thermostatted oven. The optimum column temperature depends on the boiling point of the sample and the degree of separation required. A temperature equal to or slightly above the average boiling point of a sample results in a reasonable elution time (2 to 30 min). For samples with a broad boiling range, it is often desirable to employ temperature programming, whereby the column temperature is increased either continuously or in steps as the separation proceeds.

Optimum resolution is usually associated with minimal temperature; the cost of lowered temperature, however, is an increase in elution time and therefore the time required to complete an analysis[8]

3.5.2.4 Detection Systems

GC has many types of detectors such as the Flame Ionization Detector (FID), Thermal Conductivity Detector, Electron Capture Detector, which depend on sensitivity and low noise. For rare and small sample volumes the detector of choice should be non-destructive to the sample. For this study the Flame Ionization Detector (FID) was selected. This is the most widely used detector. The reason for choosing the FID detector is because the FID exhibits a high sensitivity, large linear range, and low noise. In addition, the detector is insensitive toward non-combustible gases such as water vapour, CO_2, SO_2, and nitrogen oxide gases. These properties make the FID a most useful general

the analysis of most organic samples, including those that are contaminated with water and oxides of nitrogen and sulfur. The insensitivity of the FID to water makes it particularly useful for the detection of pollutants in natural water samples. Functional groups, such as carbonyl, alcohol, halogen, and amine, yield fewer ions or none at all in a flame. A disadvantage of the FID is that it destroys the sample. Most organic compounds, when burned at the temperature of a hydrogen/air flame, produce ions and electrons that can conduct electricity through the flame. A potential of a few hundred volts is applied across the burner tip and a collector electrode located above the flame. The resulting current is then directed into a high-impedance amplifier for measurement. [8]

3.5.3 Experimental Conditions

Two types of GC's were used for this study, a Varian 3300 using manual injection, and a Varian CP 3800 with automated injection. The solvent systems (I-IV) listed in Table 3.1 were analyzed using the manual injection mode, whereas solvent systems (V-VI) were analyzed using the automated injection mode. Tables 3.12 and 3.13 gives a summary of the GC apparatus and the specifications of the equipment used.

Table 3.12 GC apparatus and specifications for the manual injection mode

Instrument	:	Varian 3300
Detector	:	FID
Detector Range : 10 for high range pyridine in acetone or acetonitrile, 11 and 12 for low range pyridine in hexadecane and pyridine in acetone and acetonitrile.		
Column (manual injection mode) : DB1[length30m,Id(0.53mm),film(1.5μm),temp.limits(-60to300 °C)]. Initial temp. 50°C, held 1.5 min., program 15°C/min to final temp. 120°C, held 0.5 min., program 40°C/min. to final temp. 250°C.		
Injection mode	:	Manual
Carrier gas	:	Nitrogen
Flame Gases	:	Hydrogen and Air
Integrator	:	D-2000 Merck integrator

Table 3.12 (b) GC apparatus and specifications for the automated injection mode

Instrument	:	Varian CP 3800
Detector	:	FID
Column (automated injection mode) : Rtx 50 [length 30 m, Id (0.25 mm), film (0.25 µm), temp. limits 60 to 350°C. Initial temp. 50°C, held 4.0 min., temp. program 30°C/min to final temp. 140°C. Conditions for headspace analysis see section 3.4.3.1.		
Injection mode	:	Automated
Carrier gas	:	Nitrogen
Flame Gases	:	Hydrogen and Air
Integrator	:	Star Chromatography version 5.0 software

3.5.4 Preparation of Standards and Calibration Graphs

This was done to determine the concentration of pyridine and acetonitrile at the sorption equilibrium as well as at the desorption equilibrium. The areas obtained from the GC were calculated as concentration, based on the linear regression equations obtained from the calibration graphs. The large number of samples and the different equilibration times required that more than one calibration graph was used. The entire concentration range chosen in the study for pyridine and acetonitrile had to be covered. The experimental lowest and highest could not be analysed over one single detector range. This was mainly due to the detector sensitivity and detector range of the FID. Component peaks that were too flat and peaks that were off-scale would not reflect the true area determined by the GC integrator producing the chromatogram. Three different detector ranges needed to be used, as such there was a need to prepare the calibration graphs as high range, and low range for determining the concentration pyridine in hexadecane with acetone or acetonitrile additions.

3.5.4.1 Pyridine in Acetone

Pyridine (Sigma chemicals – analytical grade) and acetone (Bio Lab.-analytical grade) were used to prepare a 100 ml stock solution concentration of 10 000 mg/L. The stock solution was prepared volume by volume, using the density of pyridine (0.98 grams/ml) to determine the volume. The volume of pyridine pipetted into a 100 ml volumetric flask

was 1.02 ml, which made to the mark with acetone gave the stock solution required. The stock solution was then diluted with acetone to prepare standard solutions for calibration purposes.

One of the standard solutions prepared for pyridine in acetone calibration purposes was 2100 mg/L. The sorption kinetics of pyridine in acetone by peat was followed using the 2100 mg/L standard, this was done to determine the equilibrium time required for the remaining samples that were mixing continuously (see section 3.1.4). Due to the wide concentration range of pyridine, three calibration curves were prepared. Blanks were vials containing pyridine in acetone only for each solution concentration. These were mixed continuously over the same time period as that of the vials containing peat and the solutions of pyridine and acetone. The concentration of pyridine in the blanks was also determined for losses from the initial pyridine concentration. Pyridine losses in all cases were less than 3 % and as such no corrections were made to the calculated values for sorbed pyridine.

The equilibrium concentrations were calculated using these calibration curves. Table 3.13 represents the calibration values for both low and high and Figs. 3.8-3.10 show the linearity and the calibration equations. These were used to calculate the sorbed amounts and losses in the blank solutions.

Table 3.13 Solutions used to prepare the calibration curves for pyridine in acetone

Standard solution concentration (mg/L) – pyridine in acetone	Average area
68	11832
200	35833
400	68536
938	129409
2100	341162
2600	427940
3233	534563
3840	67381
4200	82452
4900	96484
5600	105580

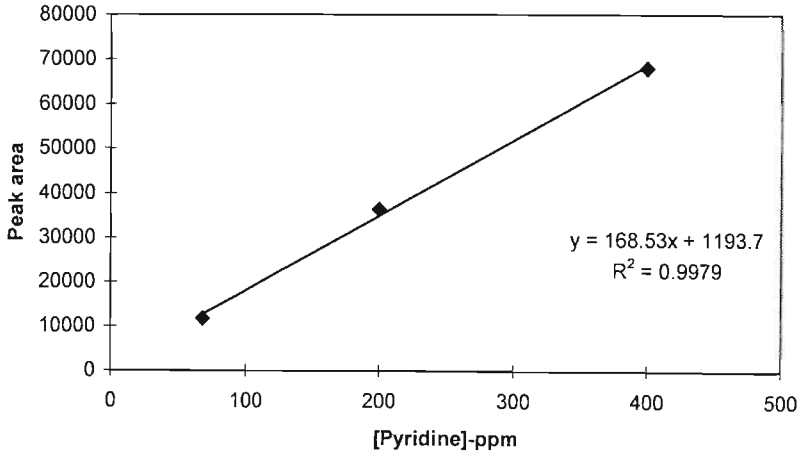


Fig. 3.8 Low range pyridine in acetone standard calibration curve

Typical GC chromatograms for pyridine in acetone are shown as Figs. 3.18 and 3.19. In Fig.3.18 pyridine is seen to elute at 4.021 minutes, this was the peak obtained for a 600 ppm pyridine concentration. An overlay with a 50 ppm pyridine concentration is shown and appears as the small peak under the large peak. Fig. 3.19 shows a chromatogram of the separation of acetone (2.300 minutes), pyridine (2.635 minutes), and hexadecane (6.361 minutes).

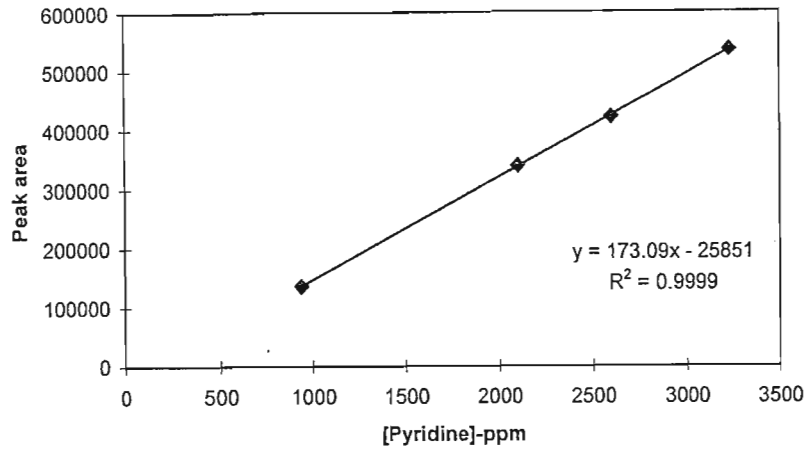


Fig. 3.9 Low range pyridine in acetone calibration curve

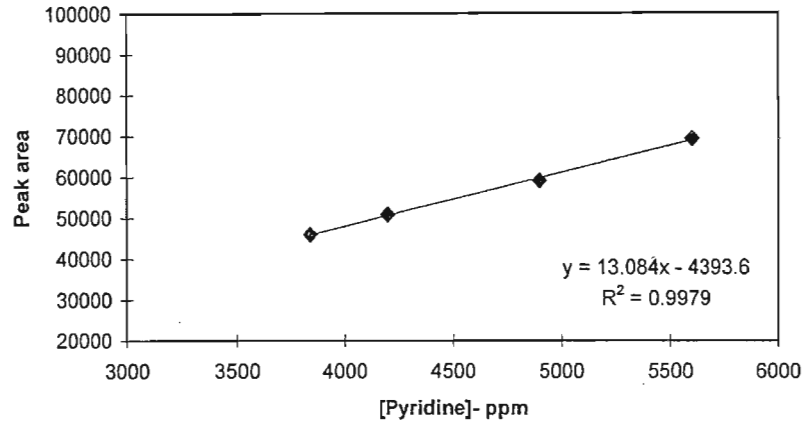


Fig. 3.10 High range pyridine in acetone calibration curve

3.5.4.2 Pyridine in Acetonitrile

Pyridine and acetonitrile (Bio Lab.-analytical grade) were used to prepare a 100 ml stock solution of concentration 10 000 mg/L. To achieve this 1.02 ml of pyridine was pipetted into a 100 ml volumetric flask and made up to the mark with acetonitrile. This solution was then used to prepare standard solutions shown in table 3.14. The calibration curves are shown in Figs. 3.11-3.13

Table 3.14 Solutions used to prepare the calibration curves for pyridine in acetonitrile

Standard solution concentration (mg/L) – pyridine in acetone	Average area
50	7614
125	19739
175	28346
345	56374
420	68633
760	75201
1440	136911
2560	267396
3900	411001
5040	528097
6516	725297
7500	774901

The standard solution of concentration 230 mg/L pyridine in acetone was used to follow the kinetics of pyridine in acetonitrile. This was for the purpose of determining the equilibrium time required for the samples that were mixing continuously. All experiments were done in duplicate. The monitoring of blanks as explained for pyridine in acetone apply to pyridine in acetonitrile as well.

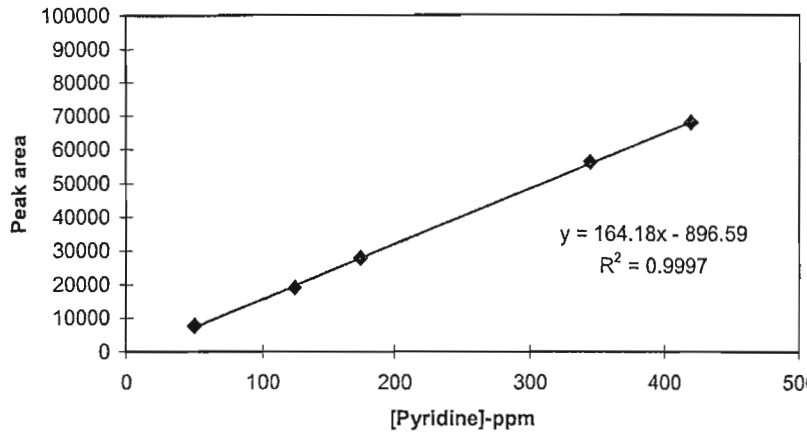


Fig. 3.11 Low range calibration curve, pyridine in acetonitrile

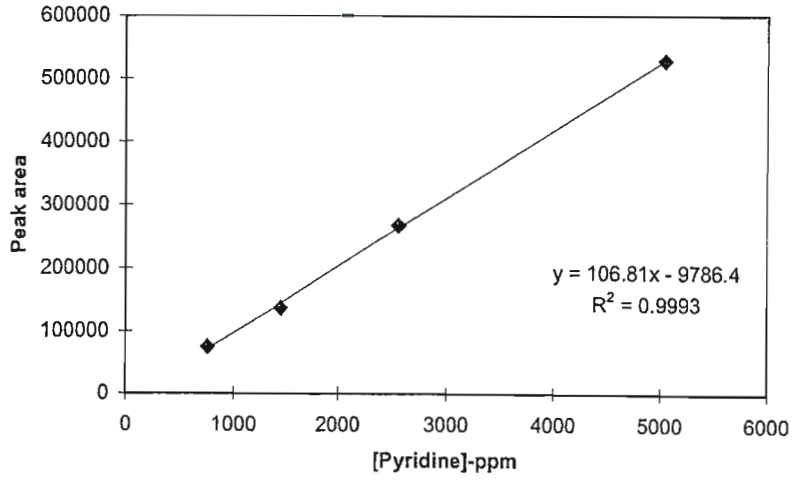


Fig. 3.12 High range calibration curve, pyridine in acetonitrile

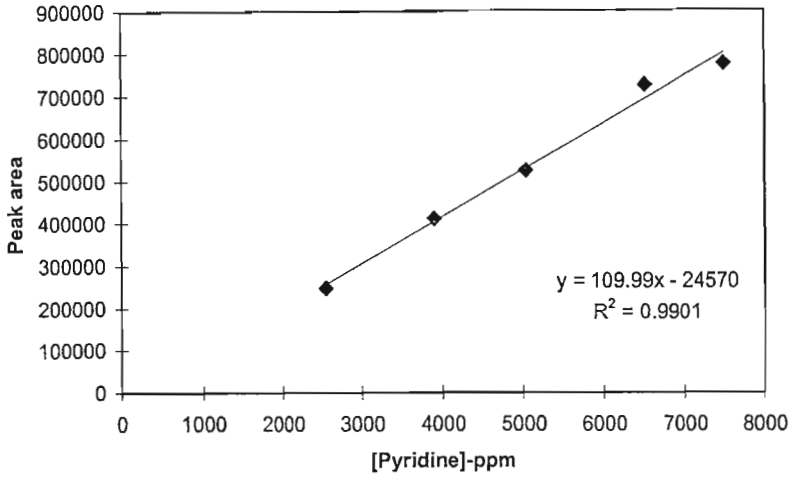


Fig. 3.13 High range calibration curve for pyridine in acetonitrile

3.5.4.3Pyridine in Hexadecane

Pyridine (Sigma chemicals – analytical grade) and hexadecane (Bio Lab.-analytical grade) were used to prepare a 100 ml stock solution concentration of 1000 mg/L. The stock solution was prepared using density of pyridine (0.98 g/ml) to determine the volume. The volume of pyridine pipetted into a 100 ml volumetric flask was 0.10 ml, which made to the mark with hexadecane, gave the stock solution (980 mg/L) required. The stock solution was then diluted with acetone to prepare standard solutions for calibration purposes. The equilibrium concentrations were calculated using the calibration curve in Fig. 3.14. Table 3.15 represents the calibration values.

