

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

**Application of Microwave Technology
To Effect On-site Regeneration of GAC**

by
K.C. Mahesh

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment of
the requirements for the degree of
Master of Science in Environmental Science (Toxicology).

1989

APPROVAL SHEET

Title of Thesis: Application of microwave technology to effect
on-site regeneration of GAC.

Name of Candidate: K.C. Mahesh

Master of Science in Environmental Science (Toxicology), 1989

Thesis and Abstract Approved:

Dr. Leonard Dauerman

Date

Associate Professor

Department of Chemical Engineering

Dr. Richard B. Traftner

Date

Associate Chairman

Department of Environmental Science

Dr. John R. Shuring

Date

Associate Professor

Department of Civil and Environmental Engineering

VITA

Name: Mahesh K.C.

Degree and date to be conferred: Master of Science in Environmental Science
-(Toxicology), 1989.

Secondary Education: St. Joseph's High School, Hassan, India, 1980.

<u>Collegiate institutions attended</u>	<u>Dates</u>	<u>Degree</u>	<u>Date of Degree</u>
N. J. Institute of Technology	01/88-12/89	M.S.Env.Sc.	December 1989
University of Mysore	8/82-12/86	B.S.C.E.	January 1987

Major: Environmental Science (Toxicology).

ABSTRACT

APPLICATION OF MICROWAVE TECHNOLOGY TO EFFECT ON-SITE REGENERATION OF GAC

K.C. Mahesh, Master of Science in Environmental Science(Tox), 1989

Thesis directed by: Dr. Leonard Dauerman

The off-site regeneration of granulated activated charcoal(GAC), spent as a result of stripping of organics from aqueous waste streams, represents a burdensome cost both because of the actual cost of regeneration and legal liability associated with shipping a hazardous waste off-site: that liability is reflected in huge potential costs associated with mishaps enroute for the self-insured or high premiums paid to the casualty insurance companies for those generators that are insured by third parties. Thus there is a need for the development of a process to effect on-site regeneration of spent GAC cost-effectively.

This thesis mainly focuses on the technical feasibility of microwave treatment to effect regeneration of GAC. This study has shown that microwave treatment of spent GAC can effect the on-site regeneration in a potentially cost-effective process. The regeneration of GAC with an adsorbed organic compound was studied. The compound was a toxic dye, namely, methylene blue. This is a polyaromatic compound containing chlorine, sulfur, and nitrogen atoms. It is a chloride salt. It is non-volatile and decomposes at $190^{\circ}C$. Our experiments showed that GAC with methylene blue adsorbed can be regenerated up to 100%; thus, even when a non-volatile compound is adsorbed on GAC, microwave technology can effect regeneration. The regeneration is effected utilizing microwave technology in a manner

consistent with its application on-site, scaled-up. The regenerability of spent GAC was investigated for three successive cycles of adsorption and regeneration. The results showed a good regeneration capacity, even at the end of fourth adsorption and, on an average, 98.2% removal of the adsorbed organic was achieved by microwave treatment.

The process appears to proceed by the following stages: water in the GAC pores are directly heated up by the microwaves leading to volatilization; the steam, thus formed, forces the air out of the pores creating an *inert atmosphere*; the GAC, a strong microwave energy absorber, heats the organic to its pyrolysis temperature; the pyrolyzed organic fuses into the GAC skeleton. This mechanism explains the observed results.

More importantly, this mechanism suggests that the most intractable soil contaminants, namely, dioxins and PCBs, can be treated by microwave technology. Assuming that soil and GAC behave similarly, it is possible that the aforementioned contaminants which are polyaromatic compounds will pyrolyze. This investigation is suggested, but not undertaken, in this thesis.

*To my wife, Asha
and my Parents.*

Acknowledgment

This work would not have been possible had it not been for my advisor, Dr. Leonard Dauerman. His great support, constant questioning and constructive criticism made this work and my education more than it would have been without him. I have learnt a great deal from him.

I am grateful to Dr. Richard B. Trattner for his constant encouragement throughout my course work and for his effort and time in reviewing this work. His comments helped to clarify some difficult concepts in the body of the text.

I am grateful to Dr. John R. Schuring for his effort and time in reviewing this work.

I would like to acknowledge G. Windgasse for her constant help with my laboratory work. Finally I would like to thank Kadur S. Manjunatha for his great help with my learning \LaTeX .

Contents

1	Introduction	1
1.0.1	Regulatory Evaluation	2
1.0.2	Experimental Design	4
2	Theory	7
3	Literature review	19
3.1	Review of regeneration techniques:	19
3.1.1	New Inventions:	23
3.2	Methylene blue:	26
4	The Adsorption Studies	28
4.1	Experimental	28
4.1.1	Measurement of Methylene blue in solution:	28
4.1.2	The Adsorption Process:	33
4.2	Results and Discussion	35
5	The Microwave Treatment	37
5.1	Experimental	37

6	The Regeneration Studies	40
6.1	Experimental	40
6.2	Results and Discussion	45
7	Extraction Studies	48
7.1	Overview	48
7.2	Experimental	49
7.2.1	Preliminary extraction studies:	49
7.2.2	Extractions using ethanol:	60
7.3	Results and Discussion	64
8	Decomposition Studies	67
8.1	Overview	67
8.2	Experimental	68
8.2.1	Solid methylene blue:	69
8.2.2	GAC saturated with methylene blue:	69
8.2.3	GAC saturated with methylene blue and in dry state:	70
8.2.4	Equipment and Parameters:	71
8.3	Results and discussion	72
9	Conclusion	73
9.1	Future studies	76
	Bibliography	78
	Appendix-1	81

List of Tables

4.1	Calibration data for methylene blue in water	31
4.2	Results of Adsorption Studies	34
6.1	Results of Regeneration Studies	43
6.2	Summary of Results	44
7.1	Calibration data for methylene blue in Ethanol	51
7.2	Calibration data for methylene blue in Acetone	52
7.3	Calibration data for methylene blue in Methanol	53
7.4	Calibration data for methylene blue in Propanol	54
7.5	priliminary Extraction Results	59
7.6	Soxhlet Extraction Results	62
7.7	Results of Extraction after Microwave Treatment	63
A.1	Properties of GAC used	82
A.2	Influence of solvents on adsorption	83

List of Figures

2.1	The Elecromagnetic Spectrum.....	8
2.2	A Plane Monochromatic Electromagnetic wave	9
2.3	Sketch of Penetrating Capability as a Function of Frequency.....	14
2.4	Variation of Dielectric Parameters with Moisture content	15
2.5	Variation of Loss tangent with Moisture content.....	16
4.1	Spctrum of methylene blue on a UV/Visible Scanner	30
4.2	Calibration Curve for methylene blue in water.....	32
5.1	Set up for Filterpaper Experiment	38
6.1	Flow Diagram showing regeneration procedure	42
7.1	Calibration Curve for methylene blue in ethanol.....	55
7.2	Calibration Curve for methylene blue in acetone.....	56
7.3	Calibration Curve for methylene blue in methanol.....	57
7.4	Calibration Curve for methylene blue in propanol	58
8.1	Setup of experiment for GC/MS analysis	68
8.2	TIC of decomposition of solid methylene blue	84
8.3	Mass spectra of decomposition products of solid methylene blue	85
8.4	NBS Library Search results for Figure-8.3	86
8.5	TIC of decomposition of adsorbed methylene blue	87
8.6	Mass spectra of decomposition products of adsorbed methylene blue	88
8.7	NBS Library Search results for Figure-8.6	88
8.8	TIC of decomposition of adsorbed methylene blue in water	89
8.9	Mass spectra of decomposition products of Saturated GAC with Water.....	90
9.0	NBS Library Search results for Figure-8.9	90
9.1	Ion chromatogram for Figure-8.8.....	91
9.2	Calibration curve for flow meter.....	92

Chapter 1

Introduction

A major operation in the treatment of waste water, industrially, and potable water, municipally, entails the adsorption of the organics by passing the aqueous stream through a bed of granulated activated charcoal(GAC). The usual practice is to have the spent GAC regenerated off-site. There are two drawbacks, one, traditional, and the other, a reflection of our present environmental concerns. The traditional drawback is cost. The cost has increased greatly because use of GAC has increased exponentially. The new consideration is the legal liability. Shipping spent GAC off-site creates a plethora of legal responsibilities. Accidents en route can lead to burdensome liabilities to remediate environmental damage and also toxic tarts. Besides, that liability is reflected in huge potential costs associated with mishaps enroute for the self-insured or high premiums paid to the casualty insurance companies for those generators that are insured by third parties (These aspects are in greater detail in following pages). Therefore a need exists to effect regeneration of GAC on-site.

On-site regeneration of GAC has been effected using externally added steam. But this has been largely confined to the use of GAC to strip off organics from the

gas phase, because, when the GAC is used in waste water treatment, it becomes water logged and regeneration must be effected by more drastic treatments like multiple hearth furnaces.

The objective of this thesis was to effect the regeneration of GAC used to cleanse aqueous streams on site. The approach that is taken in this study is to see whether or not microwave heating can effect regeneration of spent GAC. The means is to transfer the energy that can be translated into heat energy directly to the water molecules. That energy is also transferred directly to the organic molecules. Also, that energy is transferred directly to the GAC particles. The GAC particles arc if irradiated with microwave energy. The combined effects of direct heating of the water, the organics, and the GAC and, in addition, the arcing of the GAC, result in the removal and/or destruction of the adsorbed organics.

The volatiles are not environmentally acceptable. In any treatment process, the volatiles generated as part of the process, would require extra control equipment for their treatment. In the present microwave technology there is no need for an off-gas control technology because the adsorbed organic is pyrolyzed within the GAC skeleton. From this it is evident that it is technically possible to effect GAC regeneration on-site.

1.0.1 Regulatory Evaluation

The U.S. Environmental Protection Agency (EPA) has developed a complex far reaching program to regulate the management of hazardous waste in accordance with Resource Conservation and Recovery Act (RCRA). The program is designed to track and regulate hazardous waste from generation to ultimate disposal, i.e., from *cradle to grave*. EPA identifies hazardous waste based on its quantity, con-

centration, toxicity and characteristics. Based on these factors, EPA has drawn up a list of wastes to be considered as hazardous waste under RCRA program.

When the GAC is used to treat a waste which is listed, after the treatment, the used GAC will become contaminated with hazardous waste. According to subtitle C of RCRA this contaminated GAC is also considered hazardous. Any action of storing, treating, transporting and disposing will trigger RCRA.

If the truck carrying this waste meets with an accident leading to a potential spill, then it is life time liability for the parties involved. The above scenario will invoke the following laws:

- Comprehensive environmental response, compensation and liability act.

(CERCLA)

- Water pollution control act. (WPCA)
- Spill compensation control act. (SCCA)
- Hazardous material transport act. (HMTA)

On the other hand, when the generator has on-site, closed, microwave treatment facility there are potentially the following advantages:

1) The GAC being the sorbent material is desorbed using microwave treatment and it is reused thereby :

- saving the cost of activated carbon.
- once it is reused and recycled it is exempted from subtitle C of RCRA.

2) If the GAC has to be disposed of, after optimum cycles of reuse, one can desorb

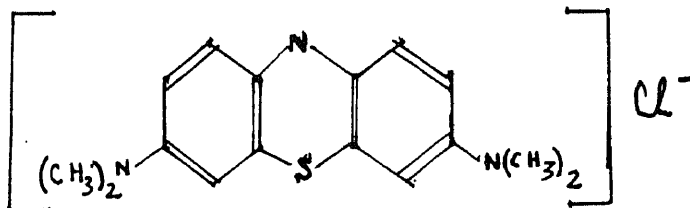
the GAC before disposal using this microwave treatment technology. The above process renders the waste non-hazardous leading to easy disposal methods.

3) There is no liability burden on the generator, in case of an accidental spill.

4) Disposal costs will be less.

1.0.2 Experimental Design

The first series of experiments were designed to determine whether or not the GAC can be regenerated. The criterion used for determination of regenerability is whether or not GAC's adsorptive capacity changes significantly after three cycles of adsorption and regeneration. The adsorbent used is methylene blue. This is a large molecule having a molecular weight of 373.90. It contains three aromatic rings one of which is heterogenous. The structure is:



It is non-volatile and a toxic dye.

This laboratory has developed a comprehensive innovative hazardous waste treatment technology utilizing low density power microwave energy. Processes studied include the following.

1. Desorption of volatiles from substrates (sand, soil, GAC, molecular sieves, sludge):

- a) Steam distillation - fixed bed
 - b) RDW-reactor- fluidized bed
2. Destruction of organics:
- a) Arcing /heating in RDW-reactor in fluidized bed
3. Immobilization of heavy metals in soils:
- a) Vitrification of contaminated soil with scrap iron to form non-conductive magnetic ferrites
4. Regeneration of spent GAC beds:
- a) Desorption of non-volatiles
 - b) Regeneration of GAC
5. Interaction of microwave with clay soils
6. Resource recovery of organics:
- a) Chemical reactions effected in the RDW reactor
7. Treatment of recalcitrant (non-biodegradable) organics:
- a) OH radicals (from persulfates, limes bleach etc.) react with recalcitrant organics adsorbed on substrates or in solution
8. On-site (no excavation) treatment of contaminated soil:
- a) modification of existing technology
9. Encapsulation of metals by spraying a mist of calcined ceramics onto a fluidized bed

This thesis will focus upon the fourth process, namely regeneration of spent GAC beds. The purpose of these studies was to demonstrate in principle that on-site regeneration of spent GAC can be effected. That having been shown, the next question is whether or not the process is feasible. These studies were done bench-scale on a common household microwave oven. Thus conclusions concerning feasibility can not be drawn. However, the overall project on the study of microwave treatment of hazardous waste, of which the present study is one part, is presently proceeding to the pilot plant and scale-up stages. Then the insights developed in this study will shape the studies on the feasibility of using microwave treatment to regenerate hazardous waste on-site. The other processes will be subjects of future reports issued by this research group.

Chapter 2

Theory

The regeneration of GAC using microwave technology involves four basic components: 1) Microwave; 2) GAC; 3) Water; 4) Methylene blue. It becomes necessary to understand the theory and properties of each of these components and also the theory behind the interaction of each of these with microwave energy. An attempt has been made to explain the theory of interaction of these four components.

Microwave (MW) is a form of electromagnetic radiation with no rest mass. The frequency of microwave ranges from 100 Mz to 300 GHz, with a wave length ranging from 3m to as small as 1mm. The microwave band can be seen at the middle of the electromagnetic spectrum as shown in Figure-2.1.

Though microwave has wide range of frequency, the frequency available for industrial users are 915 MHz and 2450 MHz. Usually all household microwave ovens operate at 2450 MHz. Microwave energy is composed of electric field and magnetic field at right angles to each other as shown in Figure-2.2. [1]

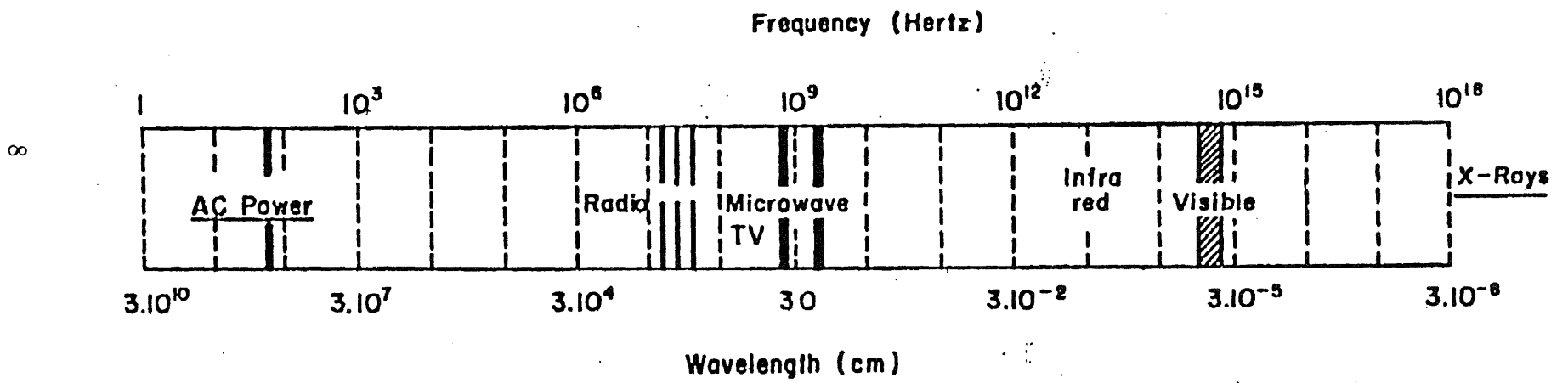


Fig.2.1 The Electromagnetic Spectrum.

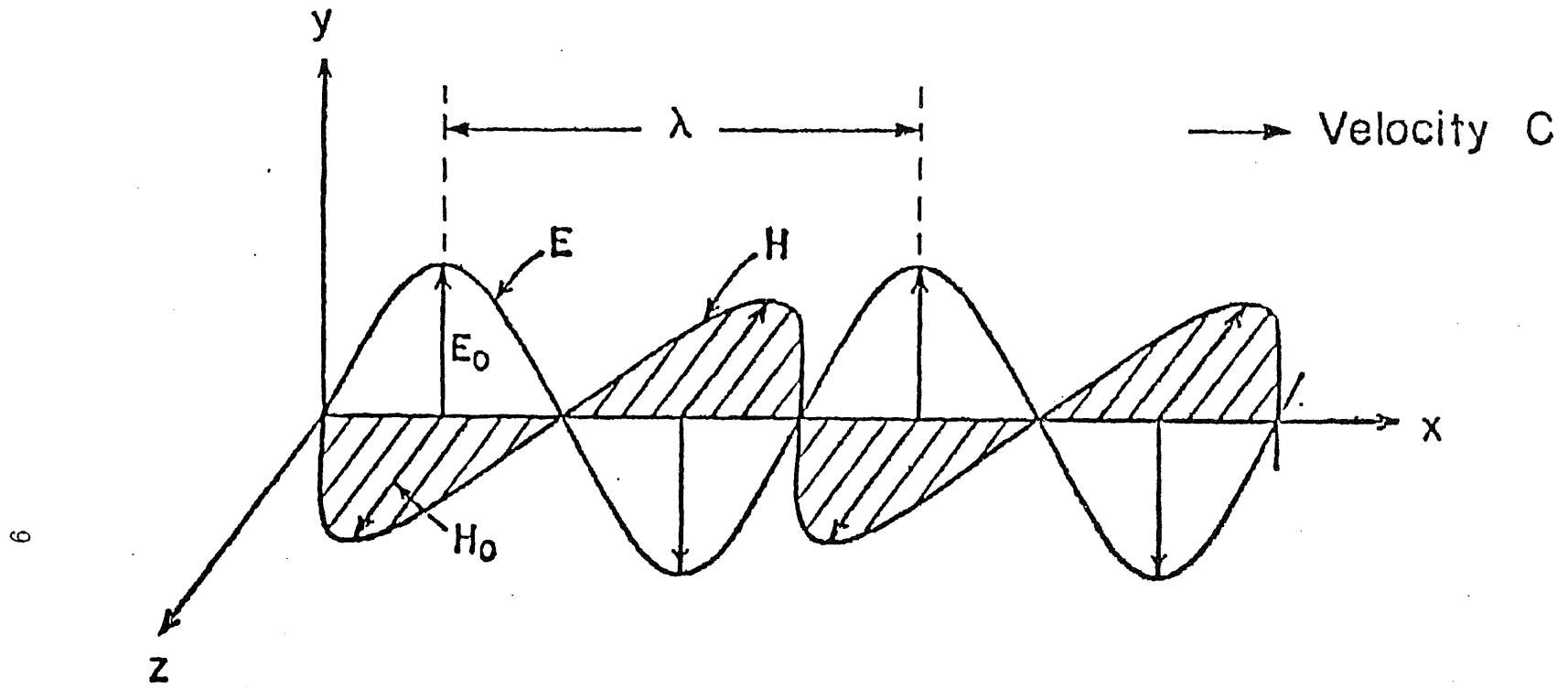


Fig.2.2 A Plane Monochromatic Electromagnetic Wave.

To understand the concept of heating by microwave, certain things about material properties should be known. There are basically three classes of materials in a microwave system: [2]

a) conductors

b) insulators

c) dielectrics

Most good conductors are metallic. These materials reflect microwave. However, absorption is “skin-deep” in a conductor. Therefore if the surface to volume ratio of a conductor is high enough, then, the conductor becomes an absorber and not a reflector. It has been observed that a metal in the form of wire absorbs microwave energy very well. The second class of materials namely insulators show a small amount of reflection and absorption but a large amount of transmission/diffraction of microwave through them, e.g: ceramics, teflon. The third class of materials, dielectrics, have properties going all the way from insulators to those of metals. A number of factors affecting the dielectric properties are discussed in following pages. The absorption of microwave energy is more complex. As microwave penetrates into any material it gets attenuated. The depth of penetration -DOP- is generally defined as the depth at which the power of the incident wave is decreased by 50%. This means that 50% of the power is absorbed between the surface of the object and the penetration depth. [1]

The interaction of the microwave radiation with any material depends on the dielectric properties of the material. There are real and imaginary parts of dielectric constant designated as ϵ' and ϵ'' respectively. Generally ϵ' is called as dielectric constant whereas ϵ'' is called loss factor. Another important parameter

is the loss tangent $\tan \delta = \epsilon'' / \epsilon'$. The penetration depth is given by the equation: [1]

$$D = \frac{0.189\lambda_0}{\sqrt{\epsilon'}\sqrt{\sqrt{1 + \tan^2\delta} - 1}}$$

where D= Depth of penetration

λ_0 = wave length in vacuum.

It is evident from the above equation that, the larger the $\tan \delta$, the smaller will be the penetration depth. Also an increase in ϵ reduces D. The absorption of microwave energy is related to loss factor(ϵ''). If the loss factor is high, most of the transmitted energy is absorbed in the material. On the other hand if the ϵ'' is small, most of the transmitted energy will pass through the material of finite thickness. Another variable is the frequency or the wave length: for reasons stated earlier this parameter can not be freely chosen.

Many dielectrics have the ability to be polarized by an applied electric field. This means that the molecules inside the material try to align themselves in a direction opposite to that of the applied field; the result is that the average internal electric field between the molecules is reduced. The amount by which the internal field is reduced is proportional to the dielectric constant of the material. As the material is polarized by an external field, it essentially reorders the molecules in the material. This occurs due to addition of potential energy to the state of each molecule. If now external field is suddenly removed or changed in direction, the molecules will try to return to their more or less random orientation. To this, the stored potential energy is converted into random energy which causes the molecules to collide and give up their extra energy in the form of heat. This loss of externally applied energy within a material is referred to as 'relaxation'. The time lag between

the applied field and the resultant polarization implies an irreversible conversion of energy to heat. This time lag is called as 'relaxation time'. Molecules which display long relaxation time can not absorb microwave energy very well, e.g: polymers. On the other hand, molecules which show strong random motion, e.g: heated steam, have a too short relaxation time, and do not absorb microwave energy either.[2]

In the microwave oven the external field changes its direction 2450 million times per second. This causes the dipoles to rotate so as to realign with the field very fast, which causes intermolecular collision generating heat.

GAC contains graphitic material. The free electrons in graphite are easily moveable and are subjected to microwave field. These free electrons change their orientation frequency times. This causes lot of heat produced in GAC and this is one reason why GAC is heated up rapidly with microwave energy. When a magnetic material is subjected to microwave energy it absorbs the magnetic component of the microwave field, which causes the material to heat up, e.g. ferrites.

The next component of interest is water. The heating effects of non-ionizing radiation depends on the penetrating power of radiation. Experiments were done on water and the data shows that the penetrating power is peak at the microwave region (Figure-2.3). [1]

The amount of moisture in a substance greatly affects the dielectric constant of the material. The reason is that water has a very high value of dielectric constant (78) , whereas many base material will have a much lower value . As the percentage of water in the material increases, its dielectric constant increases more or less proportionately. As an illustration, the variation of dielectric parameters with moisture for Douglas fir is shown in Figure-2.4.

The loss tangent increases with increasing moisture content but levels off and shows decrease on further increase of moisture Figure-2.5. In a multicomponent system the dielectric constant will always lie between the values of that of its components. [2]

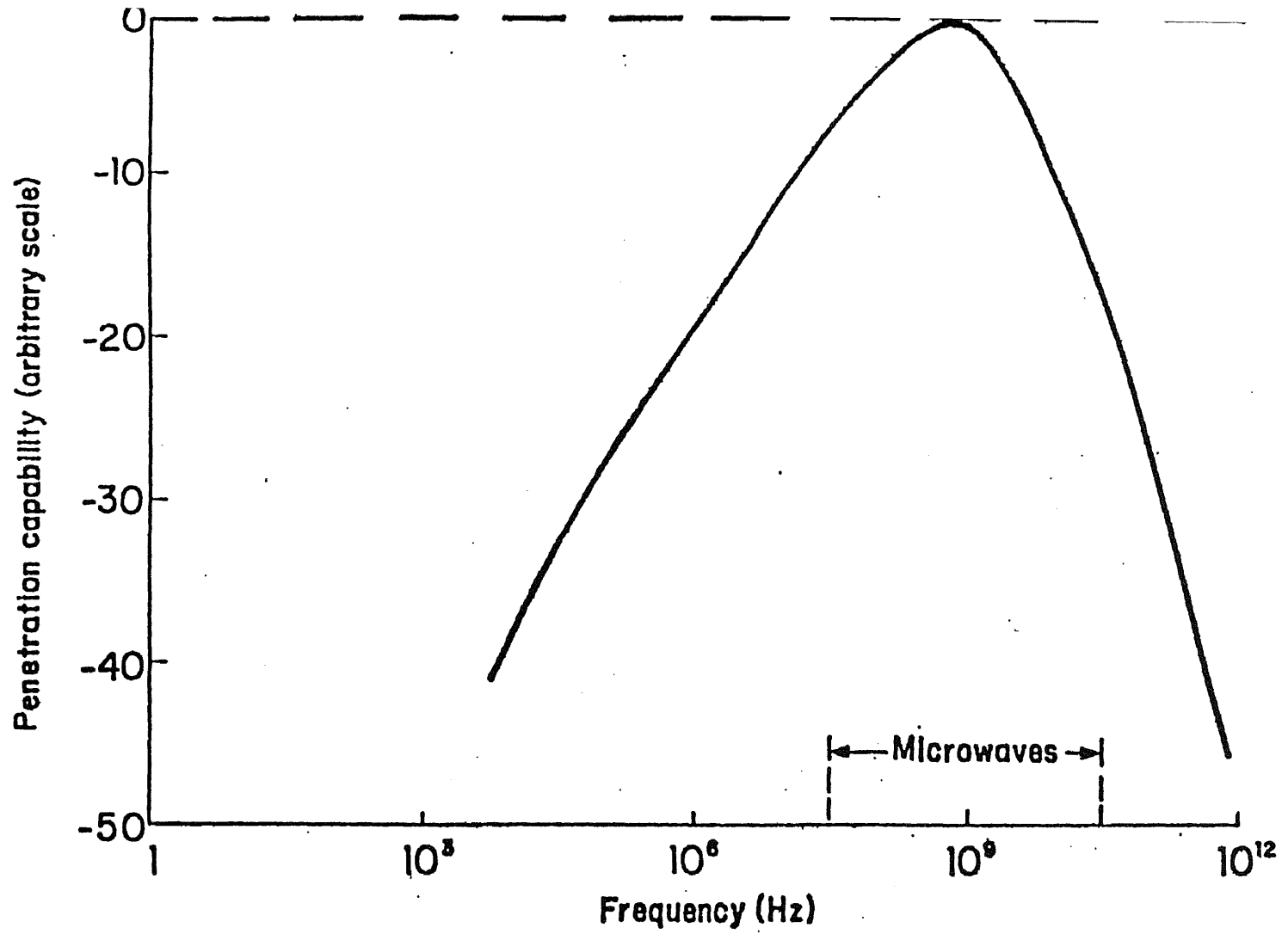
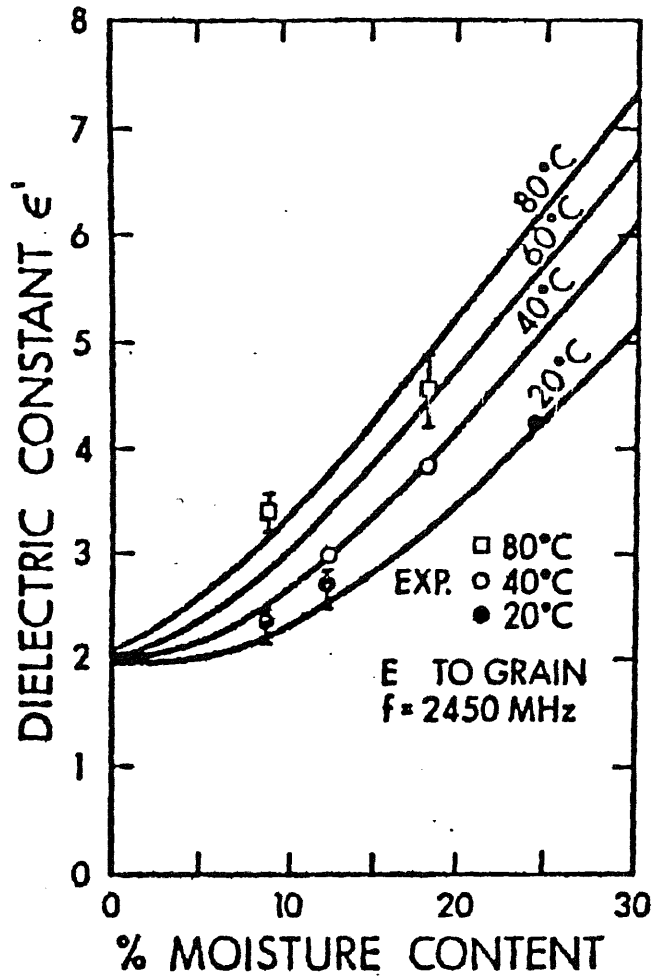
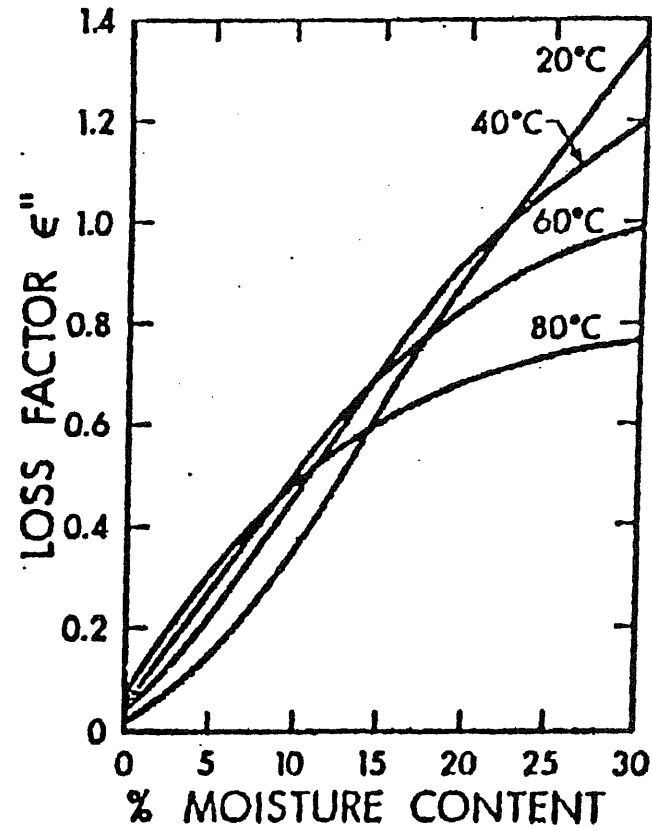


Fig. 2-3 Sketch of Penetration Capability as a Function of Frequency.

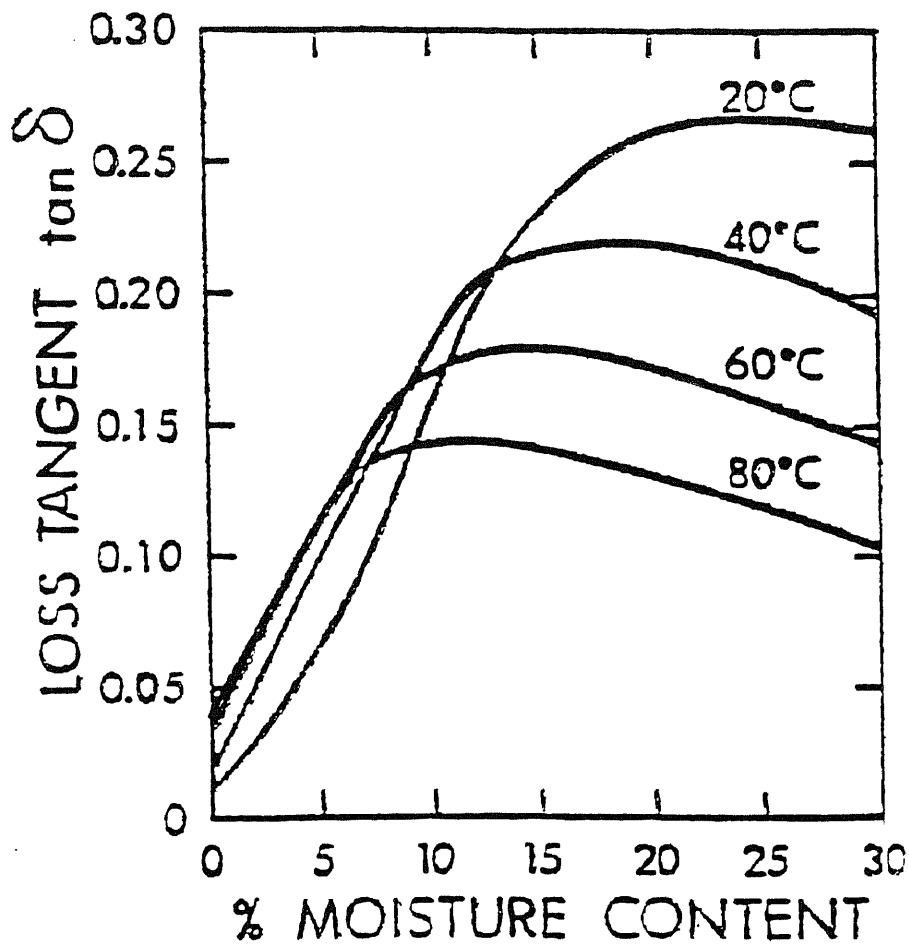
Figure-2.4 Variation of Dielectric Parameters with Moisture content



Dielectric constant versus moisture content for Douglas fir with temperature as the parameter. Theoretical values are shown by solid lines and a few experimental points are given for comparison; s.g. = 0.40.