Table 3.15 Peak areas for the pyridine in hexadecane calibration

Solution concentration (mg/L) –pyridine in hexadecane	Average Peak area
27.1	2976
49.7	5801
95.1	11548
207	24673

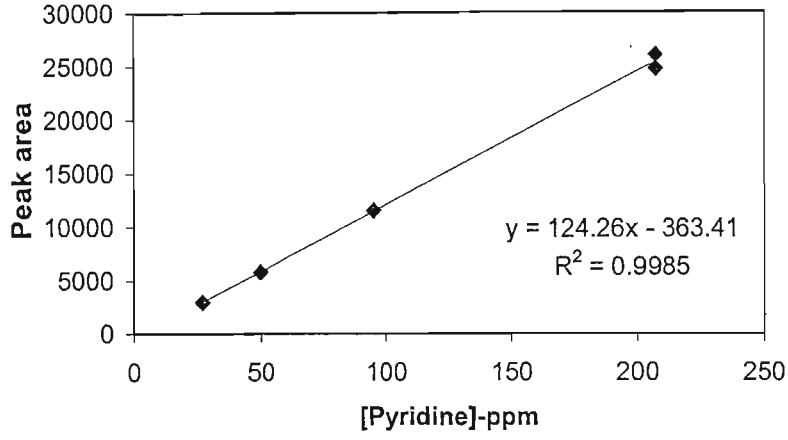


Fig. 3.14 Pyridine in hexadecane calibration curve

3.5.4.4 Acetonitrile in Hexadecane

Acetonitrile and hexadecane (Bio Lab.-analytical grade) were used to prepare a 25 ml stock solution concentration of 0.9 % by volume. The volume of acetonitrile pipetted into a 25 ml volumetric flask was 0.225 ml, which made to the mark with hexadecane, gave the stock solution required. The stock solution was then diluted with hexadecane to prepare standard solutions for calibration purposes. The equilibrium concentrations were calculated using the calibration curve in Fig. 3.15. Table 3.16 represents the calibration values.

Table 3.16 Peak areas for acetonitrile in hexadecane

Solution concentration (volume %) Acetonitrile in hexadecane	Average Peak area
0.018	5180
0.036	10200
0.072	20449
0.108	34300
0.14	37955
0.36	101473
0.48	152480
0.60	178200
0.72	212490
0.90	283570

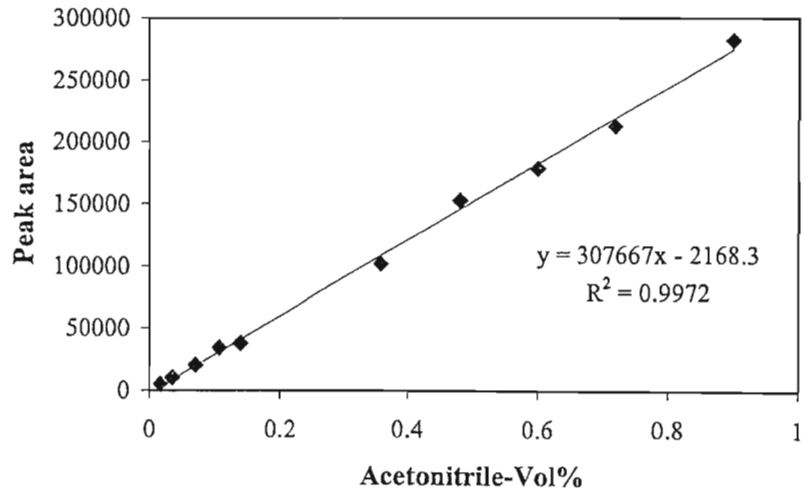


Fig. 3.15 Acetonitrile in hexadecane calibration curve

In the case of systems IV to VI all the kinetic points at equilibrium for the pyridine concentration range were included to obtain the isotherms for these systems. The desorption studies were conducted in the same way, for each pyridine concentration the desorption kinetics was studied, after desorption equilibrium for all pyridine concentrations in the desorption range the isotherms were obtained.

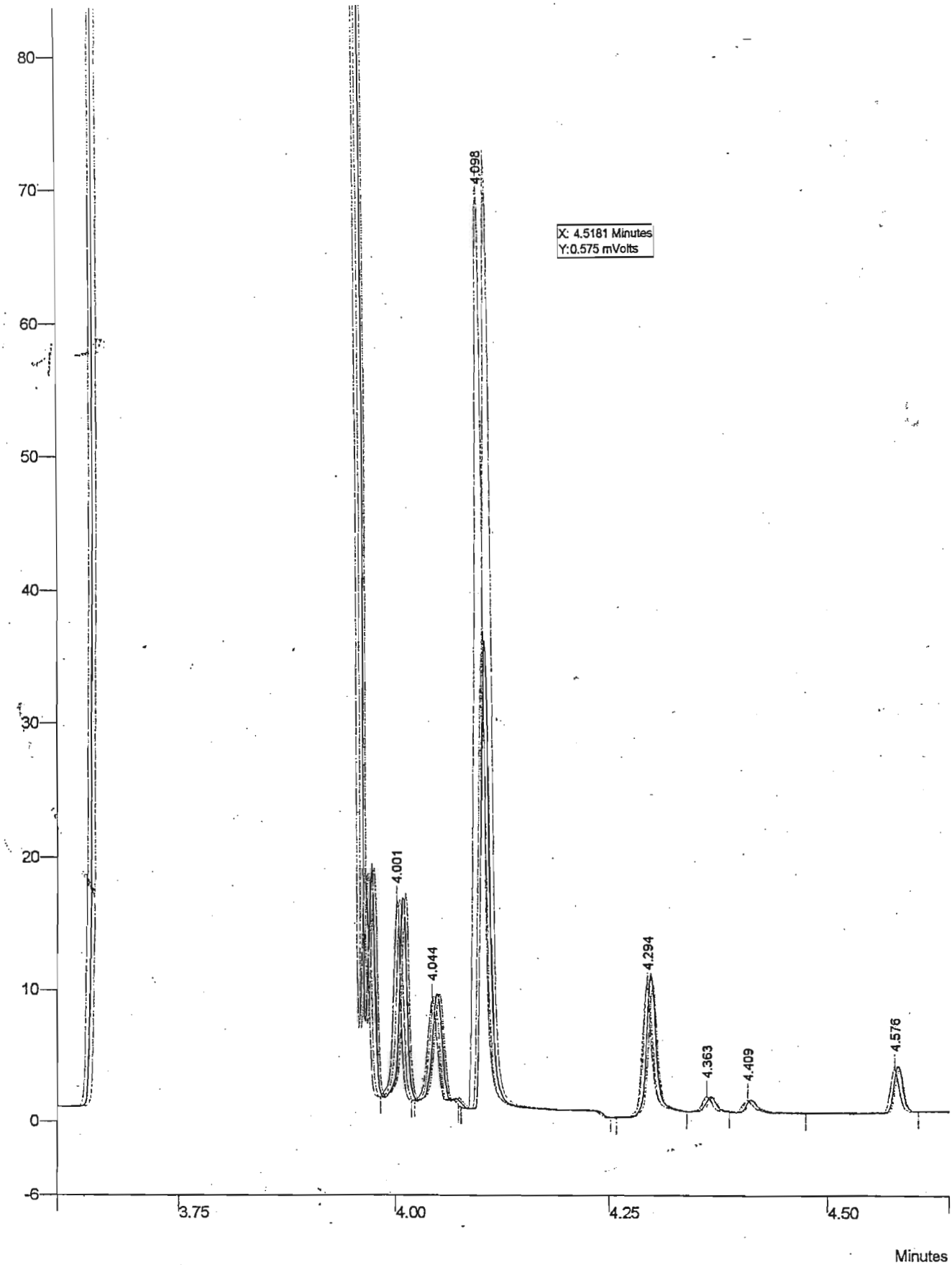


Fig. 3.16 Overlay chromatograms of dioxane extract. Pyridine eluting at 4.098 minutes. Large peak offscale eluting at 3.857 minutes is dioxane, while the other smaller peaks are extractable material from peat sorbent.

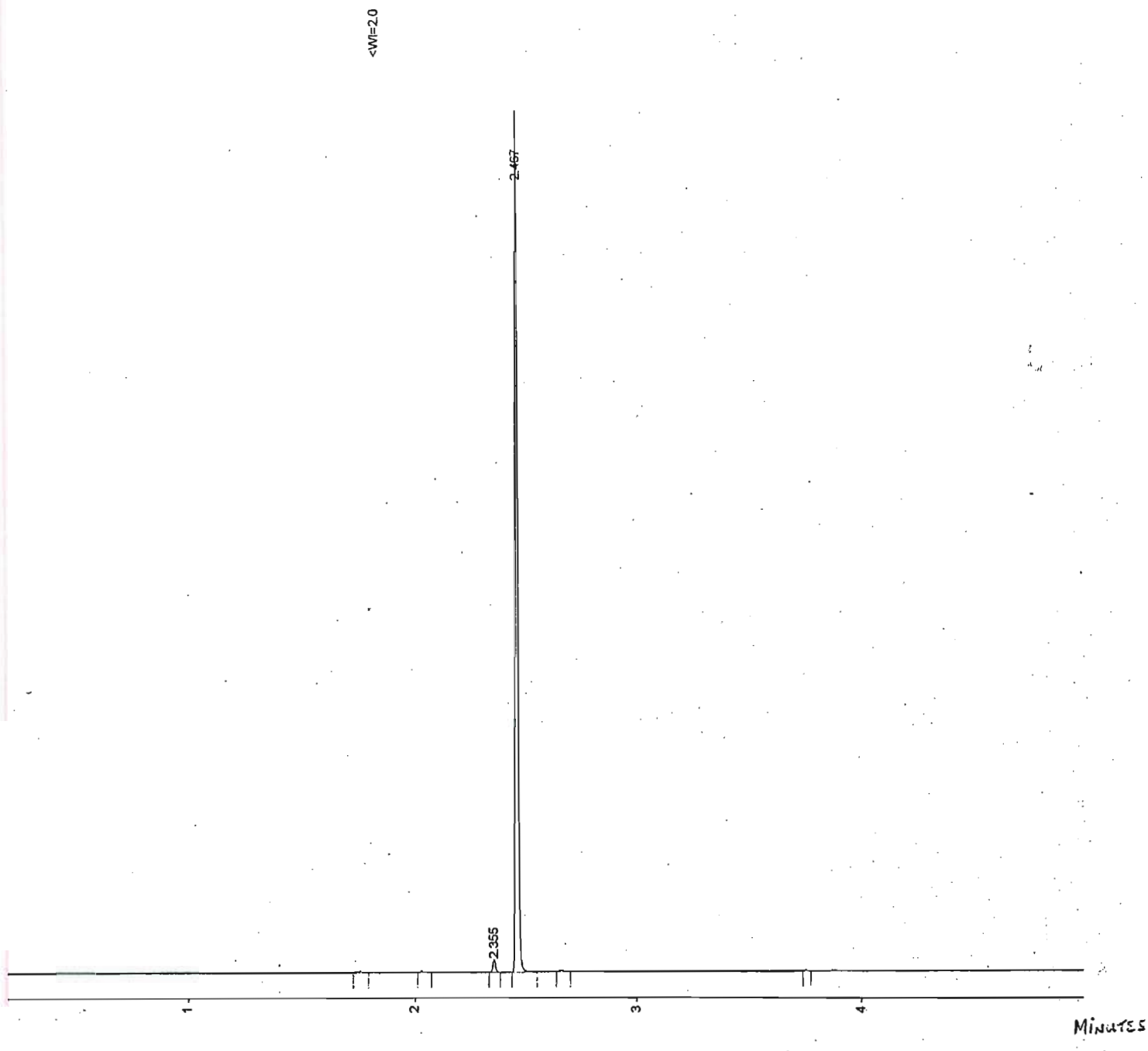


Fig. 3.17 Chromatogram of the headspace for acetonitrile, Acetonitrile elutes at 2.467 minutes

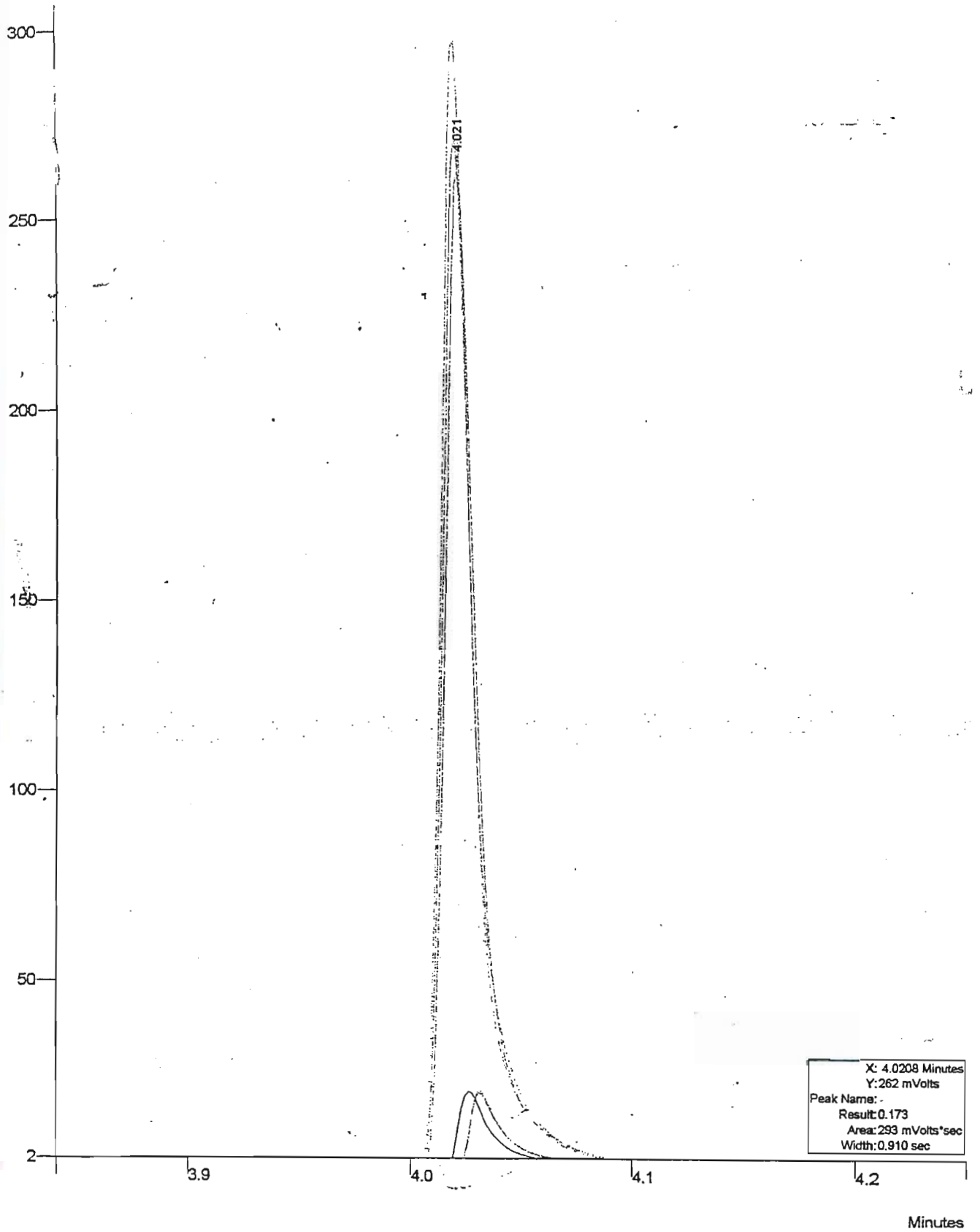


Fig. 3.18 Chromatogram of pyridine in acetone – hexadecane mixtures. Overlay scans of 50 and 600ppm. Pyridine elutes at 4.021 minutes