Dielectric loss factor of Douglas fir at 2450MHz versus moisture content with temperature as the parameter; s.g. = 0.40.



Loss tangent (loss factor \div real part of dielectric constant) of Douglas fir at 2450 MHz versus moisture content with temperature as the parameter; s.g. = 0.40.

Figure-2.5 Variation of Loss tangent with Moisture content

In the present work, the GAC and water are the two components of concern and are assumed to follow the above theory. The GAC is wet and submerged in water during the course of microwave treatment. Thus, because of moisture in the component mixture, the dielectric constants could be probably high with losses ranging from 0.1-1.

The density of a material can greatly affect the value of the dielectric constant. If the air voids are present in a material the dielectric constant and loss factor decreases. The dielectric constant of air is 1.0; air is considered transparent to microwaves. Since all other non gaseous materials have dielectric constants greater than one, air inclusions will always reduce a material's dielectric parameters. Hence as the density of the material increases its dielectric constant increases almost in a linear proportion. [2]

The void ratio of GAC is large, therefore, air will fill the pores. But when it is put in aqueous solution, the air is displaced by water or sorbate. Thus the possibility of decrease in dielectric properties of the multicomponent system in microwave due to air is overruled.

The temperature dependence of dielectric constants can be quite complex in nature, because at a given frequency the dielectric loss may increase or decrease with temperature. A typical result of variation of dielectric parameters with temperature is shown in fig-5 for Douglas fir, wherein we can see the increase in ϵ' and decrease in ϵ'' with temperature. It is known from the previous works that the temperature behaviour of a dielectric material that absorbs water is mainly dependent on the moisture content.[2] Since GAC in the present series of experiments was submerged in water when exposed to microwave, this temperature relationship may be of significance.

Another important physical parameter which have to be discussed for the present experiments is the thermal conductivity of the material. This is the ability of a substance to conduct heat throughout its volume. In our experiments, there is water both inside and outside the GAC. As the system is subjected to microwave they both (GAC and water) heat up simultaneously and independently. Water can reach a maximum temperature of $100^{\circ}C$ at which point it is converted into steam, whereas the GAC can heat up to a higher temperature. Thus there exists a thermal gradient between inside and outside the GAC particles.

The physical geometry and structure of the particle to be microwaved will also influence the interaction phenomena. With regard to granular material like GAC there will be variations in the density and size of each particle which may be the natural result of the process itself. Thus it is often difficult to determine accurately the dielectric properties of granular materials.

The fourth component of interest in our experiment is methylene blue. Methylene blue is chosen for these studies as it represents a heterogeneous, non-volatile, aromatic compound. It has a negative charge on it. It is a heavy molecule with a molecular weight of 373.9.

Chapter 3

Literature review

3.1 Review of regeneration techniques:

The use of activated carbon for the purification of potable water or the tertiary treatment of wastewaters is well known. Purification processes using activated carbon have proven very effective for industrial wastes, particularly those containing organic matter that is not easily biodegraded. It was on June 7, 1976 that the *National Resources Defense Council* reached an agreement with EPA to study a group of substances in industrial effluents, and the development of appropriate regulations for their control. These substances are known as “priority pollutants”. This list has more recently expanded in an EPA list of 129 pollutants. A massive volume of literature illustrates the need for removal of priority pollutants from wastewater. Adsorption is the most common method. Activated carbon has been used almost exclusively to adsorb the 129 priority pollutants from wastewater.[23] However, for processes using activated carbon to be economically feasible, after the carbon has been saturated, some means of regenerating it must be employed to render it suitable for reuse. Various methods of regenerating activated carbon has been proposed and implemented. These generally employ chemical, thermal or

biological processes for effecting regeneration of the spent carbon.

Carbon used for vapor phase adsorption are regenerated by passing low pressure steam through the carbon bed to evaporate the adsorbed solvent and convey it to the exit where the steam is condensed and the solvent is recovered in a liquid state. This method of regeneration by passing steam is adopted in the case of volatile adsorbates.[9]

Desorption of the adsorbate with a solvent can restore much adsorptive capacity in some applications. But these types of desorption by extraction seldom restores the full capacity. The effectiveness of the methods depends on the adsorbate and proper choice of solvent for the corresponding sorbate. Generally regeneration from liquid phase application is accomplished by thermal means. The thermal energy is used in conjunction with other desorption methods like washing the adsorbed organic using dil. NaOH, neutralization and fermentation of adsorbed organic substances. A patented work assigned by Calgon Carbon corporation, was an improved method on washing. This was a multistage washing. Activated carbon impregnated with caustic will be regenerated by using three stage wash with caustic solutions ranging from 30 to 50 % at a temperature ranging from $72^{\circ}F - 150^{\circ}F$ with a contact time of 3-24 Hrs. This method claims that it removes both organic and sulfur contaminants.[19]

Later those preliminary steps were discontinued and the carbon was directly subjected to oxidation either with air at $300 - 600^{\circ}C$ or with steam and/or CO_2 at $800 - 900^{\circ}C$. The carbon recovery was satisfactory and adsorptive capacity was restored. The thermal desorption behaviour of organic compounds loaded on activated carbon is governed by thermal stability of the adsorbate and the adsorption energy. Suitable regeneration processes and operating conditions may be selected

from the knowledge of thermal desorption pattern. Where desorption without decomposition is expected, low temperature regeneration with adsorbate recovery was employed. However in some instances where decomposition occurs, high temperature reactivation may be necessary to recover sufficient adsorbent activity.

Presently thermal treatments are the most commonly used methods of regenerating activated carbon. However these methods are characterized by large losses of activated carbon. The type of equipment employed causes further pulverizing of the carbon thereby filtering it was a big problem. This was one of the main reasons for gradual abandonment of regeneration of powdered carbon. In fact this led to the development of broad spectrum types of granular carbon useful for many industrial purification processes.[9]

Another different approach for oxidizing the impurities adsorbed on activated carbon was by using a patented *electrolysis cell*. This was a process used for regenerating activated carbon particles contaminated by oxidizable adsorbates. An electrolysis cell is divided by a liquid permeable membrane to define an anodic and a cathodic chamber therein both filled with electrolyte during operation. Recycling conduits communicate with the anode chamber and a recirculating pump to establish a fluid circuit therewith. A suspension of particles of activated carbon contaminated by oxidizable impurities suspended in an aqueous solution of an electrolyte is loaded into the fluid circuit and circuited therethrough. A voltage applied to the electrodes of the cell develops an electrolysis reaction in the aqueous solution of the electrolyte and atomic oxygen is liberated at the surface of the anode electrode. As particles of the activated carbon flow through the anode cell they come in contact with the atomic oxygen which oxidizes the impurities adsorbed by the particles. Complete oxidation was achieved after circulating for sufficient time to

oxidize all impurities. The carbon thus treated was reused for fresh adsorption.[15]

Another successful general method developed was rotary kiln. This was a combination of thermal and steam treatment. The carbon moves counter currently to a mixture of combustion gases and superheated steam. In this system the recovery was reported to be 90-95%. The multiple hearth furnace was developed to regenerate spent carbon. These were generally heated internally with gas burners. This thermal treatment was in the presence of air, to burn the carbon monoxide and hydrogen produced by regeneration reaction. The wet carbon enters the top hearth. Evaporation of moisture and carbonization of much of the adsorbed organics is accomplished on the upper hearths. The activation reaction takes place on the lower hearths. Recoveries of 90-95% are reported in this treatment. One of the recent technology was the spent carbon in the form of aqueous slurry is subjected to the action of oxidizing gases at high temperatures and elevated pressures. Under these conditions the adsorptive capacity of the carbon was restored.[9]

In recent years much research has been devoted to studies of regeneration of activated carbon. To avoid loss of activated carbon through pulverization and offset the problem of filtration associated with it, a new technique of regenerating the spent carbon was developed. By this technique the carbon particles are **fluidized** and are then treated in conjunction with either hot steam or thermal oxidation methods. Several different ways of this technique are as follows:

1. The spent carbon is dewatered to approximately 50% moisture, and a high velocity low pressure air stream carries the moist carbon in a fluidized form into a patented regenerator. Within the regenerator, the spent carbon is exposed to an oxidizing atmosphere at a controlled high temperature. The gas stream on leaving the regenerator is immediately quenched to a low temperature and no

further reaction occurs, and the regenerated carbon is separated. This method is now being operated on an industrial scale. Regeneration efficiencies range from 85-90%. [9]

2. Another fluidizing technique regenerates the activated carbon by passing it downward through a patented regenerator, while the regenerated combustion gas is passed upwardly through it. Steam, N_2 gas or CO_2 is fed to a mixing zone to raise the temperature in an upper fluidizing layer to $300 - 450^\circ C$. [25]

There are not many methods of regeneration by biological treatment. However it is very interesting to know that a patented method makes use of biological treatment to regenerate the spent carbon. This treatment was used in the course of purifying wastewater, containing organic matter which are difficult to oxidize (e.g. surfactants). The wastewater was purified by adsorption onto activated carbon, which is biologically regenerated by microorganisms attached to the granules. [16]

In the year 1986 the USSR scientists came up with a regeneration method using radiation. The carbon used to treat effluents from pesticide plants were regenerated using gamma-rays. This method combines the conventional adsorption and purification, with radiation treatment of the sorbent. [22]

3.1.1 New Inventions:

By and large all the regeneration techniques discussed so far were achieved by heating to a temperature sufficient to desorb the adsorbate typically. Effective adsorbance create a problem in regeneration since, generally, the more effective is the adsorbent, the more difficult it is to remove the adsorbate. Long regeneration times and large purge gas volumes are therefore required for a moderate temper-

ature purge gas to desorb the adsorbate. This is due in part to the poor thermal transport inherent in these methods and with these adsorbent and substrate materials. More over, heat requirements are high since not only the adsorbent (which can be very large in itself) but also the adsorbent support, the adsorbent column, associated conduits and large quantities of purge gas often must be heated. The long regeneration times are poor in efficiency and large volumes of purge gas result in effluents which are very dilute in the adsorbed component. Usefulness of the adsorbed component as a by-product is thereby reduced since more processing will be required to recover the component from the dilute gas. Higher temperature purge gas could be used for more rapid desorption but this may also degrade the adsorbent capacity.

In the prior art, dielectric heating (in particular, microwave heating) has been suggested for many heating processes including drying, vulcanization of rubber, detoxification of dangerous substances and polymerization of fiberglass laminates. For example U.S Pat.No 3,77,234 suggests the use of microwave radiation for removing volatile polar vehicles from non-polar materials (dielectric loss factors of about 0.0001 to 0.1) specifically drying of synthetic polymers. Conventional heating plus a purge gas flow is also used(see U.S Pat.No 4,011,306), but as a result of poor heat transfer this can require long regeneration times or high temperatures. German Offenlegungschrift No. 2,107,717 describes a particular circulation system for moving an activated charcoal through adsorption reactor and then through a regeneration reactor where in microwave energy is applied for releasing adsorbed gases and then the charcoal is recirculated back again through the adsorption reactor. It is inherent from such continued circulation of the charcoal adsorbent that the charcoal is readily subject to attrition and mechanical degradation. Microwave heating in the presence of an added regenerating or purge gas, such as steam,

for regenerating carbon adsorbents apparently is disclosed in Japanese Kokai No. 76/43,394 and 76/43,395. These Kokai also reveal that only certain active carbon are receptive to microwave heating of an extent adequate for desorption and regeneration with the heat treatment history of the carbon adsorbent effecting and determining whether desorption by microwaves be operable. Japanese Kokai No. 76/145,491 concerns regenerating an activated carbon through exposure to high frequency electrical field to remove adsorbed substances by discharge, using small discharge plasma.[17]

The prior art of present study also includes, such as described in U.S Patent No. 4,038,050, an electrical desorption of molecular sieve adsorbents wherein during desorption-regeneration an electrical flow is provided from one electrode and then from particle to particle of the adsorbent to another electrode. As is well known in the art, heating with microwaves provides high frequency oscillatory movement of the molecule with in the material by the combined interaction of the electric and magnetic fields associated with absorbed electromagnetic energy. The rapid temperature increase of the material is caused by this molecular friction.

A patented work, assigned by Sanyo Electric KK, makes use of the application of the microwave energy in conjunction with heated steam. In this case the substrate was heated up using microwave energy at 2450 or 915 MHz., and steam is passed at high temperature. By combined effect of these two the desorption was achieved.[13]

A work similar to present study, was carried out in Japan, and is the subject of a patent. The adsorbate used was aqueous methylene blue solution. The activated carbon was shaken for about 18 hours in the sorbate solution. The saturated carbon was heated for 10 min in the microwave oven to regenerate it. The

adsorption was tried again, the measurements were made by calorimetric analysis. It was found that as the time of microwave absorption increased, the adsorption capacity of regenerated carbon approached that of original activated carbon.[18]

3.2 Methylene blue:

Methylene blue is a polyaromatic compound containing chlorine, sulfur and nitrogen atoms. It is a chloride salt: it is also named as methylthionine chloride. It is a trihydrate, dark green, odourless crystal with bronze luster or cryst powder; color index is basic blue 9; The structure is $C_{16}H_{18}ClN_3S$: with C=60.08%, H = 5.67%, Cl=1.09%, N=13.14%, and S=10.03%. It has a molecular wt. of 373.9 and may crystallize with 3,4 and 5 moles of water. Methylene blue is non-volatile. Interestingly, its vapor pressure data is not available. From the manufacturer the value of its decomposition temperature is known to be $190^{\circ}C$ which happens to be its melting point too.[6] It is very soluble in water; 1 gm dissolves in 25 ml of water and 65 ml of alcohol: soluble in chloroform and is insoluble in ether. It is known to be incompatible with caustic alkalis dichromates, alkali-iodides and reducing agents. For analysis, a UV/visible spectrophotometer can be used. The absorption maximum is known to be 668 and 609 nm.[5]

The use of methylene blue as a dye is well known from a long time. However it has been proved that it is a toxic dye. It is one of the drugs that have clearly been shown to cause clinically significant *Hemolytic anemia*. In the year 1967 Stokinger and Mountain developed a list of industrial chemicals known to cause Hemolysis because of G-6-PD deficiency. Methylene blue is in that list.[26]

Methylene blue is used as an adsorbate compound in several studies of ad-

sorption. The studies have been done by K.Boki; S.Tanada on activated carbon and pyrolysis ash using methylene blue as sorbate.[10] Adsorption isotherm of methylene blue onto activated carbon were developed. The studies were done on activated carbon from west Germany and Japan, the equilibrium concentration of 100 ppm at $25^{\circ}C$ and at a Ph of 6.68 was 360.4 mg/gm and 52.1 mg/gm respectively for these two types of carbon. In the above studies it took 8 days to attain equilibrium adsorption at $25^{\circ}C$ with constant shaking. Methylene blue has been used as one of the sorbates in a patented work assigned by Matsuo.T. [18]In this work the methylene blue is used with activated carbon as adsorbent and regeneration using microwave energy was attempted.

Chapter 4

The Adsorption Studies

4.1 Experimental

4.1.1 Measurement of Methylene blue in solution:

Methylene blue has a CAS registry number 61-73-4 and a formula $C_{16}H_{18}N_3S.Cl$. The molecular weight is 373.90. It is very soluble in water. One gram of methylene blue dissolves completely in 25 ml of water.[5]

Procedure:

- 100 mg of methylene blue was weighed accurately with a balance having a least count of 0.1 mg and this was dissolved in distilled water in a 1000 ml Erlenmeyer flask, and made up to the volume. Thus 1000 ml, 100 mg/l methylene blue standard solution was prepared.
- From the primary standard of 100 mg/l, dilutions were made to generate different standards, which are as shown in Table-4.1.
- To measure the absorbance a UV visible spectrophotometer - Spectronic 20 of Bosch and Lomb make was used along with Bosch and Lomb special cuvetts.

The readings were taken with the wavelength set at 660 nm. This was chosen based on the spectrum of wavelength scan on Gilford UV/Visible scanner. The spectrum is as shown in Figure-4.1. The absorbance of various standard concentrations are read and tabulated as in Table-4.1.

The standard solution required filtration because of the following:

While measuring the absorbance of methylene blue sample after adsorption on GAC, the powdered carbon particles were affecting the absorbance reading. Thus the situation called for preparation of a calibration curve of Filtered Concentration vs Absorbance.

A calibration curve of absorbance Vs concentration in mg/l was prepared is as shown in Figure-4.2. The variation was almost linear and hence a *linear best fit* analysis was done on the data. This linear variation was well supported by the fact that the correlation coefficient was greater than 0.99.

SAMPLE = 1 METHYLENE BLUE

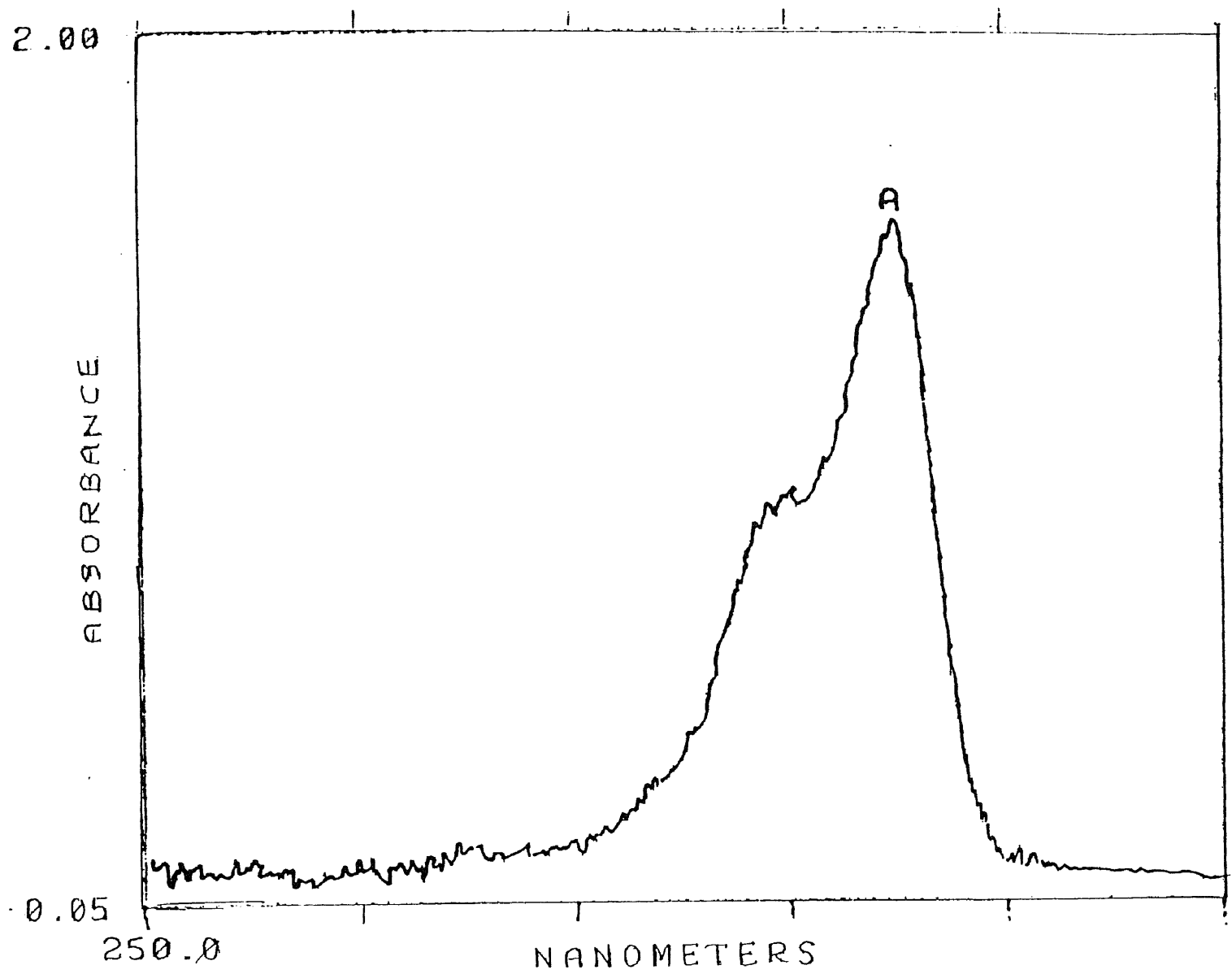


Figure-4.1 Spectrum of methylene blue on a UV/Visible Scanner

TABLE-4.1*Calibration data for methylene blue in water*

Point	Concentration (x)in mg/l	Absorbance (y)
1	0.4	0.03
2	0.6	0.03
3	0.8	0.05
4	1.4	0.06
5	1.6	0.07
6	2.0	0.09
7	8.0	0.28
8	10.0	0.39
9	15.0	0.41
10	18.0	0.51
11	20.0	0.64
12	30.0	0.85

Regression Analysis

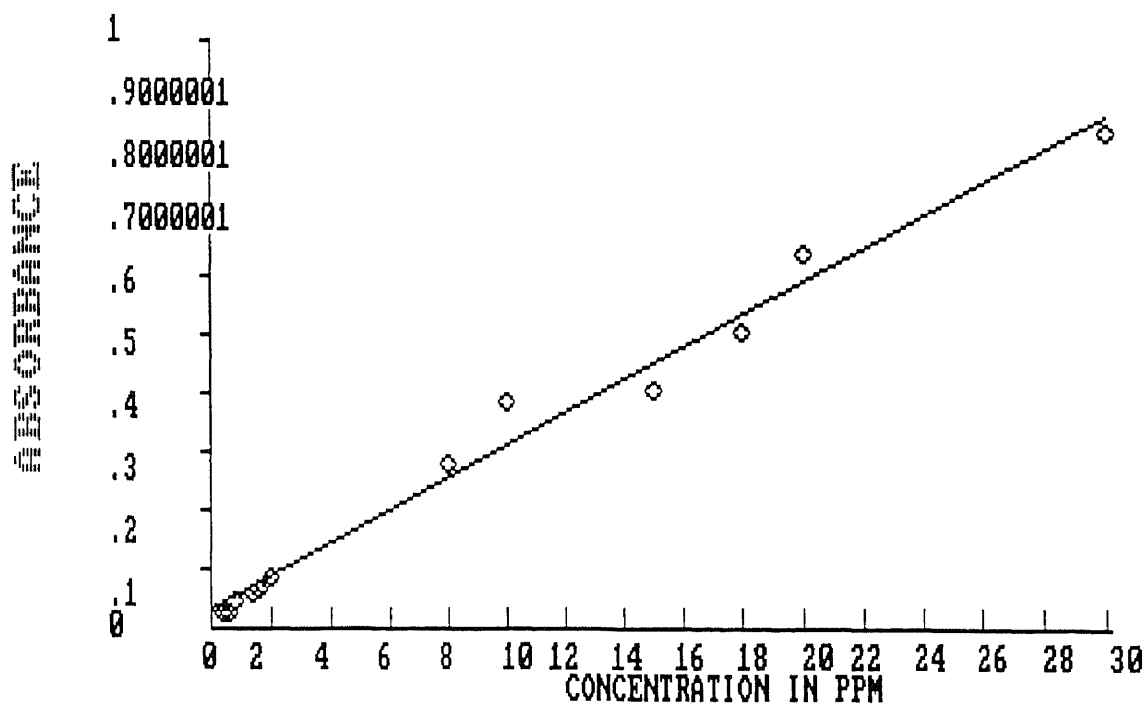
Slope = 2.80598 E-02

Intercept = 3.20957 E-02

Correlation = 0.99

Equation of bestfit is: $y = 0.0281 x + 0.03$

Figure-4.2 Calibration Curve for methylene blue in water



4.1.2 The Adsorption Process:

The adsorption of methylene blue was done on GAC samples. The GAC used was Calgon F-100/8 x 30 type. The details on the properties of GAC used are shown in Table-A.1 of Appendix-1. The procedure for adsorption is as follows:

- 100 ml of a 100 mg/l methylene blue solution was placed in a 150 ml beaker and 0.5 grams of GAC was added to it. The mixture was stirred continuously by keeping it on a magnetic stirrer using a Teflon coated stirrer at constant speed. Stirring was continued for 90 minutes. Beyond that time, it was determined in earlier experiments that the rate of adsorption slows down very much.
- Stirring was stopped after 90 minutes. Making sure that all GAC particles are at the bottom, the filtration was done. The filter paper used was Whatman No.1. First the filter paper was wetted with water, then the surface water was removed by vacuum. The methylene blue solution was poured from the beaker and 5 ml of which was allowed to rundown; after that, the filtered sample was collected in a dry cuvette.
- The absorbance reading was taken on a Spectronic 20 and recorded as in Table-4.2. The process was repeated on a number of samples and corresponding readings are tabulated as in Table-4.2.

TABLE-4.2*Results of Adsorption studies*

Sample no.	Absorbance before adsorption	Absorbance after adsorption	Final concentration in mg/l	Adsorption in mg/l	Wt. of MB adsorbed in mg	percent weight adsorbed
1	2.0	0.5	16.73	83.27	8.33	83.27
2	2.0	0.51	17.10	82.90	8.29	82.90
3	2.0	0.51	17.10	82.90	8.29	82.90
4	2.0	0.6	20.28	79.72	7.97	79.72
5	2.0	0.33	10.68	89.32	8.93	89.32
6	2.0	0.41	13.52	86.48	8.65	86.48
7	2.0	0.16	4.63	95.37	9.54	95.37

4.2 Results and Discussion

From Table-4.2, it can be seen that the values of percent weight of methylene blue adsorbed varies from a low 79.9 to a high of 95.4. This variation was due to a number of factors. Since the weight of GAC used was 0.5 gms, even a small variation in amount of GAC taken from sample to sample will alter the results. The variations can also be attributed to the concept of *active centers*. This theory postulates that adsorptive power does not exist on all portions of a surface, but that it is localised on sites called active centers. On these active centers, the surface atoms are arranged in pattern having specific affinities.[9]

Granular activated carbons are known for their good performance in purification processes. There are many parameters which affect the adsorption process of activated carbon of which solvent is very important. The adsorption of most organic compounds is less from an organic solvent than from an aqueous solution. One cause is the greater solubility of organic compounds in organic solvents. Another factor is solvent adsorption. In contrast to water which is weakly adsorbed by carbon organic solvents are strongly adsorbed. [9] Therefore methylene blue dissolved in water was used to achieve adsorption on GAC. An interesting table of data on influence of solvents on adsorption which involves methylene blue also is presented in Appendix-1 as Table-A.2.

Small polar molecules will not be adsorbed whereas large molecules like methylene blue will be adsorbed. On the other hand, methanol, ethanol, propanol and butanol will not adsorb because they are small molecules. As the carbon number increases, the adsorption increases. Methylene blue has a carbon number 16 and a complex structure. To attain equilibrium adsorption of methylene blue on

activated carbon at 25°C (room temperature) the mixture has to be shaken for 8 days.[10] Since the purpose of this study was not the determination of the adsorptive capacity of activated carbon used, it was decided to go for relative values. A shaking period of 90 minutes gave satisfactory results. The results are as shown in Table-4.2.

Temperature is also one of the factors affecting adsorption. As the temperature increases the adsorption increases. However all the experiments were carried out at room temperature.

Chapter 5

The Microwave Treatment

5.1 Experimental

This process will be in continuation with the adsorption process. The microwave oven used was : Sharp Carousel II; Convection microwave oven; power output 700 watts; frequency:2450 mhz; serial no. 19763.

- After the process of adsorption on GAC sample , the supernatant aqueous methylene blue solution was slowly and carefully decanted from the beaker. To minimize the amount of methylene blue solution adhering to the beaker walls, the sample was washed with distilled water twice and the wash water was also decanted carefully. Care was taken to minimize losses of GAC particle in this process.
- 20 ml of water was added to the same beaker containing saturated GAC sample. The mixture was heated in the *high* mode in the microwave oven for 10 minutes. It was observed that there was continuous arcing in the GAC particles in the presence of water.

- Next, the microwave irradiated dry GAC was cooled for 15-20 minutes. Now the GAC sample is ready for second adsorption.

A small experiment was conducted just out of curiosity. The GAC sample saturated with methylene blue was placed in a beaker; as usual 20 ml of water was added to it. The beaker was covered at the top with Whatman No.1 filter paper as shown in Figure 5.1.

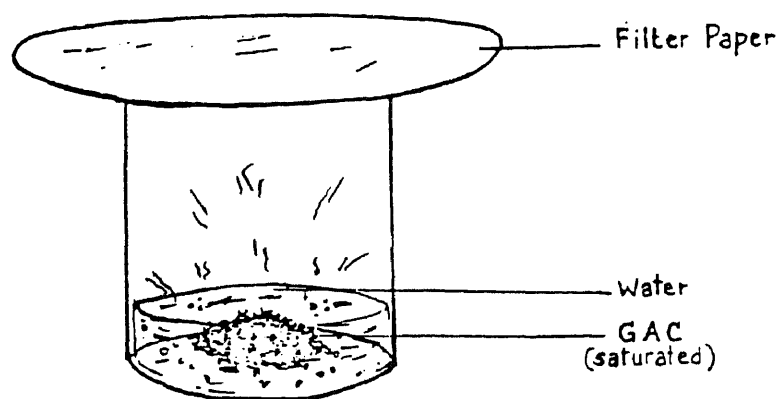


Figure 5.1 set up for filter paper experiment

The unit was placed in microwave oven and power was turned on in high mode. After 10 minutes of microwave treatment the unit was taken out. We could see the blue coloration of methylene blue on the filter paper. This experiment was repeated three times and each time the blue color appeared on the filter paper. It is not clear from the experiment whether or not the transport of methylene blue to the filter paper occurred as a result of volatilization or splattering. To distinguish

between these two mechanisms, baffles have to be placed between the mixture containing methylene blue and the filter paper. Volatile materials are not removed mechanically by baffles. To avoid the possibility that the baffles are below the dew point of a volatilized mixture of methylene blue and water, the baffles have to be arranged so that they can be heated to the temperature of the mixture.

Chapter 6

The Regeneration Studies

6.1 Experimental

The regenerability of GAC samples was studied based on three consecutive adsorptions. The process is explained as follows:

- As indicated earlier in section 5.1, after the microwave treatment, the GAC sample will be ready for second adsorption. To this GAC fresh 100 ml, 100 mg/l methylene blue solution was added and the process of adsorption was carried out as per section 4.1, for 90 minutes. After the adsorption the reading of absorbance was obtained and tabulated as shown in Table-6.1. This was the reading at the end of first cycle regeneration.
- After first cycle regeneration the GAC sample was again subjected to microwave irradiation as in section 5.1. Now the GAC sample is ready for third adsorption. The adsorption process was carried out as explained in section-4.1, which results in the absorbance reading at the end of II cycle regeneration.

- In a similar way, after the second regeneration cycle, the GAC sample was again subjected to microwave irradiation as in section-5.1, and is ready for the fourth adsorption. The adsorption process was carried out as in section-4.1.
- The readings obtained are tabulated as in Table-6.1. The procedure is depicted in the schematic flow diagram shown in Figure-6.

The overall results, namely, the percent adsorption and percent regeneration after each cycle , are tabulated as in Table-6.2.