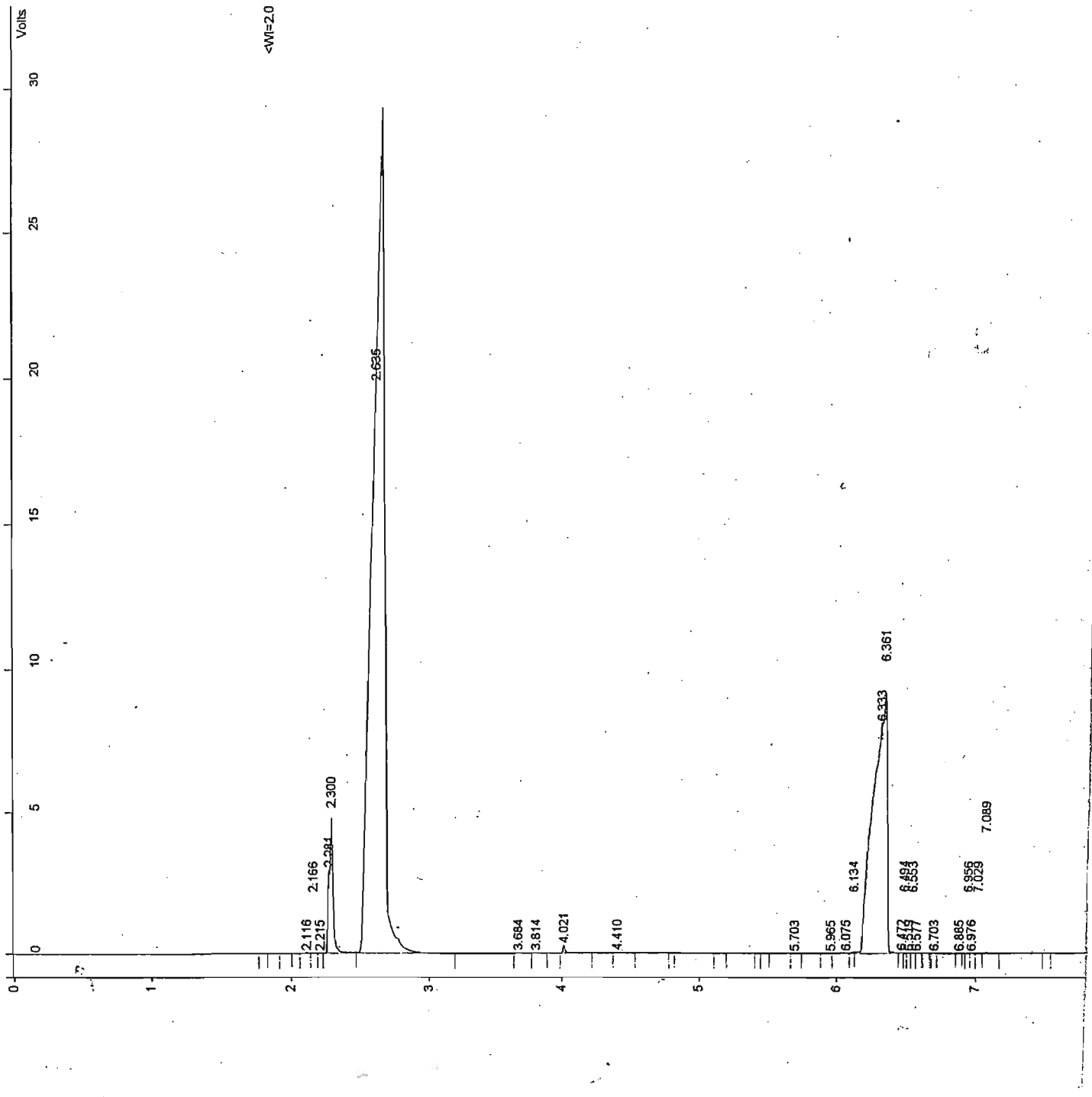


Fig. 3.19 Chromatographic separation of acetone, pyridine, and hexadecane. Pyridine elutes at 2.635 minutes, acetone at 2.300 minutes and the shoulder at 2.281 minutes. Hexadecane elutes at 6.361 sminutes and the shoulder at 6.333 minutes.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Determination of Humic Material

The absorbance readings for the blank solutions containing 10% of acetone and 10% of acetonitrile in water were measured at λ 465, and 665 nm using UV-Visible spectrophotometry. The wavelengths selected represents the three peaks that are observed for humic materials.[107] This was done so as to determine if the solvents will have any absorbance at these wavelengths. Since this will have an effect in the determination of the degree of humification. The absorbance readings obtained for both blank solutions were less than 0.001, indicating that these solvents were not going to interfere with the determination of the degree of humification of peat in the organic solvents. The degree of humification as indicated in the experimental section 3.1.2.1 for peat in aqueous extracts was compared to that of the non-aqueous solvents. The results are shown in Table 4.1 where the E4 / E6 ratio is for the two biggest absorbances, at two different time scales i.e. 12 hours and 3.5 months. The actual absorbance values are shown in Tables 3.2, 3.3, and 3.4 in section 3.2.3. Table 4.1 also indicates the standard deviation obtained from a minimum average of five readings.

Table 4.1 Degree of humification of peat in different solvent systems

Combination	**Degree of Humification (E4/E6 ratio)**	
	12 hours	**3.5 months**
Peat – H_2O	40.3 ± 1.1	82.1 ± 3.2
Peat – Acetonitrile	2.7 ± 0.1	3.0 ± 0.25
Peat – Acetone	2.0 ± 0.15	2.5 ± 0.2

Table 4.1 shows that the degree of humification is much greater in the aqueous medium as compared to the organic solvent, by a factor of 15 and 20 with respect to acetonitrile and acetone respectively in a 12 hour period. The degree of humification in aqueous-medium increases with time, such that after 3.5 months the value is twice as big

compared to the 12 hour period. In the case of organic solvents the increase over the same period is 10% and 25% for acetonitrile and acetone respectively. These results confirm that microbial degradation which originates from the peat is negligible in non-aqueous solvent compared to aqueous solvent. This is because for both time periods the dissolution of humic material into the aqueous solvent was greater than that into acetone or acetonitrile; an indication that microbial activity is higher in the aqueous medium as compared to the non-aqueous solvent. It can therefore be concluded that organic solvents are a better medium to use for studying the interactions of organic compounds, such as pyridine, with soil organic matter.

In order to support the UV-Visible results, the total organic carbon (TOC) analysis of the aqueous extracts was done and the results are shown in Table 3.6. The results indicate an increase in carbon with time which agrees with the UV-VIS results. The ratio of peat extracts after 12 hours and 3.5 months for TOC determination is 1.6. This value compares very well with the ratio of 2.0 for the degree of humification.

The similarity in ratios obtained from the two different methods indicates that the degree of humification is mainly a result of organic carbon released into the solvent media. It can therefore be concluded that the aqueous media provides better conditions for microbial to disrupt the organic matrix to a much greater degree than non-aqueous media

4.2 Determination of the Solubility of Different Solvents in One Another.

Since there is no information in the literature regarding the solubility of the solvent combinations used in this study, these had to be determined experimentally. The method described in section 3.1.3.1 was used for determining the solubility of each combination. The results which are an average of three readings are tabulated in Table 4.2.

Table 4.2 Gas Chromatographic (GC) determination of volume percentages of solvents solubilities in one another.

Solvent Combination	Solubility volume % (V/V)
Acetonitrile in hexadecane	0.90 ± 0.08
Hexadecane in acetonitrile	0.57 ± 0.02
Acetone in hexadecane	24.0 ± 0.4
Hexadecane in acetone	13.4 ± 0.2

The results obtained show that acetonitrile-hexadecane combination have very low solubilities into one another when compared to that of acetone–hexadecane combinations. The maximum solubilities for acetonitrile and acetone in hexadecane are therefore regarded to correspond to unit activity for these solvents in hexadecane.

4.3 Determination of Ostwald Coefficients

Since the equilibrium concentrations of pyridine in different solvents is best expressed as activity in the respective solvents, Ostwald Coefficients (OC) had to be determined as described in section 3.1.3.2 using equation 3.5, the results obtained are tabulated in Table 4.3

Table 4.3 Ostwald coefficients determined experimentally using GC headspace analysis.

Solution Combination	Ostwald coefficient
Pyridine (50 – 500ppm) in hexadecane + 0.5%vol. Acetonitrile	3.31 ± 0.02 [a]
Pyridine in acetone-hexadecane(50 – 6000 ppm)	4.21 ± 0.03
Pryidine in acetonitrile (50 – 6000 ppm)	4.26 ± 0.01
Acetonitrile in hexadecane (0.14 – 0.9% v/v)	1.63 ± 0.02

[a] For the calculation of pyridine activities (pyridine in hexadecane and pyridine in hexadecane with acetonitrile additions) in this study the literature value of 3.02 was used.

The Ostwald coefficient for pyridine in hexadecane – acetonitrile combination was found to be constant at 3.31 ± 0.02 over the concentration range of 50 – 500 ppm. In case of pyridine in acetone and acetonitrile concentration range 50 – 6000 ppm, the Ostwald

coefficient (OC) was found to be 4.21±0.03 and 4.26±0.01 respectively. In a concentration range of 0.1 – 0.8% volume of acetonitrile in hexadecane, the OC was 1.63 ± 0.02. This value is 7% smaller than that reported in the literature (1.74)[113] It was therefore necessary to calculate the maximum solubility of acetonitrile using the literature value and our experimental value and to compare to outcome with the experimentally determined maximum solubility shown in Table 4.2.

The measured K_d given in Table 3.8, (as described in section 3.4.4.1), for the acetonitrile of conecentration range (0.14 – 0.9% v/v) in hexadecane system found to be 43 is needed in the calculation of maximum solubility. This quantity, K_d, is unitless since solution concentration is divided by the gas phase concentration. Acetonitrile saturated vapour pressure, P at 25°C is 90.3 mm.Hg. The molar volume (V) of acetonitrile at this temperature is 52.44 cm^3 mol^{-1}. When the acetonitrile – hexadecane system is in equilibrium two phases exist, a hexadecane rich-acetonitrile poor phase, and an acetonitrile rich-hexadecane poor phase. The solubility of hexadecane in acetonitrile was determined as 0.57% v/v (Table 4.2). This can also be expressed as 0.01947 mol L^{-1}, or as a mole fraction of hexadecane 0.001027. Respectively the mole fraction of acetonirtile in this phase is 0.998973. This means that the acetonitrile activity coefficient referred to the pure compound liquid state can be considered as 1 in the acetonitrile-hexadecane system. Therefore the acetonitrile activity for this system saturated by hexadecane is given by it's mole fraction multiplied by it's activity coefficient. This means that acetonitrile concentration in the headspace over the acetonitrile-saturated solution in hexadecane is the same as the acetonitrile concentration in the headspace over the pure acetonitrile phase. The concentration may be expressed in mole per litre.

The acetonitrile concentration in the headspace, $C_{acn,soln}$, of a solution of hexadecane saturated with acetonitrile can be expressed as :

$$C_{acn,soln} = \frac{\text{Volume solubility of acetonitrile}}{\text{(Acetonitrile molar volume) x } (K_d)} \qquad (4.1)$$

This value is equal to the acetonitrile concentration in the headspace, $C_{acn,vap}$, of the pure acetonitrile. The $C_{acn,vap}$, can be calculated via the saturated vapour pressure, P, according to the Clapeyron equation 4.2, where R is the gas constant and T is the absolute temperature.

$$C_{acn,vap} = \frac{P}{(R) \times (T)} \qquad (4.2)$$

Equating equations 4.1 and 4.2, volume solubility of acetonitrile can be expressed as given in equation 4.3.

$$\text{Volume solubility of acetonitrile} = \frac{(\text{Acetonitrile molar volume}) \times (K_d) \times (P)}{(R) \times (T)} \qquad (4.3)$$

where R is the universal gas constant, and T is the absolute temperature. More importantly is that the maximum solubility of acetonitrile in hexadecane calculated by substituting the experimentally determined OC of 1.63 (Table 4.3) into equation 4.3 was 1.09% v/v. This corresponds very well to the maximum solubility of 0.9 % v/v (Table 4.2) obtained in our work. Substituting the literature[130] value for OC (1.74) the calculated solubility is 1.4% v/v, which is 56% bigger than the observed value of 0.9% v/v. Since the OC values were constant over the concentration range no correction for concentration dependance was necessary in calculating the activities.

4.4 Sorption of Organic Compounds by Peat from Organic Solvents

4.4.1 Kinetic study for the sorption of pyridine from acetonitrile and acetone.

The experimental procedure is as described in section 3.1.4. The concentration used to determine the equilibrium time was 2100 ppm. A total of 30 vials were used to determine the concentration of pyridine that remained in the vials as time progressed. The amount

of pyridine that had been taken up by peat was the difference between the initial concentration and the concentration in solution at the respective time. These values were then substituted into equation 3.2 to generate the distribution coefficient (K_d). The data obtained for both acetone and acetonitrile is tabulated in Table 4.4 as an average of three readings. These have also been represented in the form of graphs of K_d versus time, as shown in Fig. 4.1 and 4.2, for acetone and acetonitrile respectively.

Table 4.4 Kinetics for pyridine in acetone and acetonitrile systems.

	Acetone system			**Acetonitrile system**	
Time (Hours)	**Pyridine conc. In acetone (ppm)**	**K_d**	**Time (Hours)**	**Pyridine conc. In acetonitrile (ppm)**	**K_d**
24	151.6	1.35	24	167.2	4.86
48	143.8	1.55	48	160.2	5.46
72	120.5	2.29	72	143.9	6.97
168	82.6	5.14	192	121.4	9.99
240	76.2	6.06	264	125.4	10.03
648	77.1	6.13	672	96.9	14.33
1152	76.4	6.08	1176	95.1	15.46

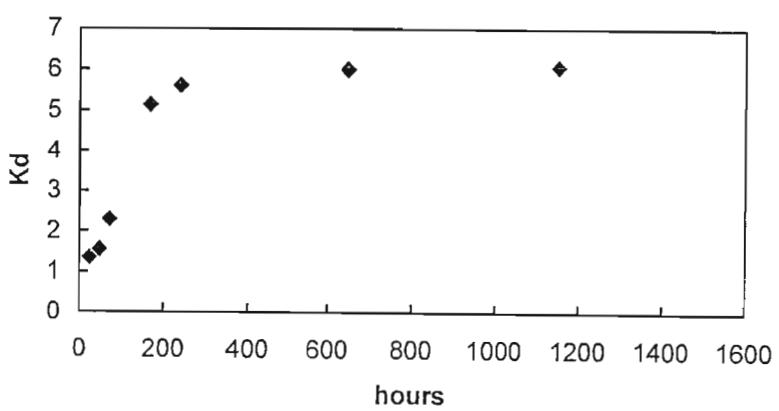


Fig. 4.1 Pyridine sorption by peat from neat acetone.

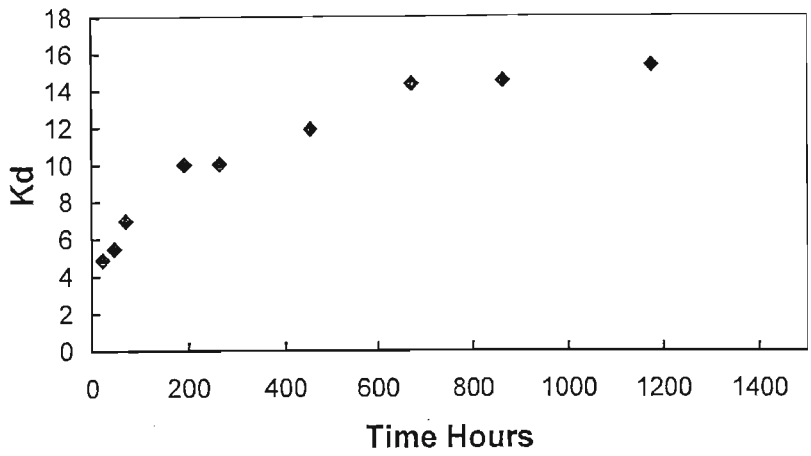


Fig. 4.2 Pyridine sorption by peat from neat acetonitrile.

The results indicate that pyridine sorption by peat in the presence of neat acetonitrile reached equilibrium after approximately 840 hours, whereas for the pyridine in acetone equilibrium was reached after 200 hours. The equilibrium distribution coefficient (K_d) for pyridine in acetonitrile was found to be 15. This value is 2.5 times greater than that from the acetone solvent which was 6. These results indicate that the driving force for sorption of pyridine into peat is solvent dependent. This observation can be attributed to the fact that acetone is a more effective electron donor than acetonitrile and as such has a stronger affinity for polar (H-bond donating) sorption sites on peat as compared to acetonitrile. The binding of acetone to the sites blocks the sorption of pyridine by peat. This is why more pyridine uptake was observed in case of the acetonitrile system.

The equilibrium times determined were used as a guide to follow the sorption of pyridine in the two organic solvents. In the case of n-hexadecane the literature value[72] of 400 hours was used. The actual times were much longer (see Table 3.1) to take into consideration the lower range of pyridine concentrations.

4.4.2 Equilibrium Studies of Sorption of Acetonitrile and Pyridine by Peat

4.4.2.1 Sorption of acetonitrile from hexadecane.

The sorption of acetonitrile by peat from hexadecane solvent was carried out as described in section 3.1.4, the initial acetonitrile concentrations are given in table 4.5. This was done so as to evaluate the masking effect by acetonitrile on the sorption of pyridine by peat from hexadecane. The sorbed amount, S_{amt}, at equilibrium was calculated using equations 3.2 and 3.3, while the sorbed volume was calculated using equation 3.4. Calibration equation given in Fig. 3.15 was used to calculate the concentration of acetonitrile in the solution at equilibrium. These concentrations at equilibrium were converted to activity using equation 3.5 (section 3.1.6.2). The data reported in Table 4.6 is an average of three readings. These have also been represented in the form of isotherm in Fig. 4.3. Included in the table are the initial acetonitrile concentration in hexadecane.

Table 4.5 Acetonitrile activities and sorbed volumes for the sorption of acetonitrile by peat from hexadecane.