Figure-6.1
Flow Diagram of Procedure to Determine the
Regenerability of GAC with Microwave Treatment

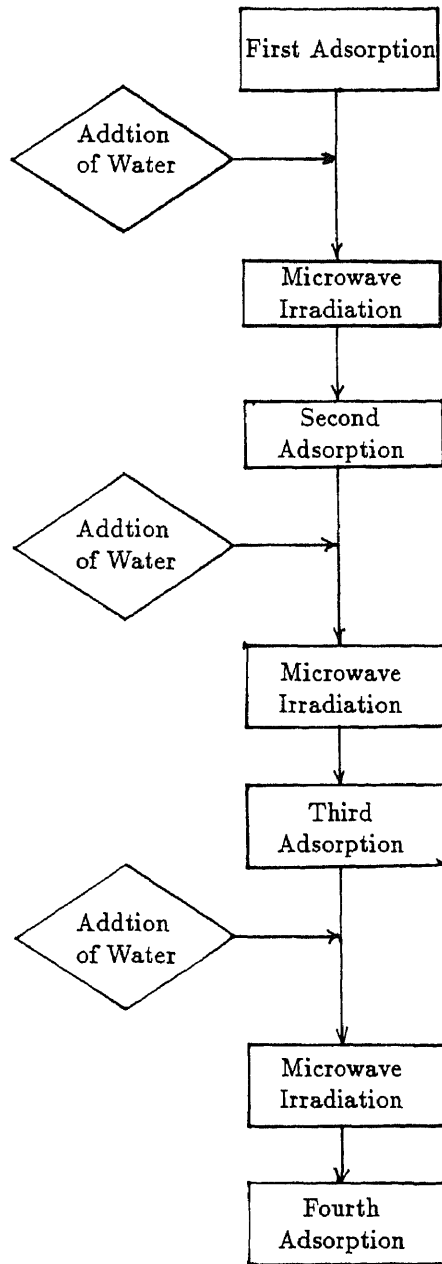


TABLE-6.1
Results of Regeneration studies

Sample no.	Cycle of adsorption	Absorbance before adsorption	Absorbance after adsorption	Final concentration in mg/l	Adsorption in mg/l	Wt. of MB adsorbed in mg	percent Regeneration
1	1	2.0	0.5	17.79	82.21	8.22	100
1	2	2.0	0.68	24.2	75.8	7.58	92.21
1	3	2.0	0.75	26.69	73.31	7.33	89.17
2	1	2.0	0.49	17.44	82.56	8.26	101.0
2	2	2.0	0.54	19.22	80.78	8.08	98.78
2	3	2.0	0.8	28.46	71.54	7.15	87.41
3	1	2.0	0.32	11.39	88.61	8.86	108.3
3	2	2.0	0.62	22.06	77.94	7.79	95.23
3	3	2.0	0.75	26.69	73.31	7.33	89.61
4	1	2.0	0.41	14.59	85.41	8.54	108.65
4	2	2.0	0.68	24.2	75.8	7.58	96.44
4	3	2.0	0.9	32.03	67.97	6.8	86.51
5	1	2.0	0.68	24.2	75.8	7.58	85.94
5	2	2.0	0.62	22.06	77.94	7.79	88.32
5	3	2.0	0.85	30.25	69.75	6.98	79.14
6	1	2.0	0.37	13.17	86.83	8.68	101.64
6	2	2.0	0.4	14.23	85.77	8.58	100.70
6	3	2.0	0.64	22.28	77.72	7.77	91.0
7	1	2.0	0.49	17.44	82.56	8.26	87.59
7	2	2.0	0.68	24.2	75.8	7.58	80.38
7	3	2.0	0.74	26.33	73.67	7.37	78.15

Note: The samples in table-3.2 have been continued for regeneration studies. Hence samples having identical sample # are same samples.

TABLE-6.2
Summary of Results

Sample no.	Percent Adsorption	Percent Regeneration after		
		I cycle	II cycle	III cycle
1	83.27	100	92.32	89.42
2	82.90	100.84	98.73	87.58
3	82.90	108.20	95.30	89.74
4	79.72	108.53	96.50	86.60
5	89.32	86.11	88.46	79.50
6	86.48	101.62	100.34	90.52
7	95.37	87.63	80.60	78.30
Mean	85.70	99.00	93.18	85.95

Specimen Calculation for Sample 1.

final concentration of methyleneblue = $(0.5-0.03)/(0.0281)=16.73$ mg/l(table 1,2)

adsorption = $100-16.73 = 83.27$ mg/l

weight of methyleneblue adsorbed = $83.27/10.0 = 8.33$ mg

percent weight adsorbed = $(8.33 \times 100)/ 10 = 83.3$

similarly after 1 cycle Wt. of methyleneblue adsorbed = 8.33 mg (table-3)

percent Regeneration = $(8.33 \times 100)/ 8.33 = 100$

similarly % Regeneration for II cycle = $(7.69 \times 100)/ 8.33 = 92.32$

6.2 Results and Discussion

It can be seen from Table-6.2, that for five out of seven samples the values for I cycle of regeneration was greater than 100% and the mean values for II cycle was 93.18% and for III cycle was 85.95%. There are variations in the results from sample to sample. This can be attributed to the size of the sample. Since the sample size taken was small, even a little variation in weight of any sample can lead to a spread in the results. But all samples show good regeneration capacity after microwave treatment. It can also be seen from Table-6.2, that the mean values of regeneration for all samples were very good. Even after three cycles of regeneration the GAC sample could adsorb 85.95% of the first adsorption.

From Tables 6.1 and 6.2 it evident that, almost all samples (but #5 and #7), surprisingly show increases in adsorption in the I cycle of regeneration. Five out of seven samples show values greater than 100% of the original adsorption. This was really a strange phenomenon: at most the desorption of the organics would be 100% and, consequently, the maximum regeneration could be 100%. But in this case the values are exceeding 100%.

Regeneration of GAC appears to follow the following steps during the microwave treatment phase: Microwave radiation will initiate two types of heating processes. Both the water and, also, the GAC are heated. GAC is a strong absorber of microwave.[7] The dielectric properties of certain material will increase with increase in moisture content in them. [2] Also microwave heats up the water inside GAC directly. Due to these two heating processes, the water inside the GAC is converted faster into steam than the water surrounding GAC. Thus microwave energy is absorbed by the GAC, water, and methylene blue individually and simul-

taneously. The temperature of the GAC rises quickly. The water present in the GAC pores is converted to steam. The steam so generated drives out the air from the pores and creates an inert atmosphere. Along with GAC, the methylene blue heats up. As a result of these combined heating effects, it is most likely that the adsorbed methylene blue gets pyrolyzed or carbonised and becomes a part of the GAC skeleton. In support of above arguments, a simple experiment was performed. Methylene blue was taken in a test tube, and heated under a Bunsen flame, initially the test tube above the methylene blue was heated to drive out air. It was observed that the methylene blue pyrolyzed to form a voluminous carbonaceous mass like sugar.

According to the above arguments, methylene blue is pyrolyzed, thereby, becoming a part of the GAC structure. Thus the adsorption should increase from one cycle to the next cycle. However, it is evident from Table-6.1 and 6.2 that, though there is good % regeneration, it is decreasing from I cycle to III cycle. The reason for this could be as follows:

After the first adsorption, microwave energy causes the adsorbed methylene blue to be pyrolyzed and become part of the GAC structure in the pores of GAC. This gives rise to an increased and fresh surface of sorbent for the next adsorption. Therefore, the adsorption might be expected to increase as compared to the previous adsorption. However, the subsequent treatment of this GAC sample with microwave energy leads to further pyrolysis or carbonization of the adsorbed methylene blue. This phenomenon continues for every treatment. A situation arises wherein, continuous deposition or pumping of the material is taking place, into a limited and fixed volume of GAC pores. This might lead to the partial clogging of the pores with greater number of cycles of regeneration. Hence, the

adsorption starts decreasing after the I cycle of regeneration.

Chapter 7

Extraction Studies

7.1 Overview

It has been postulated that the methylene blue pyrolyzes and is incorporated into the GAC skeleton. To test that mechanism, studies were carried out to determine the extractability of the methylene blue from the GAC after microwave treatment. If the proposed mechanism were correct, then, it should not be possible to extract the methylene blue. Extractions were carried out using the Soxhlet procedure to maximize the number of equilibrium stage extractions.

7.2 Experimental

7.2.1 Preliminary extraction studies:

The method of Soxhlet extraction was used for all extractions. Soxhlet extraction is a *multistage extraction*, wherein, the substrate will come in contact with pure solvent in each cycle by continuous vapourization and condensation. The solvent for extraction was chosen based on preliminary extraction studies.

A group of solvents were chosen for preliminary extraction studies. The idea was to determine the % extraction by each solvent and to use the one which has maximum value. The solvents tried were methanol, ethanol, propanol, acetone, and water. The GAC samples saturated with methylene blue were extracted using Soxhlet extraction procedure by using each of the above solvents. The extraction was carried out for a period of 3 hours in each case. Then the absorbance reading was taken and the % extraction was calculated.

For every solvent used a calibration curve was obtained with a *best fit equation*. The best fit equations were calculated by using 'Grapher' software (copyright 1988 Golden Software, Inc.). Different fits like linear, polynomial with degrees 2,3 and 4, logarithmic, power, and exponential were tried. In each case the best fit was chosen.

The experimental procedure is explained for only one solvent, i.e., ethanol. Similar procedures were carried out for other solvents also.

Measurement of methylene blue in ethanol:

- 100mg of methylene blue were weighed in a balance having a precision of 0.1mg. Then the solid was dissolved in one liter of ethanol (In the case of acetone, 10 mg

of methylene blue were dissolved).

- From the primary standard, dilutions were made to generate different standards. The absorbance reading of these standards were taken in a Spectronic-20 spectrophotometer, at a wavelength of 660 nm. The corresponding absorbances are tabulated as shown in Table-7.1. A calibration curve was prepared from the above data and is shown in Figure-7.1.

For acetone, based on data as in Table-7.2, the best fit and the calibration curves are shown in Table-7.2 and Figure-7.2, respectively.

Similarly for methanol, based on data as in Table-7.3, the best fit and the calibration curves are shown in Table-7.3 and Figure-7.3, respectively.

For propanol, based on data as presented in Table-7.4, the best fit and the calibration curves are shown in Table-7.4 and Figure-7.4, respectively.

The summary of results are tabulated as shown in Table-7.5. The maximum % extraction was obtained by using ethanol. That value was 22.73%. Thus, ethanol was chosen as a solvent for further experiments.

TABLE-7.2

Calibration data for methylene blue in Acetone

Point	Concentration (y)in mg/l	Absorbance (x)
1	0	0
2	0.1	0.03
3	0.3	0.06
4	1.0	0.12
5	3.0	0.32
6	5.0	0.50
7	10.0	0.75

Regression Analysis

Equation of bestfit curve is: $y = 10.5 x^2 + 5.31 x + 0.02$

eeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeee

Menu 1.3.6.6 Polynomial Fit Statistics

GRAPHER Copyright (C) 1988 Golden Software, Inc.

eeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeeee

points = 7	Current data file: 1	Fitting Interval Limits
points in fit interval = 7	CALIB1	0 to 10
degree	Sums of Squares of Residuals	PerCent of Residuals about Mean Explained
0	81.3343	0
1	2.27211	97
2	0.191419	100
		Polynomial Coefficients
		0.0208345
		5.30958
		10.4981