Acetonitrile initial concentration (volume %)	Acetonitrile activity (a)	Sorbed Volume, S_{vol}, (mL/g)
0.018	0.006	0.003
0.036	0.015	.005
0.072	0.031	0.011
0.108	0.061	0.013
0.14	0.063	0.021
0.36	0.230	0.038
0.48	0.318	0.046
0.6	0.456	0.047
0.72	0.513	0.065
0.9	0.699	0.068

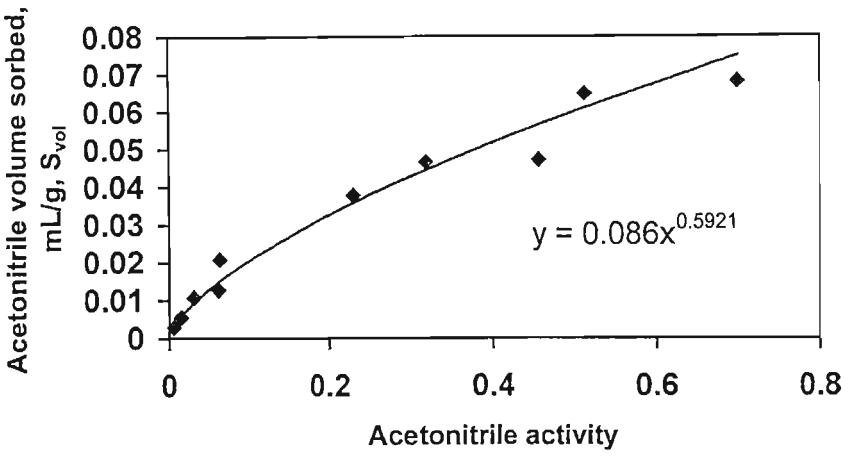


Fig. 4.3 Sorption of acetonitrile (mL/g) by peat from n-hexadecane plotted against the acetonitrile activity. The fitted curve represents Freundlich isotherm.

The isotherm in Fig. 4.3 shows that the amounts of acetonitrile sorbed by peat from n-hexadecane did not exceed 0.1 mL/g, which is the maximum absorption volume of acetonitrile by peat. Freundlich model fitting was applied to the sorption isotherm in Fig.4.3, resulting in an estimated volume sorption of acetonitrile by peat to be 0.086± 0.006 mL/g. This value was obtained using Freundlich equation $S = 0.086a^{0.59}$, where S is acetonitile sorption by peat at its solubility point in hexadecane. This indicates that a minimal swelling of the peat had occurred, and as such the masking effect of acetonitrile on pyridine sorption was not significant.

The solubility of n-hexadecane in acetonitrile was determined (Table 4.2) to be very low (0.57 ± 0.02 % vol.) and as such the acetonitrile saturated n-hexadecane solution should correspond to an acetonitrile activity of approximately 1. This means that a similar sorption isotherm of acetonitrile by peat should be observed for both peat immersed in neat acetonitrile and in acetonitrile saturated in hexadecane. Table 3.1 shows that the K_d range (10-50) of acetonitrile in hexadecane is greater than 1. This indicates that the maximum masking effect of acetonitrile sorption on pyridine would thus be a maximum

of 9% for a measured pyridine K_d value of 1. The range of K_d values (Table 3.1 solvent system IV) obtained in this study for acetonitrile in hexadecane was between 10 and 50 , and as such the masking effect of acetonitrile on pyridine sorption is negligible. A confident determination of acetone sorption to peat could not be done due to the low distribution coefficients (0.1) and high uncertainty observed for acetone sorption by peat from acetone n-hexadecane mixtures. The approximate level of acetone sorption by peat from the study was estimated to be 0.1 mL/g ± 0.1 mL/g ±0.07 mL/g for the 10% vol of acetone in n-hexadecane solvent system (which is 42% of the solubility range)). Such a sorbed amount of acetone would result in a 25% (10% vol.solubility-42%) underestimation in the distribution coefficients of pyridine in acetone when K_d is 0.3 (system I, K_d varies from 0.3 to 3, Table 3.1). The K_d range for system VI, Table 3.1, was 8-25, hence no K_d corrections for pyridine were required, because the minimum K_d (8) is greater than K_d (0.3) for a 25% underestimation by almost 30 times.

4.4.2.2Effect of pyridine additions to acetonitrile sorption

The effect of pyridine additions on the sorption of acetonitrile to peat was also studied. The aim of this part of the study was to establish if pyridine, over its concentration range in acetonitrile, allowed for more acetonitrile to be taken up by peat. This would illustrative a co-operative sorption phenomenon. Sorption and calculation of sorbed amount, S_{amt}, at equilibrium was carried out as described in section 4.4.2.1. The data shown in Table 4.5 was used to plot the isotherm containing no initial pyridine concentrations. Table 4.6 shows the data obtained, indicating the sorbed acetonitrile by peat at equilibrium at two different pyridine concentrations of 50 and 600 mg/L added to a solution of acetonitrile in hexadecane. The data is also presented in the form of isotherms in Fig. 4.4 which are plots of acetonitrile sorbed volume against acetonitrile activity. In addition these have been compared with the isotherm having no pyridine i.e. Fig. 4.3.

Table 4.6 Sorbed volume and activity for acetonitrile for different amounts of pyridine in a solution of hexadecane.

Solvent Combination in hexadecane	Acetonitrile activity (a)	Sorbed Volume (mL/g) (S_{vol})
Acetonitrile 0.036 % by volume, Pyridine 50 mg/L	0.017	0.0096
Acetonitrile 0.14 % by volume, Pyridine 50 mg/L	0.104	0.027
Acetonitrile 0.36 % by volume, Pyridine 50 mg/L	0.219	0.04
Acetonitrile 0.48 % by volume, Pyridine 50 mg/L	0.349	0.052
Acetonitrile 0.9 % by volume, Pyridine 50 mg/L	0.656	0.074
Acetonitrile 0.036 % by volume, Pyridine 600 mg/L	0.017	0.0096
Acetonitrile 0.14 % by volume, Pyridine 600 mg/L	0.106	0.0278
Acetonitrile 0.36 % by volume, Pyridine 600 mg/L	0.219	0.0398
Acetonitrile 0.48 % by volume, Pyridine 600 mg/L	0.327	0.0513
Acetonitrile 0.9 % by volume, Pyridine 600 mg/L	0.656	0.0737

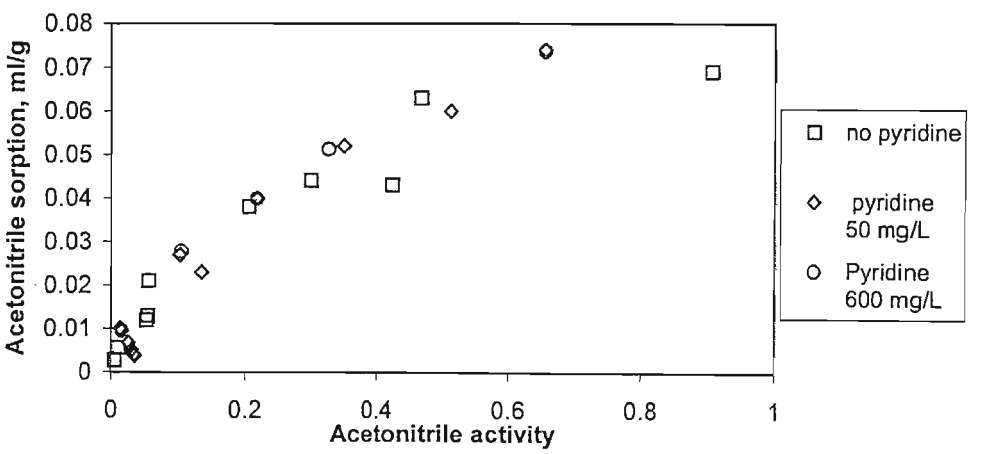


Fig. 4.4 Sorption of acetonitrile by peat for different initial pyridine concentrations in a solution of hexadecane.

The acetonitrile sorption trends shown in Fig. 4.4 indicates that overall sorption of acetonitrile does not increase with increasing the pyridine concentration. At initial acetonitrile concentration 0.036% by volume, the sorbed acetonitrile volume of 0.0096

ml/g is obtained for both 50 and 600 mg/l initial pyridine concentration. This is three times more than the sorbed volume of acetonitrile obtained (0.003 ml/g) without the presence of pyridine, as indicated in Table 4.6. A possible explanation is that at low initial acetonitrile concentrations pyridine assists in co-operative binding of acetonitrile. However, at acetonitrile concentrations greater than 0.036% by volume, acetonitrile dominates, such that additions of pyridine to the acetonitrile-hexadecane system does not show a solvent assisted sorption behaviour. This seems to indicate that pyridine is not effective in the overall solvating and disrupting the polar soil organic matter moieties to allow for more acetonitrile to be sorbed. Pyridine can therefore be considered to be a poor co-solvent for co-operative sorption of acetonitrile to peat.

4.4.2.3Pyridine sorption by peat from acetone, acetonitrile, and n-hexadecane.

The sorption of pyridine by peat from the three solvents namely acetonitrile, acetone, and hexadecane was carried out as described in section 3.1.4. The initial pyridine concentration range used in this study is given in table 3.1 (number I-III). The calibration equations used to determine the concentration of pyridine in the system are as given in Figs. 3.8 - 3.14. The concentration of pyridine taken by peat (sorbed amount) was determined as a difference between the initial concentration and the solution concentration at the respective time. Different concentration of pyridine were used for the determination of isotherms. The data reported in Table 4.7 are an average of three readings. The concentrations of pyridine in solution were converted into activity using equation 3.4 (section 3.1.6.2). These are also reported in Table 4.7 including the range of distribution coefficients, K_d values for the isotherms. Sorbed isothems were generated by plotting sorbed pyridine against pyridine activity. This is because activity takes into account the interaction of solute and solvent.

Table 4.7 Pyridine activities and sorbed amounts (mg/kg) not normalized for sorption by peat from acetone, water, acetonitrile, and hexadecane.

Pyridine in acetonitrile		**Pyridine in water[(a)]**		**Pyridine in acetone**		**Pyridine in hexadecane**	
Activity	Sorbed by peat (mg/kg)	Activity	Sorbed by peat (mg/kg)	Activity	Sorbed by peat (mg/kg)	Activity	Sorbed by peat (mg/kg)
1.86×10^{-5}	225.38	2.03×10^{-5}	360.02	2.17×10^{-5}	107.28	1.81×10^{-4}	281.45
5.11×10^{-5}	493.90	5.29×10^{-5}	559.95	1.73×10^{-4}	378.91	3.41×10^{-4}	547.03
6.57×10^{-5}	778.14	1.21×10^{-4}	1037.86	4.80×10^{-4}	458.22	8.737×10^{-4}	895.95
1.64×10^{-4}	997.82	1.96×10^{-4}	1412.94	1.37×10^{-3}	1089.37	1.96×10^{-3}	1066.61
1.85×10^{-4}	1434.3	2.82×10^{-4}	1779.96	1.72×10^{-3}	1149.31		
3.96×10^{-4}	1964.01	3.51×10^{-4}	2101.24	2.05×10^{-3}	1597.94		
7.61×10^{-4}	3569.41	6.21×10^{-4}	3068.65	2.59×10^{-3}	1613.65		
1.50×10^{-3}	4242.84	8.63×10^{-4}	4174.18	3.16×10^{-3}	1661.35		
3.01×10^{-3}	7089.13	1.735×10^{-3}	6391.49				
4.53×10^{-3}	9946.67	2.158×10^{-3}	7012.88				
K_D Range	1.5 - 9				0.3 - 3		6 - 20

[(a)] Values for pyridine sorption from water taken from literature.[145]

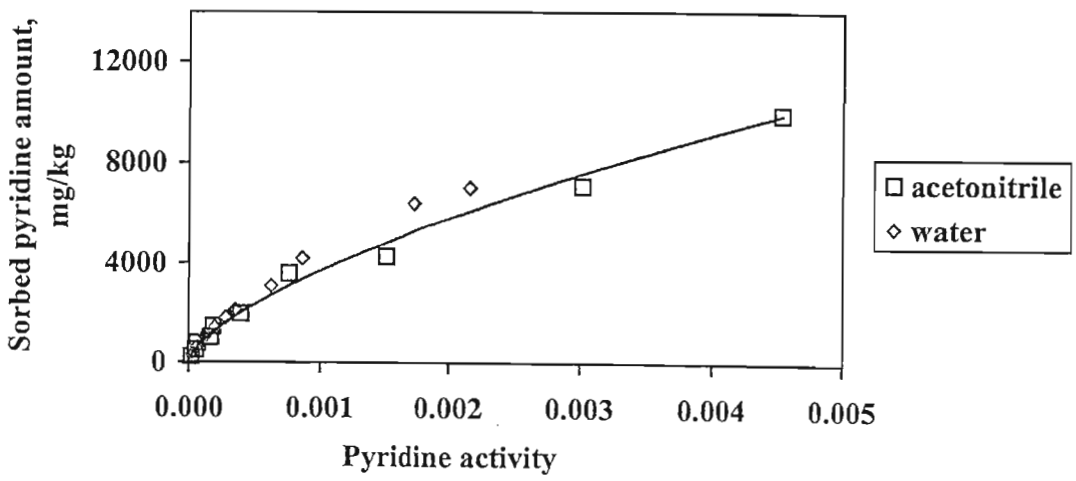


Fig. 4.5(a) Pyridine sorption by peat from acetonitrile, n-hexadecane, and acetone. Sorbed pyridine amounts shown are not normalized for peat swelling.

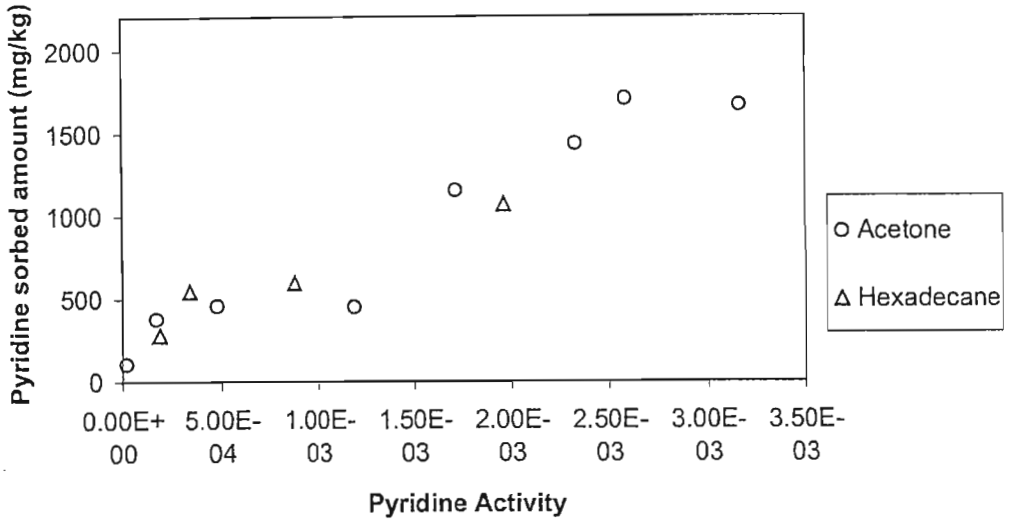


Fig. 4.5 (b) Pyridine sorption by peat from n-hexadecane and acetone. Sorbed pyridine amounts shown are not normalized for peat swelling.

Figs. 4.5(a) and 4.5(b) shows that the sorption of pyridine by peat from n-hexadecane, acetonitrile, water, and acetone (solvent systems I-III in Table 3.1) is not linear. The isotherms seem to approach a maximum value. Pyridine sorption from acetonitrile was comparable to the sorption from water but far greater than from the other two solvents. Pyridine sorption from hexadecane and acetone was comparable. The non-linearity of the isotherms indicates a hysteretic effect. This is contrary to what has been observed in case of aqueous and gaseous systems[37]. The range of measured K_d values are tabulated in Table 4.7, these values decrease with solute concentration by a factor of three in the n-hexadecane system, and by a factor of six and ten in the acetonitrile system and acetone system respectively. No K_d corrections were required, as described in section 3.1.6.3.

The normalization of pyridine sorption data to the volume of the peat phase rather than the weight of the dry peat phase did not change the trends of pyridine uptake in these solvent systems. The sorbed amounts of pyridine shown in Table 4.7 were normalized for solvent sorption (see section 3.1.6.3), the normalized data is shown in Table 4.8

Table 4.8 Pyridine activities and sorbed amounts (mg/kg) normalized for sorption by peat from acetone, water, acetonitrile, and hexadecane.

Pyridine in acetonitrile		**Pyridine in water**		**Pyridine in acetone**		**Pyridine in hexadecane**	
Activity	Sorbed by peat (mg/kg)	Activity	Sorbed by peat (mg/kg)	Activity	Sorbed by peat (mg/kg)	Activity	Sorbed by peat (mg/kg)
1.86×10^{-5}	195.20	2.03×10^{-5}	319.13	2.17×10^{-5}	116.08	1.81×10^{-4}	185.27
5.11×10^{-5}	435.26	5.29×10^{-5}	501.89	1.73×10^{-4}	444.04	3.41×10^{-4}	405.85
6.57×10^{-5}	682.73	1.21×10^{-4}	928.77	4.80×10^{-4}	631.92	8.737×10^{-4}	821.55
1.64×10^{-4}	925.49	1.96×10^{-4}	1284.45	1.37×10^{-3}	873.32	1.96×10^{-3}	1011.73
1.85×10^{-4}	1289.04	2.82×10^{-4}	1518.92	1.72×10^{-3}	1581.43		
3.96×10^{-4}	1956.05	3.51×10^{-4}	1907.14	2.05×10^{-3}	1765.26		
7.61×10^{-4}	3357.06	6.21×10^{-4}	2611.84	2.59×10^{-3}	2337.23		
1.50×10^{-3}	4336.94	8.63×10^{-4}	3670.30	3.16×10^{-3}	2691.52		
3.01×10^{-3}	7035.84	1.735×10^{-3}	5289.39				
4.53×10^{-3}	8225.48	2.158×10^{-3}	6286.17				

The graphs of pyridine sorbed amount versus pyridine activity were replotted and the trends obtained are shown in Figs. 4.6 a,b. Comparing Figs.4.5 a,b (pyridine sorption data not mormalised) and Figs. 4.6 (a) and 4.6 (b) (pyridine sorption normalized) it is clear that normalization of the pyridine sorption data per volume of the sorbed phase cannot account for the trends of pyridine uptake in the different solvent systems.

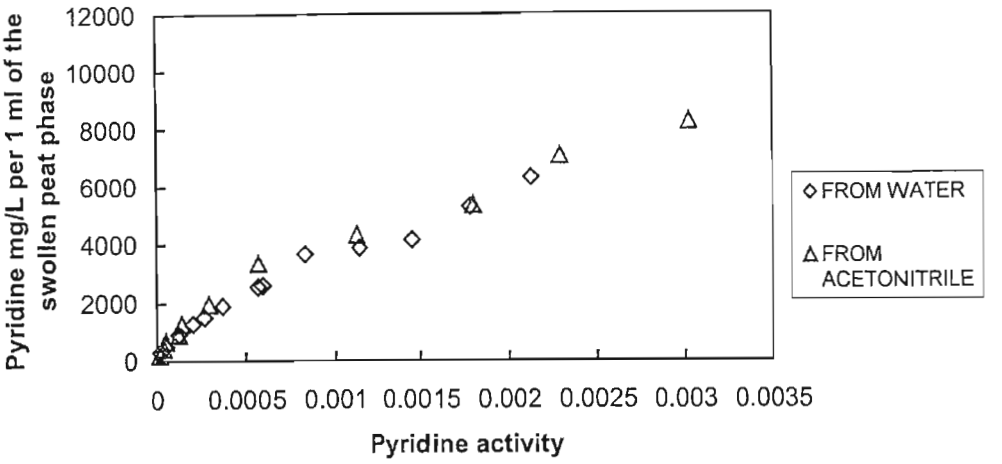


Fig. 4.6 (a) Total sorption of pyridine by peat from acetonitrile, water, acetone, and hexadecane, normalized sorbed pyridine values are shown.

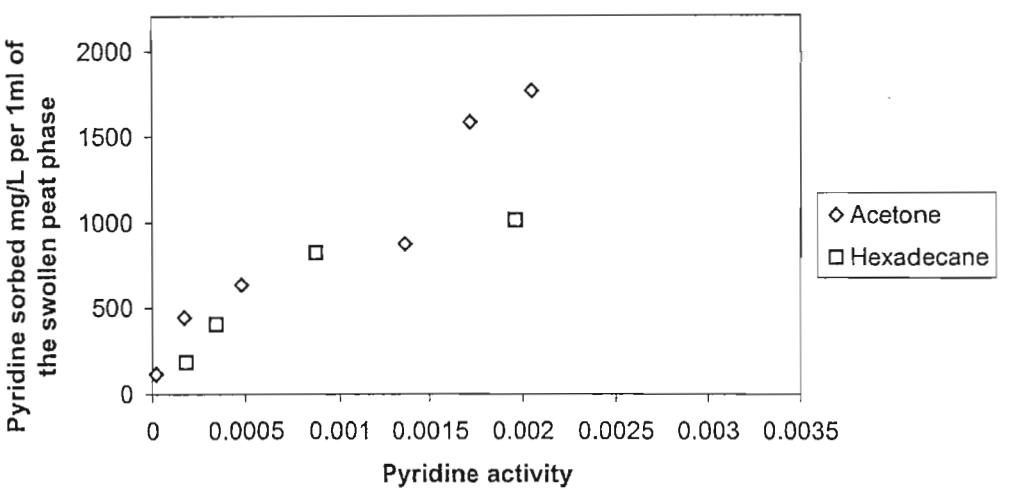


Fig. 4.6 (b) Total sorption of pyridine by peat from acetonitrile, water, acetone, and hexadecane, normalized sorbed pyridine values are shown.

The points for water were taken from literature[72], this isotherm represents the sorption of pyridine by peat in an aqueous system. Looking at the plots it can be concluded that acetonitrile behaves very much like water with regards to the solvent –assisted disruption of polar peat contacts.

A possible explanation for the suppressed pyridine sorption from hexadecane might be that *n*-hexadecane competes for "non polar" peat sites better than other organic solvents, thus suppressing pyridine sorption from *n*-hexadecane and resulting in an apparent non-competitive pyridine sorption in other solvents. However this scenario is not conclusive due to the polar nature of SOM and it's strong interactions with pyridine. It has been observed that pyridine is capable of forming strong hydrogen bonds and proton-transfer complexes with phenolic and carboxylic groups of organic compounds[95]. On the basis of the gas phase or SOM distribution coefficients, it has been shown that pyridine interacts with hydrated SOM 2,500 times stronger than its non-polar analogue benzene[114]. The gas phase sorption isotherm for aliphatic hydrocarbon, *n*-hexane, on peat is also known to be essentially linear after 2-3 weeks in the 0-0.3 activity range[128]. This supports the fact that aliphatic hydrocarbons can hardly compete with pyridine for peat sorption sites. The capability of large *n*-hexadecane molecules (molar volume 292 cm^3/mol) to penetrate into the peat framework is also reduced due to the size exclusion effect[118]. The non-effect of *n*-hexadecane on the sorption of polar compounds such as pyridine is also supported by experimental observations made in this study, when one compares the results in Figs. 4.5 (a) and (b) with those in Fig. 4.7. This being that pyridine sorption on peat is similar when determined from neat acetonitrile , Fig. 4.5 (a) and solutions of acetonitrile in *n*-hexadecane (Fig. 4.7), i.e. hexadecane does not affect the sorption of pyridine.

This non competitive effect of the solvents on pyridine sorption cannot exclude the possible complexation of pyridine with organic material released from peat into organic media such as acetonitrile and acetone which have the ability to dissolve peat components, see section 4.1 Table 4.1. However such a complexation, if significant, would result in the increase of the pyridine Ostwald coefficients in solutions, compared with Ostwald coefficients of pyridine in pure organic solvents. This was not the case since the Ostwald coefficients were found to be constant, see Table 4.3. This would mean that the sorption isotherms of pyridine in water, acetonitrile, and acetone would be shifted to the smaller activity range thus making the solvent-assisted sorption (as compared with sorption from *n*-hexadecane) even more pronounced. On the other hand, a release of peat

material into the organic solvents could result in the freeing of certain spaces in the sorbent phase thus providing new sorption sites for pyridine.

In case of acetonitrile as the solvent, strongly immobilized acetonitrile molecules (or reaction products from interaction with Humic substances) could have resulted in irreversible binding of the pyridine molecules to SOM. Although it is not clear why immobilized or transformed acetonitrile molecules may increase the sorption potential of SOM containing a multiplicity of phenolic, carboxylic (and many other) groups of high reactivity for interactions with pyridine, this assumption however cannot be eliminated. However, the hypothesis is not sufficient to explain the general non-competitive pyridine sorption observed from the solvents acetone, acetonitrile, hexadecane and water.

4.4.2.4Sorption of Pyridine by Peat from n-Hexadecane with Increasing Acetonitrile Concentrations.

The sorption of pyridine by peat from hexadecane with varying initial acetonitrile concentrations was carried out as described in section 3.1.4. The concentration used for the kinetic study are shown in Table 3.1 solvent system V. This was done so as to study the effect of initial acetonitrile concentration on the sorption of pyridine by peat. The sorbed amount of pyridine at equilibrium was calculated using equations 3.2 and 3.3. The calibration graph used to calculate the concentration of pyridine in solution is given in Fig. 3.14. Pyridine concentrations at equilibrium were converted to activity using equation 3.4 (section 3.1.6.2). The data obtained is shown in Table 4.8, while the corresponding isotherm is given in Fig. 4.7

Table 4.9 Sorbed pyridine amounts from hexadecane with different initial acetonitrile concentrations

Initial acetonitrile concentration (volume %)	Initial pyridine concentration (mg/L)	Activity	Sorbed pyridine concentration (mg/kg)
0	58	0.000188	281
0	133	0.000341	547
0	300	0.000871	892
0	600	0.001962	1067
0.05	58	0.000318	827
0.05	300	0.001044	1105
0.05	600	0.003531	2242
0.5	58	0.000169	1242
0.5	133	0.00041	2767
0.5	300	0.001659	4263
0.5	600	0.004097	6622
0.7	58	0.00012	1386
0.7	133	0.000212	3345
0.7	300	0.001344	5226
0.7	600	0.002842	9930
0.9	58	0.000254	1232
0.9	133	0.0006	2689
0.9	600	0.003998	8299

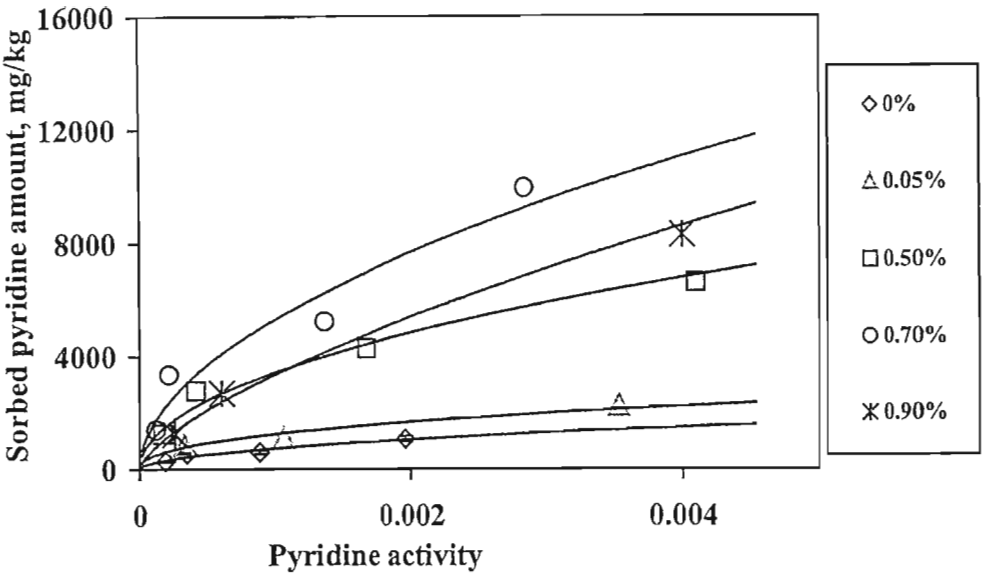


Fig. 4.7 Effect of increasing acetonitrile concentration on Pyridine sorbed by peat from hexadecane containing different initial acetonitrile concentrations

The trends seen in Fig. 4.7 indicate that the presence of acetonitrile assists the sorption of pyridine by peat from hexadecane. Pyridine sorption increases with increasing acetonitrile concentration up to a point (0.7 %) where it reaches a maximum and then starts to decrease (0.9 %). This drop can be attributed to the competitive sorption effect, acetonitrile competes with pyridine for sorption sites for concentrations of acetonitrile greater than 0.7% by volume. This acetonitrile-assisted trend for pyridine sorption was determined in a large excess of n-hexadecane (activity nearly 1). The maximum pyridine sorption of 9930 mg/kg was obtained at 0.7% by volume acetonitrile addition. This compares very well with the maximum level of pyridine sorption obtained from neat acetonitrile, this being 9947 mg/kg (see Table 4.9, Fig. 4.7). These two values are much greater than the pyridine sorption obtained from neat hexadecane, which was 1066 mg/kg (see Table 4.9, Fig. 4.7). This further indicates that the pyridine sorption trends are not due to competition between pyridine and hexadecane for the sorption sites in peat.

The ability of 0.7% acetonitrile in hexadecane to solubilize peat is greater than that of pure hexadecane. It has been reported in literature that acetonitrile has the greatest solubilizing ability, followed by acetonitrile in hexadecane, while hexadecane has the lowest ability.[132] The similarity of the pyridine sorption observed from acetonitrile (Fig. 4.6) and acetonitrile containing *n*-hexadecane (Fig. 4.8), which are solvents differing in solubilizing capability, indicates that the pyridine sorption trends are not due to the interaction of pyridine with solubilized peat materials either. This observation further emphasises the usefulness of hexadecane as an inert solvent (i.e. does to interefere with the SOM sorption potential of pyridine) in this study.

The effect of acetonitrile on the sorption of pyridine is more pronounced when the amount of pyridine sorbed is plotted against the added amount of acetonitrile at a given pyridine activity. The fixed pyridine activities choosen were 0.001 and 0.003. The data collected is shown in Table 4.10 and also shown in the form of a graph in Fig. 4.8. This data was taken from Table 4.9 for pyridine activities corresponding to 0.001 and 0.003 only.

Table 4.10 Pyridine sorbed by peat for pyridine activities 0.001 and 0.003 for different initial acetonitrile concentrations

Initial acetonitrile concentration (vol%)	Pyridine sorbed (mg/kg) at activity 0.001	Pyridine sorbed (mg/kg) at activity 0.003
0	737	NM*
0.05	1242	1961
0.2	1433	2710
0.36	2306	NM*
0.5	3442	5896
0.7	5356	9533
0.9	2866	6022
Neat acetonitrile	3526	7114

NM* - Denotes not measured

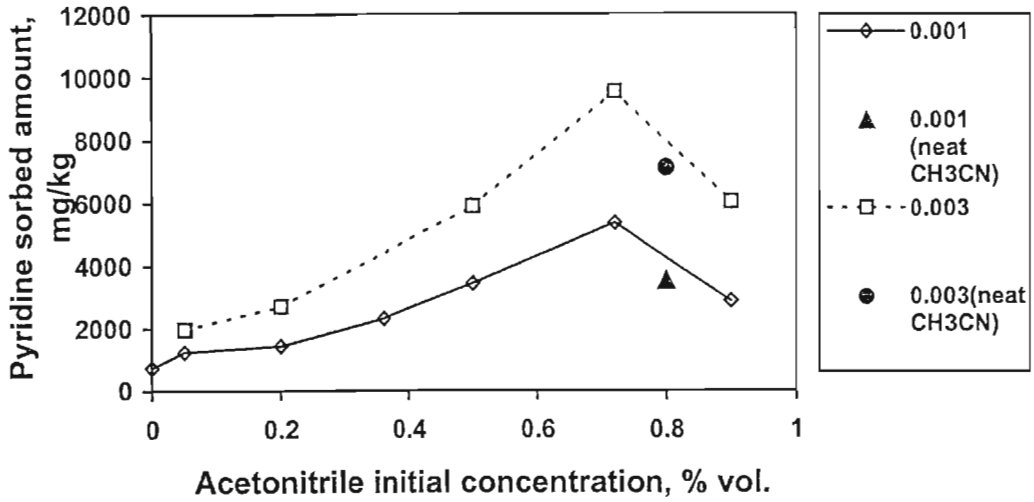


Fig. 4.8 Effect of initial acetonitrile concentration in hexadecane on pyridine sorption by peat at two pyridine activity levels. Solid and dashed lines correspond to pyridine sorption from neat acetonitrile (i.e. at the indicated pyridine activities)

Figure 4.8 shows that sorption of pyridine by peat as a function of initial acetonitrile concentration is sigmoidal, such that at lower initial acetonitrile concentrations (up to 0.36 %), there is only a small effect of acetonitrile on pyridine sorption, while at higher initial acetonitrile concentrations the effect on pyridine sorption is much greater, reaching a maximum at 0.7%.