Figure-7.1 Calibration Curve for methylene blue in ethanol

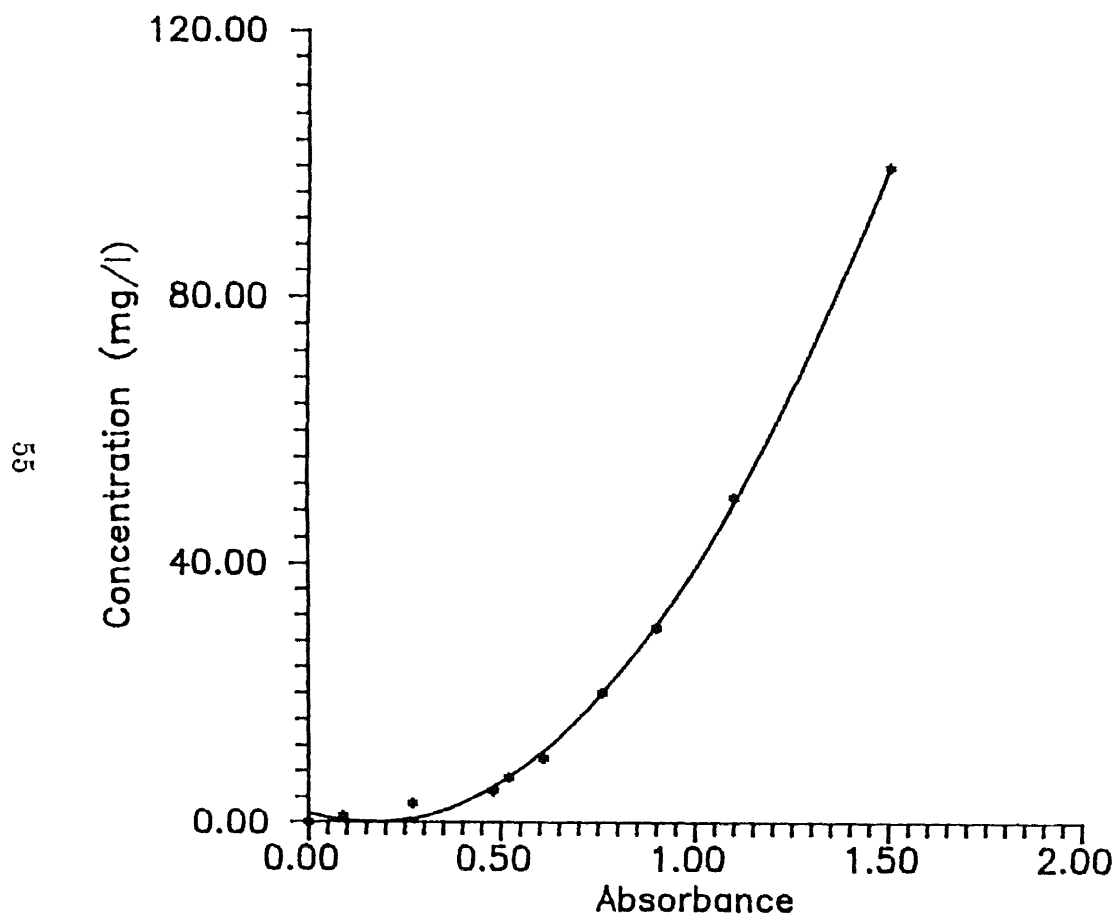


Figure-7.2 Calibration Curve for methylene blue in acetone

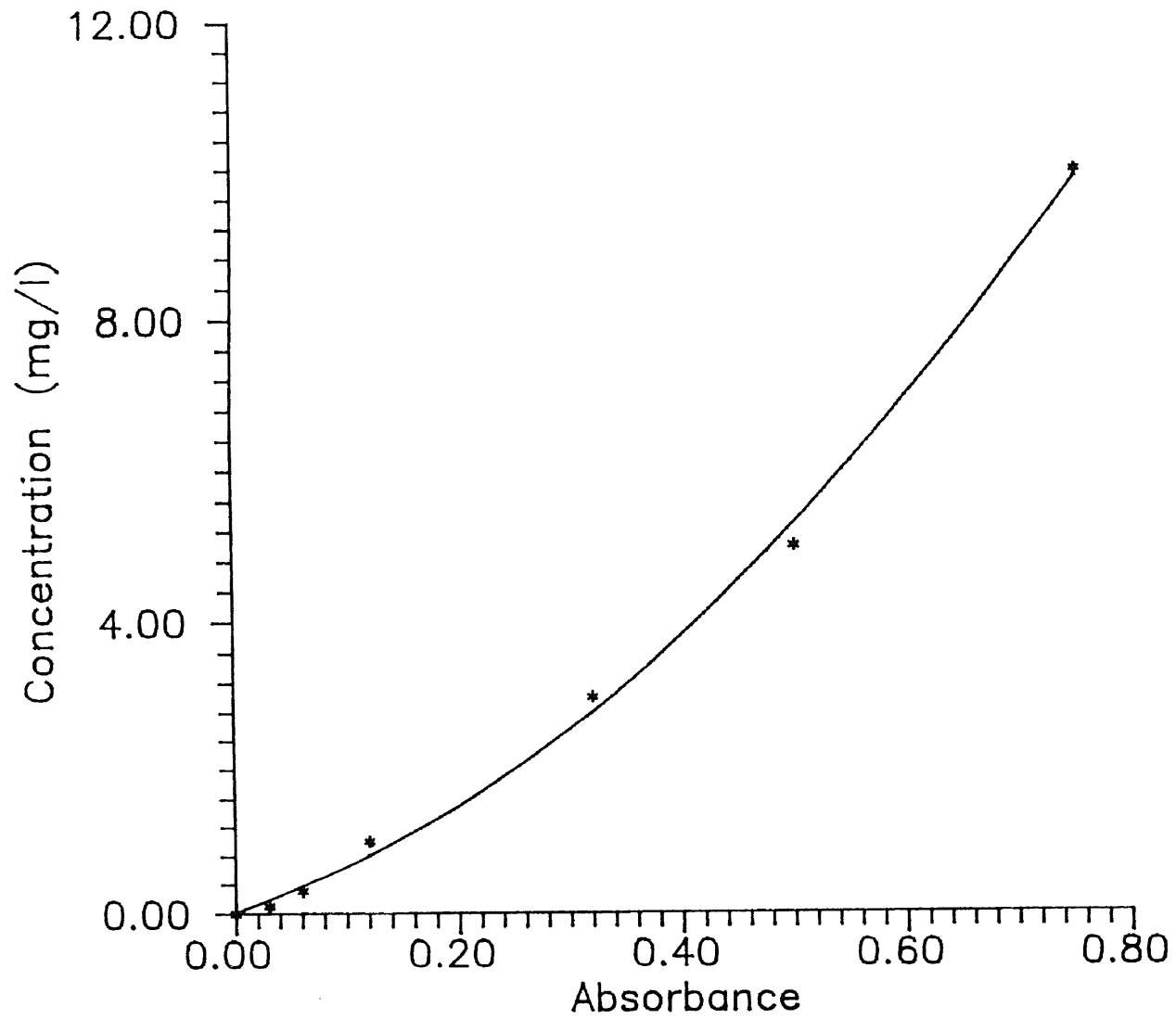


Figure-7.3 Calibration Curve for methylene blue in methanol

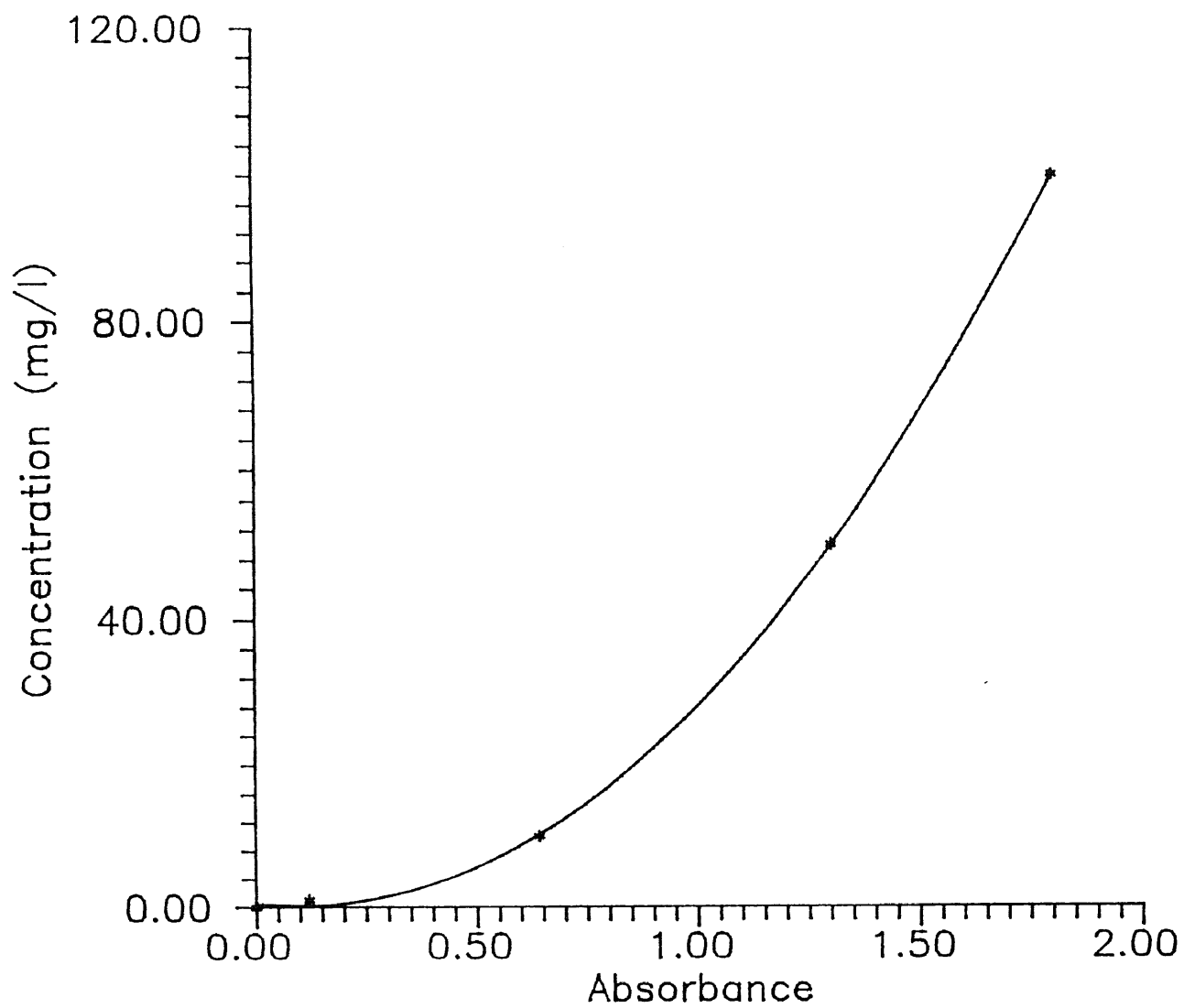


Figure-7.4 Calibration Curve for methylene blue in propanol

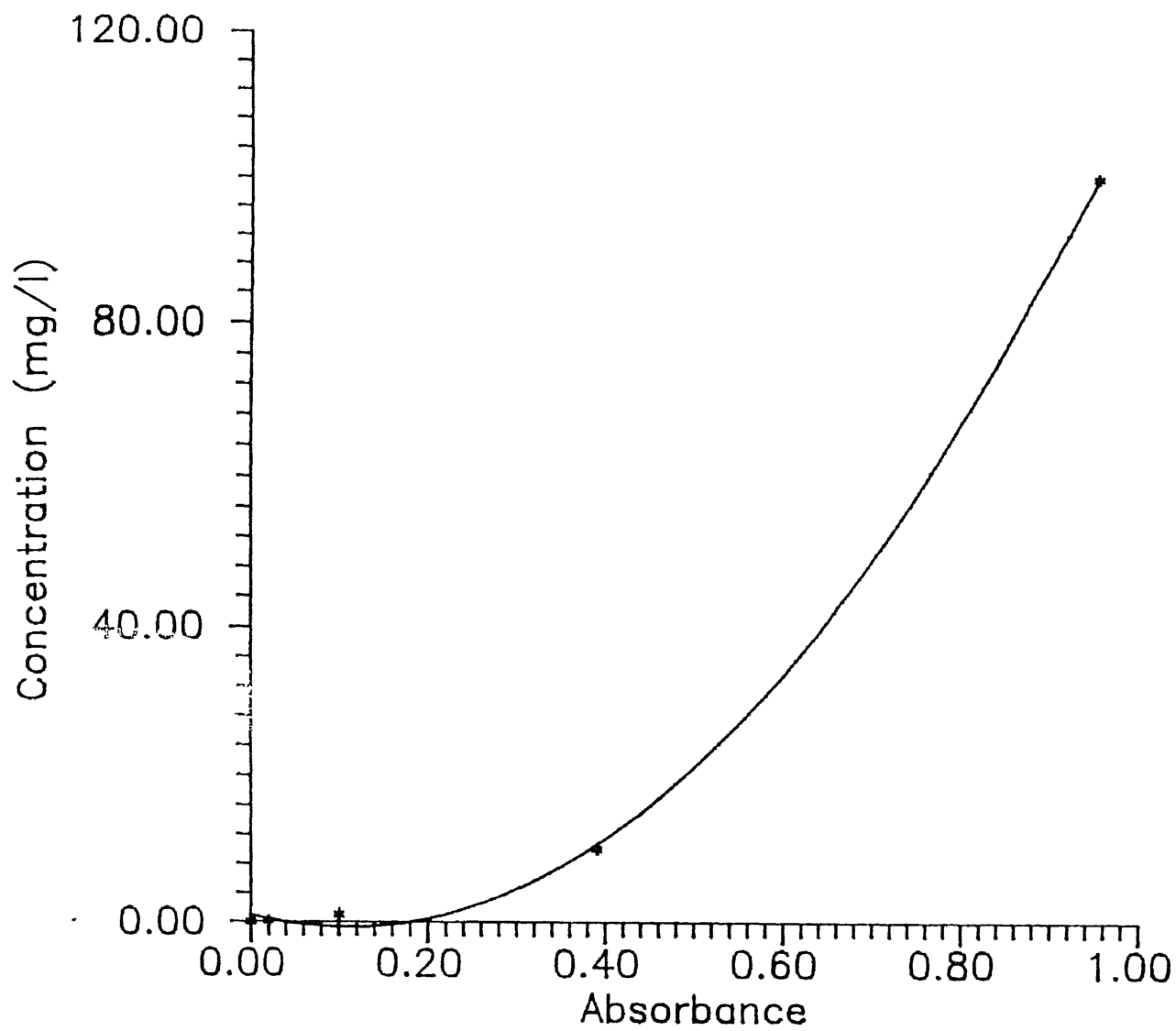


Table - 7.5
Preliminary Extraction Results

Samp. #	Wt. of MB adsorbed in mgm	Soxhlet Extraction			
		Solvent (100 ml)	Absorbance	Wt. of MB desorbed in mgm	%desorption
1	8.5	Water	--	--	--
2	9.68	Acetone	0.31	0.27	2.7
3	7.46	Methanol	0.31	0.18	2.4
4	9.90	Ethanol	0.8	2.25	22.73
5	9.94	Propanol	0.3	0.45	4.5

7.2.2 Extractions using ethanol:

To calculate the quantity of methylene blue left undesorbed on the GAC after the microwave treatment, the extraction was to be carried out. This quantity of methylene blue left undesorbed can be calculated only if the maximum percent extraction from GAC is known. Hence extractions from GAC adsorbed with known quantity of sorbates (as blank) were carried out. The procedure is explained as follows:

0.5 gm of fresh GAC was taken and saturated with methylene blue by putting it in 100ml of 100 mg/l aqueous methylene blue solution for 90 minutes. As explained earlier, the % weight of methylene blue adsorption was calculated. This GAC was washed with distilled water and dried in a desiccater for 24 hours at room temperature. The sample was subjected to Soxhlet extraction using 100 ml ethanol as solvent. The extraction was carried out for a period of 3 days. At the end of 3 days, the absorbance was read using the Spectronic 20 Spectrophotometer. The amount of methylene blue extracted was determined using the best fit equation. Care was taken to see that any loss of volume of the solvent during the process of extraction was made up before taking the reading. This procedure was repeated for 3 samples and the results are tabulated in Table-7.6.

Once the maximum extraction capacity of ethanol is determined, the next thing was to find out quantitatively the amount of methylene blue desorbed due to microwave treatment. This value could be obtained by knowing the quantity of methylene blue left over on treated GAC. To obtain this, the saturated GAC was desorbed in microwave oven as explained in section 5.1. The desorbed GAC was subjected to extraction as explained in section 7.2.2. After 3 days of extraction the

readings were taken and the % weight of methylene blue extracted was calculated. The work was carried out on four samples and the results are tabulated as shown in Table-7.7.

A German paper described a new desorption process; by: Boerje Steenberg. *Naturwissenschaften* 29; 79(1941). According to this paper, by repeated alternate extractions using chloroform and water allows recovery of all methylene blue in aqueous solution. This procedure was tried in this laboratory as follows:

The experiment was conducted with 0.5 gm GAC sample. The process of adsorption was carried out for period of 90 minutes, in 100 ml, 100 mg/l aqueous methylene blue solution. The GAC saturated with methylene blue was put to Soxhlet extraction with 100 ml of chloroform as the solvent, for a period of 3 hours. After this extraction the GAC was allowed to dry at room temperature and then extracted with 100 ml of distilled water for the same period of time. The whole procedure was repeated twice, with the two solvents alternating each other on the single GAC sample. It was found that no measurable or visible extraction was observed in the aqueous phase.

Table - 7.6
Soxhlet extraction results

Samp. #	Adsorption		Extraction in ethanol		
	Absorbance	Wt. of MB adsorbed in mgm.	Absorbance	Wt. of MB desorbed in mgm.	%desorption
1	0.45	8.5	1.3	7.2	85.0
2	0.60	8.0	1.3	7.2	90.4
3	0.84	7.15	1.2	6.0	84.0
	Mean of % Extraction				86.5

Table - 7.7

Results of extraction after MW treatment

Samp #	Adsorption		MW treatment with 20 ml. of water in minutes	Extraction in ethanol			
	Absorbance	Wt. of MB adsorbed in mgm.		Absorbance	Wt. of MB desorbed in mgm.	Wt. of MB left over on GAC	% MB left over
1	0.31	9.0	10.0	0.37	0.24	0.28	3.1
2	0.56	8.14	10.0	0.64	1.26	1.46	17.7*
3	0.52	8.26	10.0	0.26	0.1	0.12	1.4
4	0.51	8.29	10.0	0.23	0.09	0.10	1.14
	Mean of % MB left over						1.88

* Since this value was not in range of other three values, it was discarded.

7.3 Results and Discussion

The results of preliminary extraction are given in Table-7.5. From this table it can be seen that among five different solvents ethanol desorbed the highest quantity of methylene blue from saturated GAC. This value was 2.25 mg, and the corresponding percent desorption was 22.73. The results of Soxhlet extraction studies, conducted for a period of 3 days, using ethanol alone as a solvent are tabulated in Table-7.6. In this the maximum, average percent desorption or extraction was found to be 86.5.

The results in Table-7.5 were obtained by extracting the adsorbed methylene blue from saturated GAC using different solvents, for a period of three hours. Since the purpose of this preliminary extraction was only to choose one solvent out of five, which shows the highest extractability relative to other solvents, the extraction was carried out only for three hours each to obtain the relative values of the same.

The results of the extraction studies after microwave treatment are presented in Table-7.7. It was found that the average value of the percent methylene blue left over undesorbed, after microwave treatment, was 1.88. This value was computed over studies on four uniform, representative samples of saturated GAC.

It can be observed from Table-7.7 that the mean value of the quantity of methylene blue left over after microwave irradiation is 1.88% of the original adsorption. Logically if 1.88% is left over in the first adsorption, the % adsorption in the second adsorption should be reduced by 1.88%. However, going back to the results of chapter 6, from the Table- 6.2, one can infer that the samples behaving anomalously; also, from Table- 6.1, even after the second cycle of regeneration, a good number of samples show a difference of less than 1.88% in the percent adsorption

between the first and second adsorption.

The above facts are consistent with the discussion in section 6.2, and can be explained similarly:

Both GAC and water are heated up by the incident microwave energy individually and simultaneously. The GAC can heat up faster than surrounding water. In the mean time, water both inside and outside the GAC particles heat up. But the maximum temperature which can be attained by water is only 100°C . As a result there exists a temperature gradient between center and periphery of GAC particles.

The organic compound, namely, methylene blue is under the action of combined heating effect. Thus the water or moisture inside GAC gets converted into steam faster than water outside the GAC. The steam produced inside GAC will drive out all air in the pores, also, outside water cannot enter into the hot steaming GAC. In many cases, material exposed to microwave will absorb less energy the less moisture it contains: this is referred to as *moisture leveling*. On the other hand, if one succeeds in pumping the microwave energy into a low moisture content material, the heating rate increases as the material temperature goes up. This causes red hot condition of the material.[2]

The situation in the present case can be well compared to the above theory. When the moisture inside the GAC is driven out of the GAC pores, due to this state of lack of moisture, the GAC can get red hot. The reported ignition temperature for carbon, range from a low of 300°C to over 600°C . Also it is reported that the temperature at which a carbon will ignite depends to some extent on the temperature at which the prior carbonization and activation were conducted.[9] The decomposition temperature of methylene blue is 190°C : the condition inside any pore would be like an *autoclave*. In the absence of air or oxygen, the adsorbed

methylene blue will be subjected to a temperature greater than 190°C and hence it gets pyrolyzed inside the pore. Since methylene blue is a large organic molecule with aromatic rings, it could probably become a part of the GAC structure. This naturally increases the available surface for adsorption, which is the proposed reason for the increase in adsorption above 100% after the microwave treatment, even though 1.9% of the material was left over undesorbed.

In connection with above explanation a simple experiment was conducted. Methylene blue powder was taken in a test tube and was heated thermally in the absence of air. With sufficient heating methylene blue formed a voluminous, carbonaceous mass, like sugar. Hence in this case it was clear that methylene blue pyrolyzed in the absence of air.

Chapter 8

Decomposition Studies

8.1 Overview

It has been postulated in this thesis that the regeneration of GAC saturated with methylene blue is effected by the pyrolysis of the methylene blue: Since methylene blue is non-volatile it can not be steam stripped, therefore, this alternate path is inferred. In the previous section it was shown that microwave treatment did remove approximately 99% of adsorbed methylene blue. The purpose of the studies in this section was to determine whether or not methylene blue or its reaction/decomposition products could be detected in the gas phase.