Since the acetonitrile-assisted sorption of pyridine is clearly observed up to an initial concenteration of 0.7 % by volume of acetonitrile, this indicates that there was no competition for peat sorption sites between acetonitrile and pyridine over the 0.05-0.7 % by volume acetonitrile concentration range. This is despite the fact that both compounds are capable of strong specific interactions and could be expected to compete on the basis of their non-linear isotherms (Figs. 4.5, 4.6, 4.7, and 4.8). The trendlines shown for the neat acetonitrile was taken for sorption of pyridine from acetonitrile, data shown in Table 4.7. At initial acetonitrile concentrations less than 0.7 %, the sigmoidal nature of the

pyridine sorption isotherms suggest there is a co-operative effect on pyridine sorption. At initial acetonitrile concentrations greater than 0.7 %, pyridine sorption decreased, leading to the observed maximum in Fig. 4.8. This indicates that at initial acetonitrile concentrations greater than 0.7 % acetonitrile competes with pyridine for peat sorption sites.

4.4.2.5Pyridine Sorption by Peat From n-Hexadecane With Increasing Acetone Concentrations.

The effect of initial acetone concentrations (volume %) on the sorption of pyridine by peat from hexadecane was also studied. The experimental procedure is again as set out in section 3.1.4. The sorbed pyridine amount at equilibrium was calculated using equations 3.2 and 3.3. Calibration equations given in Figs. 3.8-3.10 were used to calculate the pyridine solution concentrations. The data reported in Table 4.11 is an average of three readings.

Table 4.11 Pyridine sorbed amounts (mg/kg) for different initial acetone concentrations. Effect of increasing acetone concentration on pyridine sorption.

Solvent System	Pyridine sorbed (mg/kg) for100 ppm initial pyridine	Pyridine sorbed (mg/kg) for 600 ppm initial pyridine
5%acetone in hexadecane	478	2057
10%acetone in hexadecane	453	2158
15%acetone in hexadecane	432	2058

The results obtained in Table 4.11 indicate non-competitive pyridine sorption by peat as the initial acetone concentration is increased.

The results indicate that tripling the acetone concentration (5-15%) had no effect on the sorption pyridine by peat. Acetone is therefore a much better solvating medium for pyridine than hexadecane, this is evident from the comparison of the Ostwald

Coefficients, shown in Table 4.3. A larger Ostwald Coefficient indicates a better solvating medium[126]. This means that an increase in the acetone concentration in hexadecane should have resulted in an increase in solvation of pyridine and hence a decrease in pyridine sorption should have been observed. This trend was not observed indicating that sorption of pyridine by peat is therefore not assisted by acetone additions, unlike the effect of acetonitrile additions on pyridine sorption which showed a definite solvent-assisted trend.

4.5 Desorption and Extraction of Organic Compounds From Peat

4.5.1 Desorption and Extraction of Acetonitrile From Peat

The desorption and extraction of acetonitrile from peat was carried out as described in section 3.1.5. This was done so as to determine the desorption behavior of acetonitrile from peat. Calibration equation given in Fig. 3.15 was used to calculate the concentrations of acetonitrile in the solution. The amount acetonitrile (ml/g) remaining in peat after the desorption process and solvent extraction was calculated using equation 3.1. The data obtained is reported in Tables 4.12, these are an average of three readings.

Included is the fraction of the desorbed acetonitrile and the solvent (hexadecane) extracted acetonitrile. These values have been converted into percentage and reported as the % of acetonitrile recovered. In addition the table shows the amount of acetonitrile that cannot be removed from peat from the desorption and extraction processes. These values are the difference between the sorbed amount of acetonitrile on peat less the desorption and extracted amount.

The data in Table 4.13 is an expansion of the results obtained in Table 4.12, where only one concentration of acetonitrile in this case 0.36% by volume is chosen (solvent system IV in Table 3.1). The table gives the detailed desorption values of acetonitrile with respect to time, and that of extraction using dioxane and DMSO at desorption equilibrium. The data is reported in terms of the amount of acetonitrile remaining in peat.

The kinetic data on the desorption process is represented in Fig. 4.9, as a plot of the sorbed amount of acetonitrile on peat versus time, included are the two points corresponding to extraction using dioxane and DMSO. The plot clearly shows that the DMSO has a highest extraction ability

Table 4.12 Sorbed amounts (ml/g) and fractions of acetonitrile remaining on peat and removed after the process of desorption into hexadecane and extraction with polar solvents dioxane and DMSO.

Initial acetonitrile concentration Vol %	Sorbed onto peat (ml/g)	Desorption (hexadecane) (ml/g) removed		Combined Solvent extraction (ml/g) removed		Acetonitrile not removable		% Acetonitrile recovered
		ml/g	fraction	ml/g	Fraction	ml/g	%	
0.072	0.011	0.0028	0.25	0.007	0.67	0.0008	8	92
0.14	0.021	0.0063	0.30	0.012	0.57	0.0027	13	87
0.36*	0.038	0.010	0.27	0.024	0.63	0.0038	10	90
0.9	0.068	0.018	0.27	0.041	0.61	0.0082	12	88

*The results have been expanded in Table 4.13.

Table 4.13 Sorbed amounts (mL/g) of acetonitrile after desorption and extraction processes with time for the 0.36 % by volume acetonitrile in hexadecane system.

Time in Hours	Acetonitrile sorbed to peat after (ml/g)-hexadecane desorption		Acetonitrile sorbed to peat after ml/g)-dioxane extraction		Acetonitrile sorbed to peat after (ml/g)-DMSO extraction	
	Amount (ml/g)	% removed	Amount (ml/g)	% removed	Amount (ml/g)	% removed
0	0.038		0.038	0	0.038	0
144	0.027					
288	0.025					
480	0.025	35	0.018	18	0.0038	37

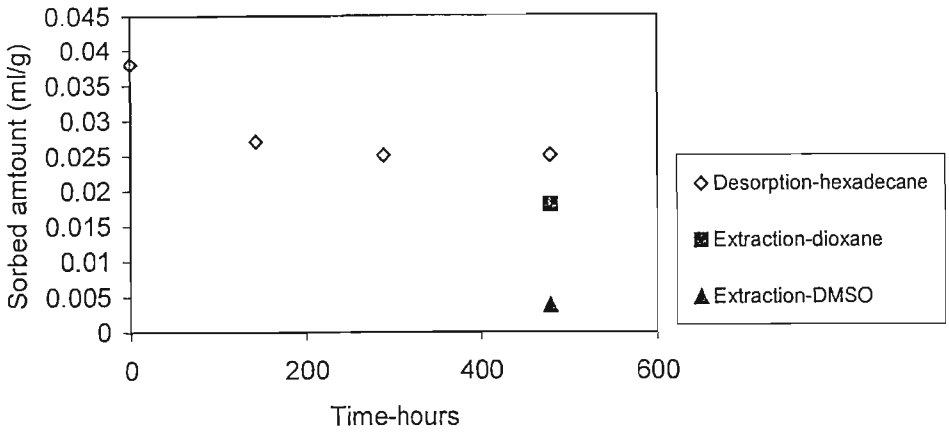


Fig. 4.9 Desorption kinetics of acetonitrile using hexadecane and solvent extraction of acetonitrile at equilibrium using dioxane and DMSO from peat that has been subjected to acetonitrile-hexadecane system.

Figure 4.9 shows that the desorption of acetonitrile from peat into hexadecane was hysteretic, i.e acetonitrile was resistant to desorption and not fully removable in a single desorption or extraction step. The physical and chemical binding forces ensured that multiple steps of desorption and extraction were needed to remove a major portion of the initially sorbed acetonitrile. The plot shows that desorption equilibrium was reached after approximately 200 hours. Table 4.12 shows that the fraction of acetonitrile removed by desorption of acetonitrile was approximately 0.27. The largest fraction of acetonitrile removed via solvent extraction was 0.62. The average acetonitrile recovered was approximately 90%. This indicate that on average10 % of acetonitrile was not recovered, an indication that this must have been binded irreversibly with SOM.

The effect of pyridine on the desorption and extraction of acetonitrile was also studied. The process as described in section 3.1.5 was used in the study. This was done so as to determine the desorption behavior of acetonitrile from peat in the presence of pyridine. Calibration equation given in Fig. 3.15 was used to calculate the concentrations of acetonitrile in the solution. The amount of acetonitrile (ml/g) remaining in peat after the desorption process and solvent extraction was calculated using equation 3.1. The data

obtained is reported in Table 4.14, these are an average of three readings, also included in the table is the the non-removable fraction of acetonitrile.

Table 4.14 Acetonitrile fraction not removable for initial pyridine additions to the acetonitrile in hexadecane system.

Initial pyridine concentration (mg/L)	Initial acetonitrile concentration (vol.%)	Fraction of non-removable acetonitrile
0	0.9	0.12 ± 0.02
58	0.9	0.61 ± 0.02
600	0.9	0.52 ± 0.04
0	0.36	0.10 ± 0.01
58	0.36	0.49 ± 0.01

The results in Table 4.14 show that in the presence of pyridine a significant fraction of acetonitrile is not removed from peat., averaging a fraction of 0.54 as pyridine is increased from 58 to 600 mg/L. The fraction of non-recoverable acetonitrile with no pyridine additions is 0.12 for the 0.9% acetonitrile in hexadecane system, and a fraction of 0.10 for the 0.36% acetonitrile system. This indicates that for the addition of pyridine, irrespective of the concentration of pyridine, a significant increase in the amount of non-removable acetonitrile is observed when compared to the non-removable fraction of acetonitrile when no pyridine is present. When one considers the 0.9% acetonitrile system, a 58 mg/L pyridine addition increases the fraction of non-removable acetonitrile by 49%. Looking at the difference in the order of magnitude in the initial pyridine concentration (58 to 600 mg/L increase) for the 0.9% acetonitrile in hexadecane system, a 9% difference in the percentage of non-removable acetonitrile was observed, from 0.61 to 0.52. For the 0.9% acetonitrile system 58 mg/L of mobilized pyridine produces a 0.49 (0.441% by volume or 4410 mg/L) increase in the fraction of non-removable acetonitrile. For 600 mg/L mobilized pyridine a 0.4 (0.400% by volume or 4000 mg/L) increase in the fraction of non-removable acetonitrile is produced It is clear that the non-removable acetonitrile fraction produced is not dependent on the concentration of pyridine, rather just the presence of pyridine. If one assumes a 1:1 stoichiometric interaction between acetonitrile and pyridine, the results indicate that the non-removable acetonitrile fraction

is not due to a chemical reaction between pyridine and acetonitrile since for a ten fold increase, 58 to 600 mg/L initial pyridine, a reduction of 9% (0.61 to 0.52) in the non-removable fraction of acetonitrile is observed. Also the amount of non-removable acetonitrile (4200 mg/L on average) is between 7 –72 times greater than the amount of mobilized pyridine (58 – 600 mg/L), which further indicates that chemical ratios for interaction with pyridine to ensure non-removable acetonitrile cannot be the reason of the acetonitrile behavior. This discounts the possibility of a chemical reaction between pyridine and acetonitrile.

Figure 4.4 showed that pyridine additions did not affect the volume of acetonitrile taken up by peat. Table 4.14 showed that in the absence of pyridine addition a fraction of 0.12 of the initial acetonitrile was not removable. However the presence of pyridine increased the fraction of non-removable pyridine to 0.56 on average for the 0.9% acetonitrile system. The high level of non-removable acetonitrile can be explained to be due to the fact that in the mixture pyridine possibly acts as a Lewis base, catalyzing a reaction between acetonitrile and peat.

4.5.2. Desorption and Extraction of Pyridine From Peat

The desorption and extraction of pyridine from peat was carried out as described in section 3.1.5. This was done so as to determine the desorption behavior of pyridine from peat. Calibration equation given in Fig. 3.14 was used to calculate the concentrations of pyridine in the solution. The amount of pyridine (mg/kg) remaining in peat after the desorption process and solvent extraction was calculated using equation 3.1. The data obtained is reported in Tables 4.15. These are an average of three readings. The data shows the non-recoverable fraction of pyridine for solvent systems pyridine in hexadecane, pyridine-acetonitrile in hexadecane, and pyridine-acetone in hexadecane.

Table 4.15 Non-recoverable fraction of pyridine after desorption and extraction for the different solvent systems studied.

Pyridine concentration (mg/L)	Polar solvent Concentration (volume %)	Fraction of non-recovered pyridine	Percentage of pyridine removed via desorption and solvent extraction. (%)
27	-	0.45±0.15	55
207	-	0.45±0.08	55
	Acetonitrile		
58**	0.9	0.58±0.09	42
600	0.9	0.55±0.04	45
	Acetone		
100	5	0.49±0.03	51
600	5	0.52±0.04	48
100	15	0.52±0.01	48
600	15	0.51±0.02	49

** These results have been expanded in Table 4.16

The data shown in Table 4.16 is an expansion of one of the results obtained in Table 4.15, where the 58 mg/L pyridine-0.9% acetonitrile in hexadecane solution is used in displaying the trend of desorption and extraction of pyridine. All the data reported in Table 4.15 were obtained through the same process. Included in Table 4.16 is the percentage of pyridine removed for each extraction step using dioxane and DMSO. The sorbed pyridine amounts (mg/kg) have been converted into percentage and reported as the % of pyridine recovered. These values are the difference between the sorbed amount of pyridine on peat less the desorption and extracted amount. The data in Table 4.16 (column 2) are an average of three readings representing the kinetic observation of the desorption of acetonitrile from peat by hexadecane with respect to time. Included in the table are values of extraction of pyridine with dioxane and DMSO. The data is also presented graphically in Figure 4.10. The observed trend was similar to the other solvent systems namely pyridine in hexadecane and pyridine-acetone in hexadecane.

Table 4.16 Pyridine sorbed amounts (mg/kg) onto peat after the desorption and extraction processess with time for the 0.9 % by volume acetonitrile-58 mg/L pyridine in hexadecane system.

Time in Hours	Amount of pyridine (mg/kg) sorbed to peat after hexadecane desorption		Amount of pyridine (mg/kg) sorbed to peat after dioxane extraction		Amount of pyridine (mg/kg) sorbed to peat after DMSO extraction	
	Amount	% removed	Amount	% removed	Amount	% removed
0	1232		1232	0	1232	0
192	1150					
336	1145	7	1121	2	712	33

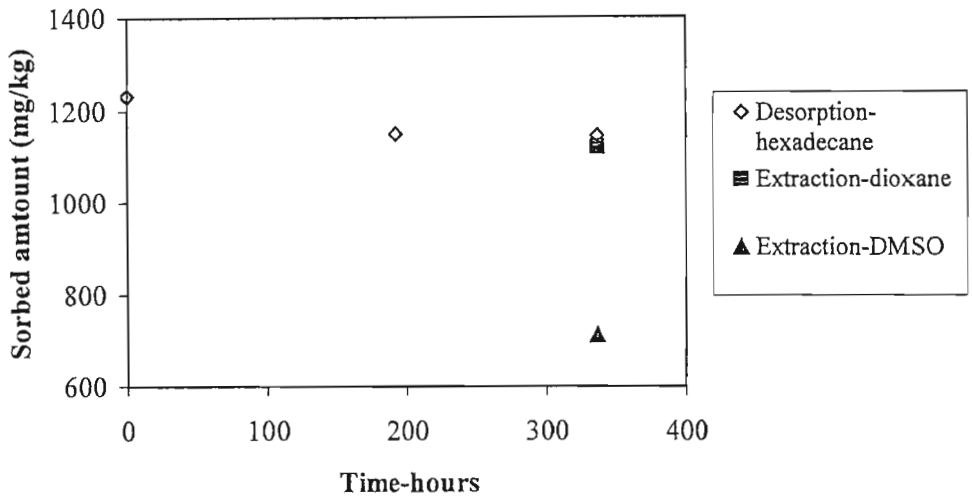


Fig. 4.10 Change of pyridine sorbed amount onto peat for the desorption and solvent extraction processess of pyridine from peat for the 0.9 % acetonitrile- 58 mg/L pyridine in hexadecane system.

The results in Figure. 4.10 show that desorption of pyridine was hysteretic. It can also be deduced from the table that the amount of non-recoverable pyridine is not dependant on the initial pyridine concentration, and also not dependant on the polarity of the solvent combination. This pyridine non-recoverable fraction is in agreement with the observation

reported in literature which states that soil extraction by pyridine results in nitrogen enrichment of Humic substances.[111] This is because pyridine binds strongly to Humic substances thereby increasing the amount of nitrogen in the soil system.