8.2 Experimental

Experiments to determine the volatiles from the microwave treatment of methylene blue were carried out as follows:

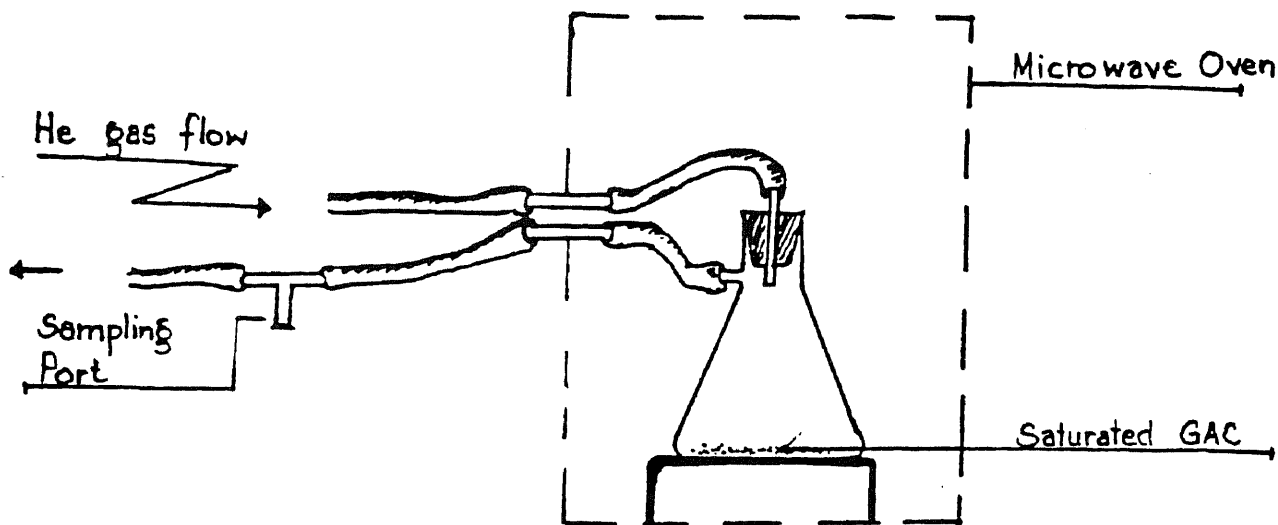


Figure 8.1 set up of experiment for GC/MS analysis

The set up is shown in Figure 8.1. The sample is placed in Erlenmeyer flask and inserted in the microwave oven as shown. Through the top inlet helium gas is blown at a very slow rate of 0.1 l/min, so as to drive out the off gases produced during microwave treatment. The flow meter was calibrated for this purpose. The calibration curve and the results of the regression analysis are shown in Appendix-1. The outlet from the Erlenmeyer flask carries out the off gases. The gas samples are sampled at the port shown in Figure-8.1 using a 10 ul syringe.

Experiments were performed on three types of samples to know the behavior of adsorbed methylene blue on GAC. A GC/MS is used for analysis.

- 1) Solid methylene blue
- 2) GAC saturated with methylene blue.
- 3) GAC saturate with methylene blue in a dry state.

8.2.1 Solid methylene blue:

Solid dry methylene blue powder was put inside the Erlenmeyer flask. In order to avoid the powder being blown away from the helium gas flow, glass wool was placed over methylene blue sample. The helium gas flow was started and, at the same time the microwave was turned on in high mode. It was observed that after 5 minutes, fumes started coming out through the outlet. The off gas was sampled using a 10ul syringe and was injected into GC/MS data system. The total ion chromatogram (TIC) the mass spectrum and the library search result for compound identification was obtained. All these results are given in Appendix-1 (Figures 8.2,8.3, and 8.4 respectively)

8.2.2 GAC saturated with methylene blue:

The sample was 2.0gm GAC saturated with methylene blue in 20ml of water. This experiment was carried out similar to the one described in section 8.2.1. It was observed that steam appeared in the outlet. After 6 minutes, the gas sample was taken and injected into the GC/MS. The TIC, mass spectrum, and the search results obtained are shown in Figures 8.8,8.9, and 9 respectively. (Appendix-1)

8.2.3 GAC saturated with methylene blue and in dry state:

This sample was 2.0gms of GAC saturated with methylene blue. The saturated GAC was dried in a desiccator at room temperature for 48 hours. This experiment was carried out similar to the one described in section 8.2.1. The gas sample, obtained after 5 minutes of microwave treatment, was injected into GC/MS. The TIC,MS, and library search results are shown in Appendix-1 (Figures 8.5, 8.6, 8.7).

The tests which were performed were of qualitative in nature. The MS gives for every compound a characteristic pattern of charged molecule fractions. Which is accomplished by ionising every molecule in an electron source. Ultimately these molecules are broken into small fragments which are positively charged. These cations are accelerated and guided into a quadrupole magnet. The quadrupole is tuned to allow only one ionic species at a time to reach the detector at the end of quadrupole. However the MS can scan a wide range of masses in a short time. For every mass scanned, the number of ions detected is listed. The abundance of detected masses in one scan gives the characteristic spectrum for a compound. [7] [8]

In each run the gas sample is injected into the GC, the separated compounds leave the column one after another and enter the MS. Each compound is broken into its characteristic masses which are detected and counted. The sum of all ions counted gives the total ion chromatogram (TIC) at that time. Hence the TIC over the total sum is same as the graph from a GC. The data from every run is digitally stored and can be manipulated in many ways to obtain different other information like selective ion chromatogram, mass spectrum at desired points on TIC, etc.. The

spectrum obtained can be compared with 38,000 spectra stored in the NBS library files. The library search gives 10 best matches out of it's files with the quality of the match as in percentage.

8.2.4 Equipment and Parameters:

SHARP carousel II convection microwave oven ; serial number.19763

GC-MS: Hewlett-Packard: GC 5890 serial # 2738A1309

MSD 5970B serial # 2716A10 472

Chemstation computer system 8725K 59784

Column:PONA 50m x 0.2 mm

Syringe : Hamilton 10.0ul, #801

Helium flow rate = 0.1 l/min.

8.3 Results and discussion

The data obtained from GC/MS are: total ion chromatogram, Mass spectrum and the library search results. All GC/MS data obtained are presented in Appendix-1. To separate and identify the off gases, analysis with a GC/MS was necessary.

The mass spectrum obtained for the decomposition products of pure solid methylene blue (Figure-8.3) will quite clearly match with the mass spectrum obtained for the decomposition products of methylene blue adsorbed on GAC.(Figure-8.6)

(but the NBS library searches for these twocases, Figure-8.4 and Figure-8.7, show a different match group). Hence it can be concluded that the adsorbed methylene blue also absorbs microwave simultaneously with the GAC and when it reaches its decomposition temperature of $190^{\circ}C$, it decomposes giving products which are almost identical to the pure solid methylene blue decomposition products(by comparing the mass spectra).

It was very interesting to note that no prominent peaks were observed in the case of experiment with saturated GAC and 20 ml of water(section 8.2.2). As it is evident from the mass spectra and corresponding NBS library search (Figures 8.9 and 9), only water is detected. The ion range of 372-374 was tried to see any methylene blue peak (Figure-9.1) but nothing came out. The reason may be that the concentration of the decomposed product was too small, or if methylene blue was desorbed from the GAC, it was too large to be detected in this 50 m capillary column. The aqueous methylene blue and methylene blue in ethanol solvent were injected separately into GC/MS, the corresponding peaks were not detected.

Chapter 9

Conclusion

Experiments show that, with 3 cycles of regeneration, i.e, the adsorption and desorption process, the GAC shows considerable regenerability. Results show that the spent GAC can be regenerated up 100% in the first cycle and then it decreases for further cycles. Considering only the mean values from Table-6.2, the regenerability goes down from 99% to 93.18% and then to 85.95% in the third cycle. These values suggest the potential use of microwave treatment for the on-site regeneration of GAC.

From the extraction studies it can be concluded that on an average, microwave treatment of spent GAC can desorb 98.1% of the adsorbed methylene blue. Though 1.9% of the adsorbed methylene blue was left over after the microwave treatment, we could see that regeneration was greater than 100% in most of the samples. From the different types of experiments conducted, it can be argued that this increase is predominantly due to the effect of "*pyrolysis*" or "*carbonization*" of methylene blue molecule, in the pores of GAC. By analyzing the conditions like the absence of air, and temperature of GAC pores greater than the decomposition temperature of methylene blue, it can be concluded that the adsorbed methylene

blue gets pyrolyzed. This causes the increase in the available surface for adsorption. This could be a strong reason for increase in % adsorption in the second adsorption. The wide range in the % adsorption can be due to a number of factors like :

1) Difference in weight of GAC taken. Since the amount used was very small (0.5 gms), even a small variation may alter the results of adsorption.

2) Due to different active centers.

3) Variations in the available surface area from sample to sample.

The overall conclusion can be summarized as follows :

1. Regeneration of spent GAC is possible even though a non-volatile compound is adsorbed.
2. The major mechanism of regeneration of the GAC, adsorbed with a non-volatile compound like methylene blue is pyrolysis or carbonization. The GAC heats up the adsorbed organic to its pyrolysis temperature, in an anaerobic atmosphere created by absence of air in the pores.
3. The pyrolyzed methylene blue is becoming a part of the GAC structure, therefore there is an increase in adsorption in the I cycle of regeneration.
4. 100% regeneration can be achieved in the first cycle and 93.2% and 85.95% can be achieved in the second and third cycles of regeneration, respectively.
5. The decrease in the adsorption and % regeneration, in the second and third

cycle could be due to clogging of GAC pores fully and/or partly by carbonized methylene blue.

6. Complete and effective removal of contaminants depend on the properties of the contaminant.
7. The microwave irradiation process is successful not only in low molecular weight organics but also in high molecular weight compounds like methylene blue.
8. Regeneration using microwave is consistent with a mechanism involving fusion, subsequent to pyrolysis in the absence of air. This type of simple regeneration can not be achieved by available technologies. They are all based upon heating the spent GAC to elevated temperatures in the presence of air to burn out the adsorbed organics. Unlike the aforementioned microwave process, the thermal processes lead to degradation of GAC as a result of oxidation caused by high temperatures and frictional loss due to tumbling of particles to effect optimum thermal heating.
9. The major problem is to regenerate *spent* GAC on-site. Microwave technology can effect the regeneration of GAC with non-volatiles adsorbed. Also, of greatest significance, there is no need for an offgas control technology because pyrolysis occurs within the GAC producing carbon which adds to the GAC skeleton. Thus it is technically possible to effect GAC regeneration on-site because of the simplicity of the needed microwave technology.

9.1 Future studies

Future studies have to investigate the following problems :

- Other non-volatile organic materials have to be investigated.
- Does this system work with volatile and non-volatile inorganics as well.?
- To find the optimum moisture content of the substrate (GAC) and the optimum time exposure to microwave.
- Is it possible to destroy or transform the products of microwave irradiation process into a non-toxic waste stream either in bed or by fixing a temporary module containing a bed of microwave heated ceramic, which is chemically non-reactive, modular, portable, non-degenerative, and that it's effectiveness would be predicted upon microwave absorption. To that end lossy solids were studied , that is solids which heat up rapidly to high temperatures in the microwave fields. These can be called as "regeneration modules". Such solids in addition to heating can also create arcs. Previously, in this laboratory, GAC was studied. In this regard silicon carbide is also being studied. It is suggested that a module consisting of a bed of pulvarized silicon carbide can be fabricated and fixed to a spent GAC bed to effect the aforementioned properties.
- Will the technology work on-site ? In-situ ?
- Is the process of regeneration cost-effective ?
- The pilot plant and scale-up stages of these microwave treatment technologies have to be considered for the future studies. Then the insights developed

in this study will shape the studies on the feasibility of using microwave treatment to regenerate hazardous waste on-site.

Bibliography

1. John m.Osepchuk, "*Basic Principles of Microwave Ovens*", copy right IMPI Ltd. Canada, 1975
2. W.R.Tinga, "*Interactions of Microwave with Materials*", copy right IMPI Ltd. Canada, 1970
3. CRC Hand book 1986/87
4. Jerome R.White, "*Why Materials Heat*", copy right IMPI Ltd. Canada, may 1971
5. Merck Index
6. Kodak Laboratory and Research Products
7. G. Windgasse, "*A New Hazardous Waste Treatment Technology Utilizing Low Power Density Microwave Energy*", A Master's Thesis, NJIT, 1987
8. Douglas A.Skoog, "*Principles of Instrumental Analysis*", third edition, Saunders Golden Sunburst Series, 1985
9. John W.Hussler, "*Purification with ACTIVATED CARBON*", Chemical Publishing Co, Inc. New York, NY, 1974
10. K. Boki, S. Tanada, T. Kita, T. Nakamura, H. Onishi and T. Hanasaki, "*Intraparticle Diffusivity of Methylene blue into Pores of Pyrolysis Ashes Derived from Sewage Sludge*", Environ. Tech. Letters vol-5, pp 171-176, 1984
11. Robert F.Schiffmann, "*Microwave Heating Applications in Industry*", copy right IMPI Ltd. Canada

12. Patience C.Ho and C. Staurt Daw, "*Adsorption and Desorption of Dinitrotoluene On Activated Carbon*", Environ.Sci.Technol. vol 22, No.8 , 1988.
13. Sanyo Electric KK patent JP 50152994, 09/12/75 and JP 810449848, 11/25/81. "*Regeneration of activated carbon using steam at high temperature in microwave field*".
14. Mohamed A.El-Dib; Ahmed S.Moursy, "*Role of adsorbents in the removal of soluble aromatic hydrocarbons from drinking waters*", Water Research, vol.12, pp 1131, 1978.
15. U.S. Patent 4,217,191 Aug. 12.1980, "*process for regenerating contaminated activated carbon*".
16. Soyu patent SU 722852 1980 "*Biological regeneration of sorbent*".
17. U.S. Patent 4,322,394, mar 30/82, "*Adsorbent regeneration and gas separation utilizing microwave heating*".
18. Japanese patent 57056310, dated 04/03/82, "*Regeneration of activated carbon by saturating with gas or liquid and subjecting it to high frequency dielectric heating*".
19. U.S. Patent 4,558,022, 12/10/85, "*Regeneration of caustic impregnated activated carbons*".
20. U.S. Patent 4,535,065, 08/13/85, "*Method for Regeneration of moist powder adsorption agents*".
21. Dickson, L.W: Singh, "*A review of applications of radiolysis in the adsorbed state*". Canadian nuclear society proceedings of the seventh annual conference " 1986, Furonto, Ontario; Canada.

22. Brusentseva, S.A; Shubin, "*Radiation-adsorption and purification of effluents containing pesticides*", Radiation.phys. & chem.(GB) vol.28, no.5-6, 1986.
23. Timothy A.Wolfe, "*Adsorption of organic pollutants on montmorillonite treated with amines*", Journal WPCF, vol.58, no.1, Jan 1986.
24. Liu, P.K.T.; Felth, S.M Wagner, N.J.Calgon carbon Corp. Pittsburgh, PA, USA." *Thermal desorption behaviour of aliphatic and aromatic hydrocarbons loaded on activated carbon*". Ind. Eng Chem. Res- Vol26, no.8. 1540-5, Aug 1987.
25. Japanese Patent 62286541, 12/12/87, "*Regeneration of activated carbon*".
26. Edward J.Calabrese, "*Ecogenetics*", A Wiley-interscience publication, John Wiley and Sons., NY.

APPENDIX-1

Table-A.1

Properties of GAC used

The GAC used was from Calgon Carbon Corporation. The properties listed here were directly taken from the manufacturer's catalog. The type of GAC used was Filtrasorb 100, having a specification as F-100/ 8 x 30.

Total surface area in m ² /gm.....	850-900
Particle density wetted in water in g/c	1.4-1.5
Moisture as packed (max %)	2.0
Abration Number(min)	75
Iodine Number(min)	850

Sieve Analysis-Sieve size U.S Std. Series

Larger than No. 8 (max%)	15
Larger than No. 12 (max%)	-
Smaller than No. 30 (max%)	4
Smaller than No. 40 (max%)	-
Uniformity Coefficient(max)	1.9
Effective Size in mm	0.8-1.0

Table-A.2

INFLUENCE OF SOLVENT ON ADSORPTION OF DYE*

Carbon Code	<i>Methylene Blue^a</i>		<i>Malachite Green^a</i>		<i>Alizarin Red^a</i>	
	In water	In ethanol	In water	In ethanol	In water	In ethano
A	0.84	0.26	1.07	0.113	1.25	0.35
C	0.70	0.15	0.74	0.029	1.00	0.43
D	0.37	0.07	0.45	0.017	0.62	0.14
E	0.30	0.08	0.34	0.008	0.45	0.17
F	0.44	0.12	0.19	0.018	0.39	0.12
H	0.73	0.07	1.10	0.050	0.95	0.24

^a Millimoles per gram of carbon at a concentration of 0.1 millimoles per liter in equilibrium solution.

* Data from *Ind. Eng. Chem.* 37 : 645 (1945); reprinted by permission of the American Chemical Society.