Looking at the general trend of total sorption behavior of pyridine in this study as shown in Figures 4.5 (a, b), it can be assumed that the non-removable portion is due to experimental losses and not chemical binding to peat. If this is true, the sorption trends after subtracting the non-removable pyridine at each activity would differ from the total pyridine sorption trend. In order to prove that the observed trend for pyridine is an accurate reflection of it's interaction with SOM, a table of data showing the removable pyridine at each activity is given in Table 4.17. The pyridine extractable contribution amounts is the difference between pyridine sorbed amount listed in Table 4.7 and the amount of pyridine still sorbed onto peat. This data has been plotted against pyridine activity to show the expected trend as can be seen in Fig. 4.11.

Table 4.17 Pyridine removable amount from peat at each activity from different media

Pyridine in acetonitrile		**Pyridine in acetone**		**Pyridine in hexadecane**	
Activity	Removed from peat (mg/kg)	Activity	Removed from peat (mg/kg)	Activity	Removed from peat (mg/kg)
1.86×10^{-5}	96.91	2.17×10^{-5}	57.93	1.81×10^{-4}	154.79
5.11×10^{-5}	212.38	1.73×10^{-4}	204.61	3.41×10^{-4}	300.87
6.57×10^{-5}	334.6	4.80×10^{-4}	247.44	8.737×10^{-4}	327.77
1.64×10^{-4}	429.06	1.37×10^{-3}	588.26	1.96×10^{-3}	586.64
1.85×10^{-4}	616.76	1.72×10^{-3}	620.63		
3.96×10^{-4}	844.52	2.05×10^{-3}	862.89		
7.61×10^{-4}	1534.85	2.59×10^{-3}	1173.77		
1.50×10^{-3}	1824.42	3.16×10^{-3}	897.13		
3.01×10^{-3}	3048.33				
4.53×10^{-3}	427707				

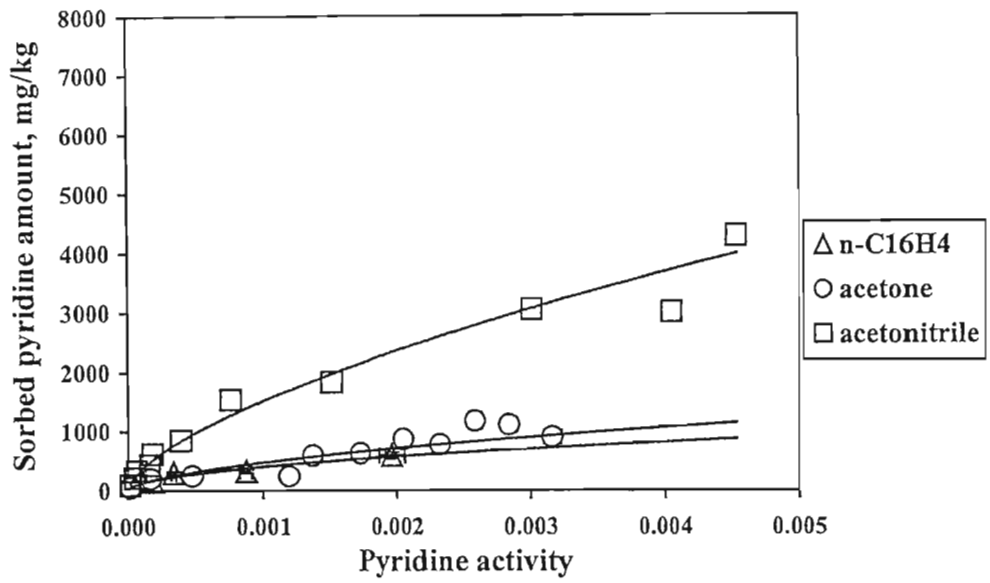


Fig. 4.11 Extractable pyridine sorbed amounts (mg per kg) from peat through desorption and extraction plotted against pyridine activity for acetonitrile,acetone,and hexadecane.

Fig. 4.11 show that the general sorption trends of pyridine to peat from acetone, acetonitrile, and hexadecane as shown in Figs. 4.5(a) and 4.5 (b), are not affected by removing the non-removable portion of pyridine. The observed trend before and after removing the non-removable pyridine are similar to each other for all the solvent systems. This clearly indicated that the non-removable pyridine is due to chemical interaction with peat.

It may be argued that the polar solvents dioxane and DMSO used for extraction at room temperature may not be sufficient to reverse the pyridine-SOM interactions. However DMSO is well know for its ability to disrupt and solubilize SOM[9].

Comparing the amount of pyridine removed for the pyridine in hexadecane system (Table 4.15) with the amount of acetonitrile removed (Table 4.12) after extraction with dioxane and DMSO provides an indication of the strength of pyridine and acetonitrile binding to peat. In the case of acetonitrile, it can be seen that a larger amount of acetonitrile (90 %)

is removed as compared with the smaller amount of pyridine (fraction removed 0.55 or 55%). Thus it can be concluded that pyridine binds more strongly than acetonitrile to peat.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the degree of humification study it can be concluded that a non-aqueous organic solvent medium is better for studying the interactions of specifically interacting organic compounds such as pyridine with peat. It was shown in Table 4.1 that the degree of humification of peat in water is greater than in the organic co-solvents used in the study. Therefore more peat would be solubilized in the aqueous media and as such the sorption trends would not reflect the true interactions within the macromolecular structure of peat.

It can also be concluded that sorption trends of pyridine to peat from the different solvent media, namely, pure water, pure acetone, pure acetonitrile, and pure hexadecane, are not affected by the volume sorption of the different solvent media by peat. The data in Figure 4.5 a,b and Figure 4.6 showed that the sorption trends remained the same after normalizing the sorbed pyridine amount (mg/kg) to reflect pyridine volume sorption (mg/L) per 1ml of the swollen peat phase. This confirmed that the trends for pyridine sorption are a true reflection of the interactions of pyridine with peat.

In case of sorption of pyridine and acetonitrile to peat in a multisolvent system it can be concluded that a solvent assisted and solvent competitive behaviour does exist. This is supported by results in Figure 4.7. At low solvent activities competition was less apparent than the solvent assisted effect. At higher solvent activities competition between acetonitrile and pyridine for peat sorption sites became more energetically favourable to acetonitrile, thereby dominating the sorption to peat over pyridine, resulting in a decreased sorption of pyridine to peat. An important aspect of this is that pyridine alone has only a limited ability to disrupt peat polar contacts in the dry phase. If acetonitrile would have disrupted the polar peat contacts by solvating only the potential compound sorption sites, pyridine would not have been able to compete effectively with acetonitrile for those sites. This however was not observed, as such acetonitrile must have solvated

the partner (functional moiety) of the disrupted polar peat contact that does not directly interact with pyridine. It can also be concluded that a co-operation between acetonitrile and pyridine exists which showed a solvent assisted sorption in the presence of a potential competitor. As such for a given system the interplay between solvent assisted penetration into polar peat contacts, and the solvent or solute competition for new sites at those disrupted contacts will determine the overall solvent effect on sorption of specifically interacting compounds such as pyridine.

A solvent non-assisted effect can be seen in Table 4.11. Increasing the acetone concentrations three fold had no effect on the sorption of pyridine to peat. It is known that acetone has a greater H-bonding basicity[113] compared to acetonitrile, and is also the more effective electron donor (according to Gutman's donor number)[129]. This would ensure that acetone would be more effective than acetonitrile at competing for peat sorption sites. This phenomena was evident in this study, whereby pyridine sorption to peat was lower from acetone than from acetonitrile as seen in Figure 4.5 a,b.

Desorption and extraction studies concluded that a sorbate assisted behaviour exists with respect to the chemical binding of the co-solvent acetonitrile to peat. Table 4.14 showed that the amount of non-removable acetonitrile increased by 80% in the presence of pyridine compared to the amount non-removable without pyridine additions, although pyridne does not have any effect on the sorption of acetonitrile as displayed in Figure 4.4. It can also be concluded that pyridine acts as a Lewis base catalyzing a reaction between acetonitrile and peat. This co-operative behavior was not seen for the amount of non-removable pyridine in the presence of co-solvents acetonitrile and acetone, as indicated in Table 4.15. Thus the presence of co-solvents did not facilitate the irreversible binding of pyridine to peat.

Three possible scenarios for the interaction of pyridine with peat in the presence of organic co-solvents acetone and acetonitrile can be proposed after considering all the results obtained in this study.

The first is when the sorbate (pyridine) lacks the ability to penetrate into polar contacts of peat in a dehydrated system (hexadecane medium), but may interact with sites not requiring bond disruption. Upon solvation, the solvent may create new sorption sites via disruption of polar bonds, but sorbate molecules are unable to compete with the solvent for these new sites. No solvent-assisted sorption will be observed in this case. This behavior was seen for the sorption of pyridine from acetone (Figure 4.5), where acetone as the solvent solvated peat but did not promote the sorption of pyridine. This is more evident when one considers that pyridine sorption from hexadecane was similar to that of acetone, although hexadecane is known for it's very poor solvation ability and poor penetration of the peat macromolecular matrix.

The second is when the sorbate is not effective at penetrating into a polar peat contact alone. Penetration occurs together with solvation of all the SOM moieties that make up the contact. The sorbate competes favorably with the solvent for newly created sorption sites. An overall solvent-assisted sorption effect will be found. A solvent-assisted effect was observed (Figure 4.7) for pyridine in the presence of increasing acetonitrile concentrations.

The third is expected when a sorbate is effective at penetrating into dry SOM contacts, and solvation results in a decrease of sorption due to competition. This was observed in Figure 4.8, acetonitrile assisted the sorption of pyridine at low activities, at high activities a competition for the polar peat sites had occurred, pyridine sorption was reduced at the expense of the more energetically favorable sorption of acetonitrile to peat.

Considering the above scenarios and sorbate molecular characteristics such as size, polarizability, dipole moment, H-bond donating and accepting capability to name a few, sorption behavior may be classified and related to intensity of intra-SOM interactions. This will provide a basis for estimating the solvation effect on sorption of organic compounds by SOM.

5.2 Recommendations for Future Work

Two concepts for the nature of SOM exist in the literature. The first is that SOM consists of glassy and rubbery regions, similar to that of glassy and rubbery polymers.[11, 27, 29, 35, 36] The second concept is that SOM consists of nonpolar aggregates formed by inter and intra molecular binding between polar groups in the SOM macromolecule. [7, 127, 145] The fact that a physical and structural understanding of soil organic matter is still incomplete, and is still the subject of cutting-edge research activity, makes it clear that both concepts are central points in the understanding of organic compound binding in SOM.

The way forward with regards to the "glassy-rubbery" model would be to conduct Differential Scanning Calorimetry (DSC) studies on Humic materials. Should a glass transition be observed, sorption studies of polar and non-polar compounds from aqueous and non-aqueous systems should be conducted. This should be conducted over the temperatures spanning the temperature of the glass transition. More information can be gathered with regards to step increases in isotherm linearity for the glassy-rubber transition.

The way forward with regards to the "cross-linked" structure would be to evaluate the effect of solute polarity. Possible isomers that can be used for the study are *o*, *m*, *p*-dichloro- and dinitrobenzenes. Isomers within each set have different permanent dipole moments while the molecules are of approximately equal size. The results will demonstrate the significance of polarity effects. To test the effect of steric hindrances in such isomeric pairs, the lower polarity diethyl-substituted isomeric benzenes, which have nearly the same molar volumes as dinitrobenzenes, should be tested. This will provide more information with regards to the effects of different forces on the affinity of organic compounds for SOM.

This proposed future work will contribute to the goal of arriving at an integrated model for soil organic matter, which can elucidate the relationships between organic compound sorption, and the chemical and physical structure of SOM.

REFERENCES

1. J.L. Alrichs, "The soil environment". In: C.A.I. Goring and J.W.Hamaker (eds.) "Organic chemicals in the soil environment", Marcel Dekker, New York, Vol. 1,1972, 465-582.
2. F.J. Stevenson, "Humus Chemistry" , John Wiley, New York, 1982, 443.
3. W. Flaig, H. Beutelspacher, and E. Rietz, "Chemical composition and physical properties of humic substances", In: J.E. Gieseking (ed.) Soil components 1: "Organic compounds", Springer-Verlag, New York, 1975, 130-190, 336-402.
4. F.J. Stevenson, and M.S. Ardankani, "Organic matter reactions involving micronutrients in soils". In: J.J Mortvedt, P.M. Giordano, and W.L. Lindsay(eds.) Micronutrients in Agriculture, *Soil Science. Soc.*, Amer. Madison,1972, 79-114.
5. J.M. Tisdale, and J.M. Oades, Organic matter and water stable aggregates in soil, *J. Soil Sci,* 32, 1982, 141-163.
6. R.L. Wershaw, *Environ. Sci. Tech.*, 1993, 27, 814-816.
7. H. Schulten, and Schnitzer, *Naturwissenschaften* , 1993, 80, 29.
8. R.P. Schwarzenbach, P.M. Gschwend, and D.M. Imboden,. "Environmental Organic Chemistry", JohnWiley and Sons Inc., New York, 1993, 262-398.
9. M. Schnitzer, and S.U. Khan, "Soil Organic Matter", Elsevier, Amsterdam, The Netherlands, 1978, 5-99.
10. H. Schulten, H. *Fres., J. Anal. Chem.*, 1995, 351, 62-73.
11. Xing, B. and Pignatello, J.J. *Environ. Sci. Techonol.* 1997, 31, 792-799.
12. Weber, W.J. and Huang, H. *Environ. Sci. Techinol.* 1996, 30, 881-888.
13. H. Fujita, In: J. Crank, and G.S. Park, "Diffusion in polymers", Academic, London, 1968, 565.
14. M. Schnitzer, "Humic substances chemistry in the Environment." In: M.Schnitzer, S.U. Khan, (eds) "Soil Organic Matter", Elsevier, Amsterdam ,1978, 1-64.
15. M.B.H. Hayes, R.S. Swift, "The Chemistry of soil organic colloids." In: D.J. Greenland, M.H.B. Hayes, (eds) "The chemistry of soil constituents", Wiley, New York, 1978, 179-320.

16. F.J. Stevenson, "Humus Chemistry: Genesis, Composition, Reactions", Wiley, New York, 1982, 443.

17. S.A. Visser, "Surface active phenomena by humic substances of aquatic origin", *Rev Franc Sci Eau,* 1982, 1, 285-296.

18. M. Tschapek, C. Warsowski, "The surface activity of humic acid." *Geochim Cosmochim Acta*, 1967, 40, 1343-1345.

19. Y. Chen, M. Schnitzer, "The surface tension of aqueous solutions of soil humic substances", *Soil Sci,* 1978, 125, 7-15.

20. N. Senesi, M. Schnitzer, "Effects of pH, reaction time, chemical reduction and irradiation on ESR spectra of fulvic acid", *Soil Sci,* 1977, 123, 224-234.

21. N. Senesi, C. Steelink, "Application of ESR spectroscopy to the study of humic substances and their interactions with organic xenobiotics and metal ions", 1989, In: M.H.B. Hayes, P. MacCarthy, R.L. Malcom, R.S. Swift (eds) "*Humic Substances:In search for structure*", Wiley, New York, 1990, 3-35.

22. J.B. Weber, "Fate of organics in sludges applied to the land." Abs 5th Nat Conf "Acceptable sludges disposal techniques", Orlando-Fla, Iform Transfer Inc., 1978, 31, 117-124.

23. J.B. Weber, "Interaction of organic pesticides with particulate matter in aquatic an soil systems.", *Adv. Chemical series*, 1972, 111, 55-120.

24. G. Vettorazzi, "State of the art of toxicological evaluation carried out by the joint FAQ/WHO Expert committee on pesticide residues 3. Miscellaneous pesticides used in agriculture and public health", *Res Rev*, 1977, 66, 138-184.

25. A. Caldebank, "The bipyridilium herbicides", *Adv Pest control Res*, 1968, 8, 127-190

26. D. Wolfhart, "Controls needed on killer Herbicide", *Pac Island*, 1980, 51, 7-10.

27. R. Haque, S. Lilley, Infrared spectroscopic studies of charge transfer complexes of diquat and paraquat, *J Agric Food Chem,* 1972, 20, 57-58.

28. A.T. Kan, G. Fu, M.A. Hunter, and M.B. Tomson, *Environ. Sci. Technol.* 1997, 31, 2176-2185.

29. A.T. Kan, G. Fu, M.A. Hunter, W. Chen, C.H. Ward, and M.B. Tomson, *Environ. Sci. Technol.* 1998, 32, 892-902.

30. D.C. Scott, J.B. Weber, Herbicide phytotoxicity as influenced by absorption, *Soil Sci,* 1967, 104, 151-158.

31. B.V. Tucker, D.E. Pack, J.N. Ospenson, Absorption of bipiridylium herbicides in soil, *J Agric Food Chem,* 1969, 15, 1005-1008.

32. J.B. Weber, Interaction of organic pesticides with particulate matter in aquatic and soil systems, *Adv Chem Series,* 1972, 111, 55-120.

33. M.C. Carter, Amitrole,. In: Kearney P.C., Kaufman(eds), "Herbicides: Chemistry, Degradation and Mode of action", Dekker, New York, 1975, 377-398.

34. F.M. Armstrong, T.J. Sheets, The relationship of soil adsorption of EPTC to oats injury in various soil types, *Weeds,* 1967, 7, 88-90.

35. J.B. Weber, S.B. Weed, Effect of soil on the biological activity of pesticides. J.Series North Carolina State Univ Agric Experim Station, Raleigh-NC, 4087, 223-256.

36. L. Eliasson, V. Hallman, E. Tolf, Leaching of picloram fro different soils, 1969, *Sver Skogsvardsforb Tidskr*, 67, 491-501.

37. K.D. Courtney, D.W. Gaylor, M.D. Hogan, H.L. Falk, R.R. Bates, I. Mitchell, Teratogenic evaluation of 1,4,5-T, *Science,* 1970, 168, 864-866.

38. J.B. Weber, S.B. Weed, T.W. Waldrup, Effect of soil constituents on herbicide activity in modified soil field plots, 1974, p112-120.

39. C.R. Harris, Influence of soil type on the activity of insecticides in soil, *J Econ Entomol,* 1966, 59, 1221-1225.

40. S.U. Khan, H.A Hamilton, E.C. Hague, Fonofos residues in organic soil and vegatable srops following treatment of the soil with insecticide, *Pestic Sci,* 1976, 7, 553-558.

41. S.U. Khan, Adsorption of dyfonate (o-ethyl-s-phenylethyl-phosphonodithioate) on humic acid, *Can J Soil Sci,* 1977, 57, 9-13.

42. D.G. Crosby, A.S. Wong, J.R. Plimmer, E.A. Woolson, Photodecomposition of chlorinated dibenzo-p-dioxins, *Science,* 1971, 173, 748-749.

43. E.A. Woolson, R.F. Thomas, P.D.J. Ensor, Survey of polychlorodibenzo-p-dioxin in selected pesticides, *J Agric Food Chem,* 1972, 20, 351-354.

44. Y. Lutz-Ostertag, H. Lutz, Action de l'herbicide 2,4-D sur le developpement embryonaire et la feconidte due gibier a plumes, *C R Acad Sci Paris*, 1970, Series D 271, 2418-2421.

45. H.D. Dubey, R.E. Sigafus, J.F. Freeman, Effect of soil properties on the persistence of linuron and diphenamid in soils, *J Agron*, 1966, 58, 221-231.

46. R.L. Douding, J.F. Freeman, Residual phytotoxicity of fluomethuron in soils, *Weed Sci*, 1968, 16, 226-229.

47. R.G. Nash, Plant uptake of 14C-diuron in modified soil, *Agron,* 1968, *J* 60, 177-179.

48. E.G. Jarwoski, Chloracetamides. In Kearney P.C., Kaufman DD(eds) *Herbicides: Chemistry, degradation and mode of action*, Dekker, New York, 1975, 349-376.

49. T.W.R., Systems and Energy, Carcinogens Relating to coal conversion processes, 1976, US Energy Research and Development Administration, Oak Ridge, TN

50. L.H. Keith, W.A. Telliard, Priority pollutants. A perspective view, 1979, *Environ Sci Technol,* 13, 416-423.

51. W.W. Youngblood, M., Blumer, Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments, *Geochim Cosmochim Acta,* 1975, 39, 1303-1314.

52. J.A. Cole, Groundwater pollution in Europe, Water information Center, Port Washington, New York, 1975

53. M.C. Bowman, M.S. Schechter, R.L.Carter, Behavior of chlorinated insecticides in a broad spectrum of soil types, *J Agric Food Chem,* 1965, 13, 360-365.

54. W.J. Farmer, W.F.Spencer, R.A. Shepherd, M.M. Cliath, Effect of flooding and organic matter applications on DDT residues in soil, *J Environ Qual,* 1974, 3, 343-346.

55. E.P. Lichtenstein, Adsorption of some chlorinated hydrocarbon insecticides from soils into various crops, *J Agric Food Chem,* 1959, 7, 430-433.

56. T.M. Ballard, Role of humic sarrier substances in DDT movement through forest soils, *Soil Sci Soc Am Proc,* 1971, 25, 145-147.

57. J.R. Peterson, R.S. Adams, L.K. Jr. Cutcamp, Soil properties influencing DDT bioactivity, *Soil Sci Soc Am Proc*, 1971, 35, 72-78.

58. J.N. Pitts, D.Jr. Grosjean, T.M. Mischke, Mutagenic activity of airborne particulate organic pollutants, *Toxicol Lett,* 1977, 1, 65-67.

59. S.G. Wakeham, C. Schaffner, W. Giger, Polycyclic aromatic hydrocarbons in lake sediments. II. Compounds derived from biogenic precursors during early diagenesis, *Geochim Cosmochim Acta,* 1980, 44, 415-429.

60. A.C. Greiner, C, Spyckerelle, P. Albrecht, G, Ourisson, Hydrocarbures aromatiques dórigin geologiue. V Derives mon-et diaromatiques du hopane, *J Chem Soc,* 1977 , 3973-3993.

61. Z. Aizenshtat, Perylene and its geochemical signifance, *Geochim Cosmochim Acta,* 1973, 37, 559-597.

62. W. Haung, T.M. Young, M.A. Schlautman, H. Yu, and W.J. Weber, *Environ. Sci. Technlo,* 1997, 31, 1703-1710.

63. C.T. Chiou, and D.E. Kile, *Environ. Sci. Technol.* 1998, 32, 338-343.

64. Z. Chen., B. Xing, W.B. McGill, and M.J. Dudas, *Can. J. Soil. Sci.* 1996, 76, 513-522.

65. T.D. Gauthier, W.R. Setz, and C.L. Grant, *Environ. Sci. Technol* 1987, 21, 243-248.

66. D.W. Rutherford, C.T. Chiou, and D.E. Kile, Environ. Sci. *Technol* 1992, 26, 336-340.

67. P. Garthwohl, *Environ. Sci. Technol* 1990, 24, 1687-1693.

68. B. Xing, W.B. McGill, and M.J. Dudas, *Chemosphere* 1994, 28, 145-153.

69. B. Xing, W.B. McGill, and M.J. Dudas, *Environ. Sci. Technol.* 1994, 28, 1929-1933.

70. S.C. Wu, and P.M. Gschwend, *Environ. Sci. Technol.* 1986, 20, 717-725.

71. M.H.B. Hayes, Adsorption of triazine herbicides on soil organic matter, including a short review on soil organi matter chemistry, *Res Rev,* 1975, 32, 131-174.

72. M.D. Borisover, E.R. Graber, *Environ Sci. Technol,* 1998, 34, 1761–1776.

73. I.G. Burnes, M.H.B. Hayes, Stacey M, Spectroscopic studies on the mechanisms of adsorption of paraquat by humic acid and model compounds, *Pestic Sci,* 1973, 4, 201-209.

74. J. Katan, T.W. Fuhreman, E.P. Lichtendtein, Binding of ^{14}C-parathion in soil: a reassessment of pesticide persistence, *Science,* 1976, 193, 891-894.

75. S. Burchill, M.H.B. Hayes, D.J. Greenland, "Adsorption of organic molecules. In: Greenland" D.J., Hayes, M.H.B., (eds) "The Chemistry of Soil Processes", Wiley, New York, Chapt 6, 1981, 221-400.

76. T.D. Gauthier, K.A. Booth, C.L. Grant, W.R. Seitz, Fluoresence quenching studies of interactions between polynuclear aromitic hydrocarbons and humicmaterials., *Am Chem Soc-Div Environ Chem,* 1987, 27(1), 246-248.

77. S.U. Khan, Adsorption of bipyridilium herbicides by humic acids., , *J Environ Qua,l* 1974, 3, 202-206.

78. S.U. Khan, Equilibrium and kinetic studies of the adsorption of 2,4-D- and picloram on humic acid, *Can J Soil Sci,* 1973, 53, 429-434.

79. D.R. Narine, R.D. Guy, Binding of diquat and paraquat to humic acid in aquatic environments, S*oil Sci,* 1982, 133, 356-363.

80. C. Maqueda, J.L. Perez Rodriguez, Martin F, Hermosin MC, A study of the interaction between chlordimeform and humic acid from a typic chromoxevert soil, *Soil Sci,* 1983, 136. 75-81.

81. R. Turski, A. Steinbirch, Studies on the possibilities of binding herbicides of triazine derivates by humic acids, *Polish J Soil Sci,* 1971, 4, 120-124.

82. M.H.B. Hayes, Adsorption of triazine herbicides on soil organic matter, including a short review on soil organic matter chemistry, *Res Rev*, 1970, 32, 131-174.

83. J.D.Sulivan, G.T.Felbeck, A study of the interaction of s-triazine herbicides with humic acids from three different soils, *Soil Sci,* 1968, 106, 42-50.

84. G.C. Li, G.T. Felbeck, A study of the mechanism of atrazine adsorption by humic acid from muck soil, *Soil Sci,* 1972, 113, 140-148.

85. P. Gaillardon, R. Calvert, J.C. Gaudry, Adsorption of quelques phenylurees herbicides par des acides humiques, *Weed Res*, 1980, 20, 201-204.

86. N. Senesi, C. Testini, T.M. Miano, The environmental fate of hebicides: the role of humic substances, *Ecological Bull Stockolm*, 1980, 35, 477-490.

87. R.D. Carringer, J.B. Weber, T.J. Monaco, Adsorption-desorption of selected pesticides by organic matter and montmorillonite, *J Agric Food Chem,* 1975, 23,

569-572 88. J.A. Leeneer, J.L. Aldrichs, A kinetic and equilibrium study of the adsorption of cabaryl and parathion upon soil organic matter surfaces, *Soil Sci Soc Am Proc,* 1971, 35, 700-705.

89. N. Senesi, G. Padovano, E. Loffredo, Testini, Interactions of Amitrole, alachlor, and cycloate with humic acids.,1986b, Proc 2nd *Int Conf Environmental Contamination*, Amsterdam 1986, pp 169-171.

90. S.U. Khan, Equilibrium and kinetic studies of the adsorption of 2,4-D and picloram on humic acid, *Can J Soil Sci,* 1973a, 53, 429-434.

91. J. Kozak, Adsorption of prometryn and metachlor by selected soil organic matter fractions, *Soil Sci,* 1983, 136, 94-101.

92. H.J. Sterk, J.B. Weber, Behavior of polychlorinated biphenyls (PCBs) in soil and plants, *Environ Pollut.A*, 1982, 28, 291-312.

93. J.B. Weber, Interaction of organic pesticides with particulate matter in aquatic and soil systems, *Adv Chem Series*, 1972, 111, 55-120.

94. R.H. Pierce, C.E. Olney, G.T. Felbeck, Pesticide adsorption in soils and sediments, Environ Lett, 1971, 1, 157-172.

95. I. Lindqvist, Charge-transfer interaction of humic acids with donor molecules in aqueous solutions, *Swed J Agric Res,* 1982, 12, 105-109.

96. N. Senesi, C. Testini, Spectroscopic investigations of electron donor-acceptor processes involving organic free radicals in the adsorption of substituted urea herbicides by humic acids, *Pestic Sci,* 1983b, 14, 79-89.

97. U. Muller-Wegener, Uber die Bindung von s-Triazinen an Huminsauren, Geoderma, 1977, 19, 227-235.

98. N. Senesi, C. Testini, D. Metta, Binding of chlorophenoxyalkanoaic hervicides from aqueous solution by soil humic acids. Proc Int Conf Environmental Contamination, London 1984, CEP Cons Ltd. Edinburgh, pp 96-101

99. G.G. Briggs, "Molecular structure of herbicides and their sorption by soils", 1969, *Nature* 223:1288.

100. M.C. Melcer, M.S. Zalewski, J.P. Hassett, M.A. Brisk, Nature of the binding interactions between humic substances and hydrophobic molecules, *Am Chem Soc-Div Enviro Chem,* 1987, 27(1), 414-416.

101. T.S. Hsu, R, Bartha, Interaction of pesticide-derived chloroaniline residues with soil organic matter, *Soil Sci,* 1974, 116, 444-452.

102. G.E. Parris, Covalent binding of aromatic amines to humates. 1. Reactions with carbonyls and quinones, *Environ Sci Technol,* 1980, 14, 1099-1106.

103. E.P. Lichtenstein, J. Katan, B.N. Anderegg, Binding of "persistent" and "non-persistent" ^{14}C- labeled insectides in an agricultural soil, *J Argic Food Chem,* 1977, 25, 43-47.

104. H. De Jonge, Sorption, bioavailability and mineralization of hydrocarbons in contaminated soils. PhD Thesis, University of Amsterdam, Amsterdam, The Netherlands 1996.

105. M.L. Brusseau, and P.S.C. Rao, *Chemosphere* 1989, 18, 1691-1706.

106. M.L. Brusseau, R.E. Jessup, and P.S.C.Rao, *Environ. Sci. Technol.* 1991, 25, 134-142.

107. M.L. Brusseau, R.E. Jessup, and P.S.C. Rao, *Environ. Sci. Technol.* 1991, 25, 1501-1506.

108. M.L. Brusseau, and P.S.C. Rao, *Environ. Control* 1989, 19, 33-99.

109. H. Fujita, *Fres., J Anal. Chem.*, 1995, 351, 62-73.

110. J. Farrel, and M. Reinhard, *Environ. Sci. Technol.* 1994, 28, 63-72.

111. M.H.B. Hayes, "Humic Substances in Soil, Sediment, and Water", eds, John Wiley and Sons, Hemisphere Publishing Corporation, New York, 1985, 345-361.

112. C. Raymond, Crippen, Identification of Organic Compounds with the Aid of Gas Chromatography, eds, McGraw Hill Book Company, New York, 1973, 43 – 50.

113. M.H. Abraham, J. Andonian-Haftvan, G.S. Whiting, A. Leo, R.S. Taft, *Journal Chemistry Society*, Perkin Trans. 2 1994, 1777-1791.

114. M.D. Borisover, E.R. Graber, *Chemosphere,* 34, 1761-1776.

115. J.J Kipling, Adsorption from Solutions of Non-Electrolytes, Academic Press, London New York, 1965, 28-29.

116. W.G. Lyon, D.E. Rhodes, *Environ. Toxicol. Chem*, 1993, 12, 1405-1412.

117. T.E. Daubert, R.P. Danner, Physical and Thermodynamic Properties of Pure Chemicals, eds, Hemisphere Publishing Corporation, 1989, 2-202.

118. W.G. Lyon, D.E. Rhodes, The swelling properties of soil organic matter and their relation to sorption of non-ionic organic compounds, EPA–600/2-91/033, 1990.

119. V.V. Gorbatchuk, S.A. Smirnov, B.N. Solomonov, A.I. Konovalov, *J. Gen. Chem. USSR (Engl. Transl.)*, 1990, *60*, 1069-1074.

120. V.V. Gorbatchuk, M.A. Ziganshin, B.N. Solomonov, *Biophysical Chemistry*, 1999, *81*, 107-123.

121. D.W. Rutherford, C.T. Chiou, *Environ. Sci. Technol., 1992, 26*, 965-970.

122. M.M. Kononova, "Soil Organic Matter", eds, Pergamon Press, Oxford, 1966, p 544.

123. V.I Kasatochin, *Soil Science*, 1974, 8, 80.

124. C.N.R. Rao, "Ultraviolet and Visible Spectroscopy Chemical Applications", Butterworths 3rd edition, 1975, 270-286

125. D.A. Skoog, F.J. Holler, T.A. Nieman, "Principles of Instrumental Analysis", Saunders Colledge Publishing, 1992, 842-846.

126. H. Hachenberg, P.A. Schmidt, "Gas Chromatographic Headspace Analysis", Heyden, 1977, pp 30-40, 80-96.

127. R.C. Shriner, R.C. Fuson, D.Y. Curtin, "Systematic Identification of Organic Compounds", 4th ed., John Wiley & Sons, Inc., New York, 1959

128. C.T. Chiou, D.E. Kile, *Environ. Sci. Technol*, 1994, 26 (6), 1339-1144.

129. R.W. Taft, N.J. Pienta, M.J. Kamlet, E.M. Arnett, *J Org. Chem.*, 1981, 46, 661-667.