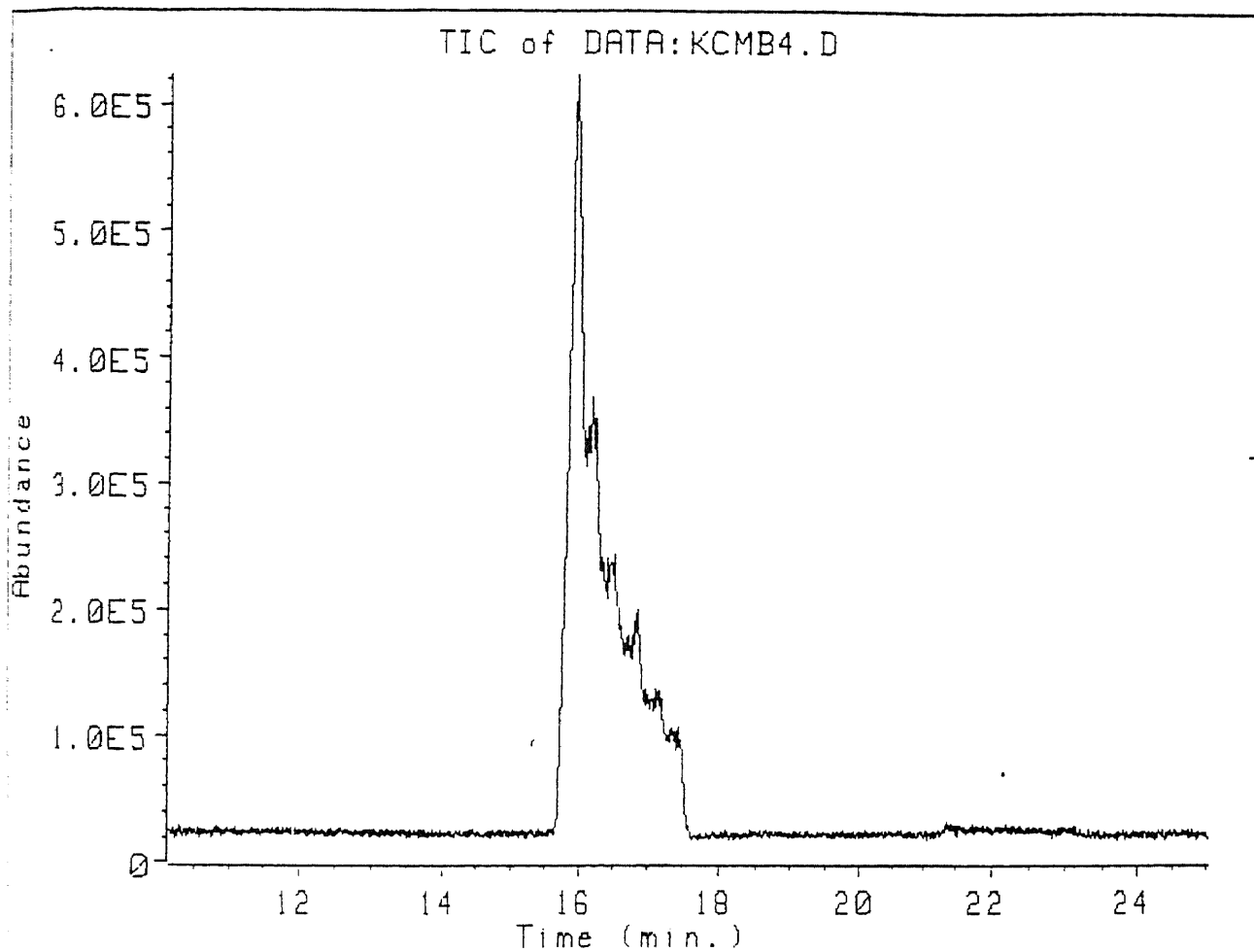


Figure-8.2 TIC of decomposition of solid methylene blue

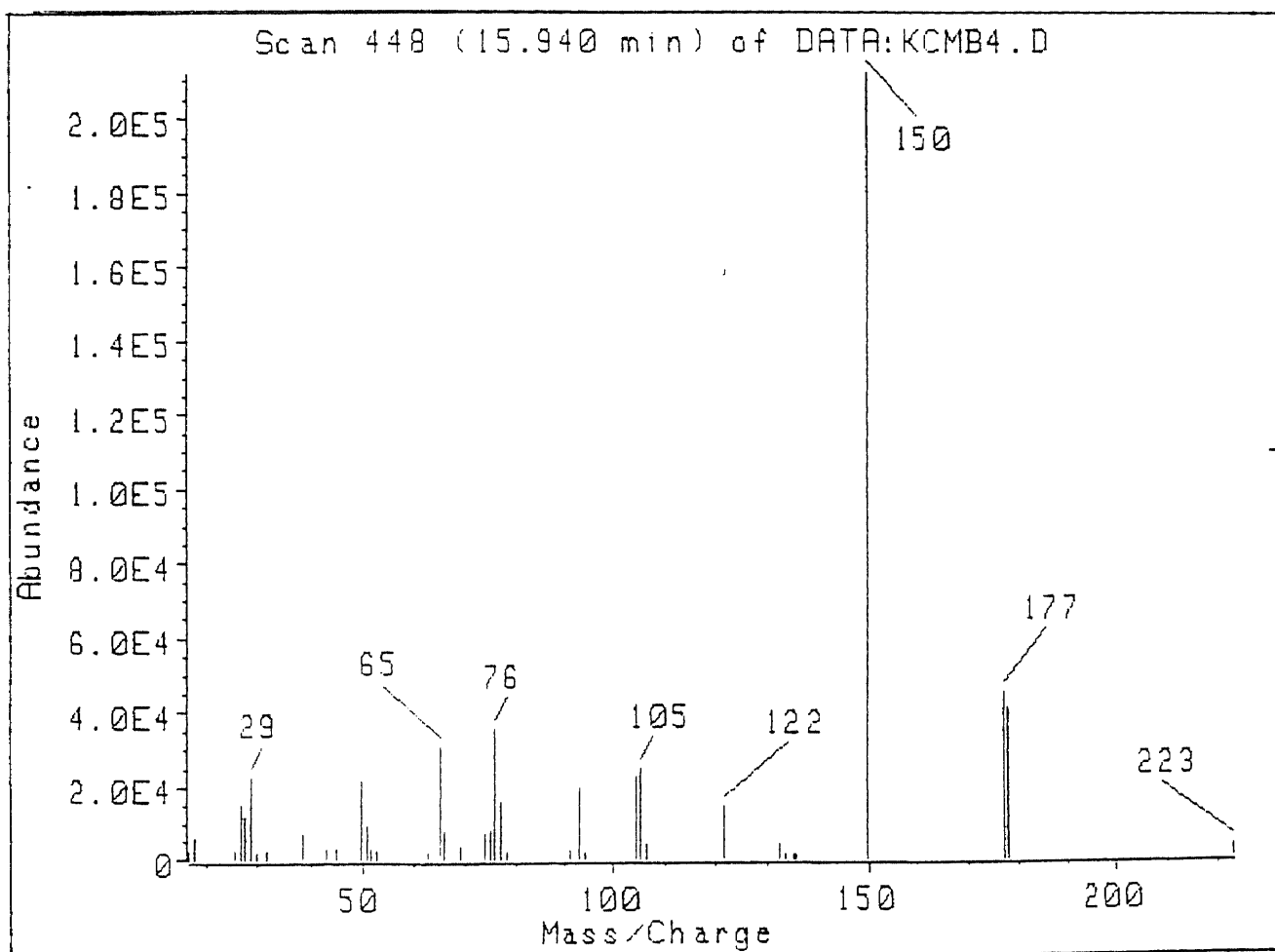


Figure-8.3 Mass spectra of decomposition products of solid
methylene blue

LIBRARY SEARCH RESULTS

Scan 448 (15.940 min) of DATA:KCM84.D
 TRIAL3 SOLID MB IN MIC .W IN He FLUID DECOM. PROD

Library file: DATA:NBS_REVE.L
 Library name: NBS MASS SPECTRAL DATABASE

	CAS #	Library Index #	Match Quality
1: 2,4-Imidazolidinedione, 1-[[[5-nitro-2-f	67209	20651	9667
2: 1,2-Benzenedicarboxylic acid, diethyl es	84662	18444	9535
3: 1,2-Benzenedicarboxylic acid, bis(2-meth	117828	25230	9303
4: 1,2-Benzenedicarboxylic acid, butyl 2-me	17851535	24887	9282
5: 1,2-Benzenedicarboxylic acid, dipropyl e	131168	21930	9262
6: 1,2-Benzenedicarboxylic acid, bis(1-meth	605458	21931	9146
7: Ethaneperoxoic acid, 1-cyano-1-[2-(2-phe	58422927	30714	9128
8: 1,2-Benzenedicarboxylic acid, diheptyl e	3648213	31658	9117
9: Phenol, 2-methyl-4-(1,1,3,3-tetramethylb	2219843	18243	8992
10: 1,2-Benzenedicarboxylic acid, bis(1-meth	131157	33127	8984

Which match (1 to 10):

Figure-8.4 NBS Library Search results for Figure-7.3

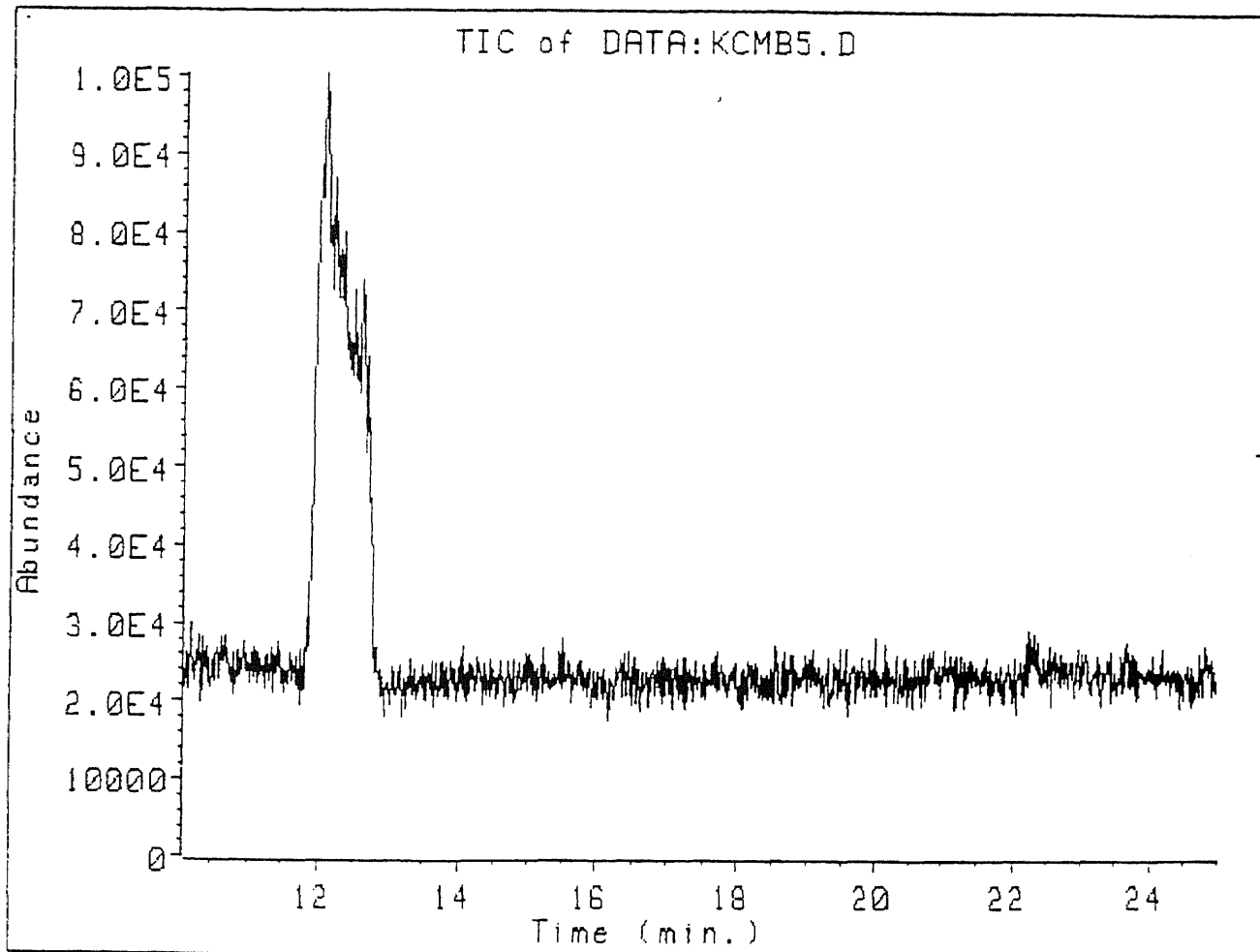
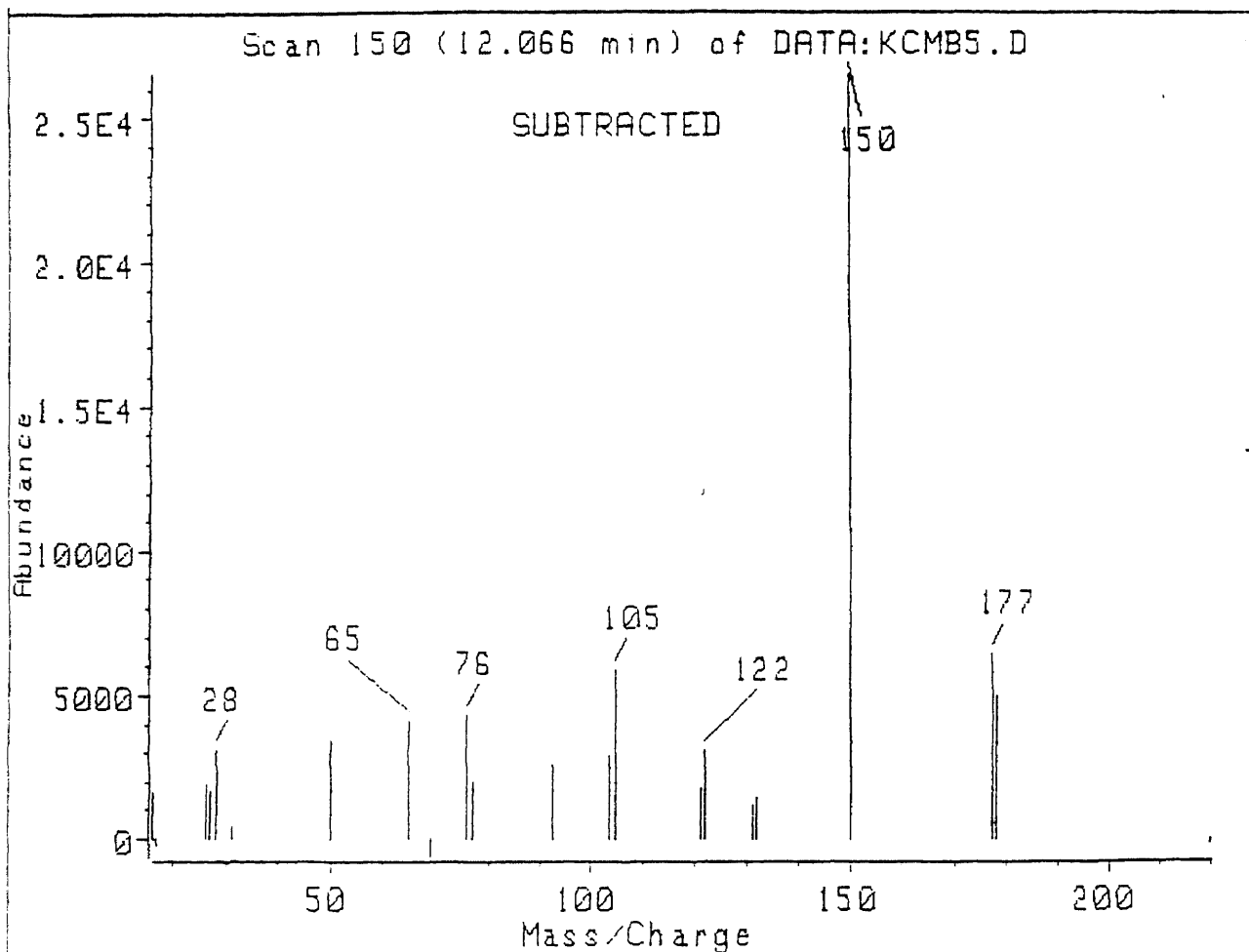


Figure-8.5 TIC of decomposition of adsorbed methylene blue

Figure-8.6 Mass spectra of decomposition products of adsorbed methylene blue



LIBRARY SEARCH RESULTS

Scan 150 (12.066 min) of DATA:KCMB5.D
 TRIAL 3 SOLID MB IN MW IN He MEDIA 5MINS, KCMB2.A

Library file: DATA:NBS_REVE.L
 Library name: NBS MASS SPECTRAL DATABASE

	CAS #	Library Index #	Match Quality
1: 2H-1-Benzopyran-7-ol, 3-[2-(acetyloxy)-4	38822069	31255	8848
2: Benzoic acid, 2-nitro-, methyl ester (9C	606279	12526	8816
3: Benzamide, N-methyl-4-nitro-N-(4-nitroph	33675693	27119	8815
4: Benzo[b]thiophene-4-ol, methylcarbamate	1079330	16450	8784
5: Benzothiazole, 2-(sec-butylamino)- (8C1)	28291738	16266	8734
6: Benzenebutanoic acid, 3-nitro-, gamma.-ox	6328003	19662	8720
7: Ethanone, 1-(3-nitrophenyl)- (9C1)	121891	9798	8708
8: Ethanone, 1-(2-nitrophenyl)- (9C1)	577593	9799	8703
9: Benzamide, 4-methoxy-3-nitro-N-phenyl- (97325	24274	8701
10: 1-Pentyn-3-ol, 3-methyl-, 4-nitrobenzoat	56009235	21566	8681

Figure-8.7 NBS Library Search results for Figure-7.6

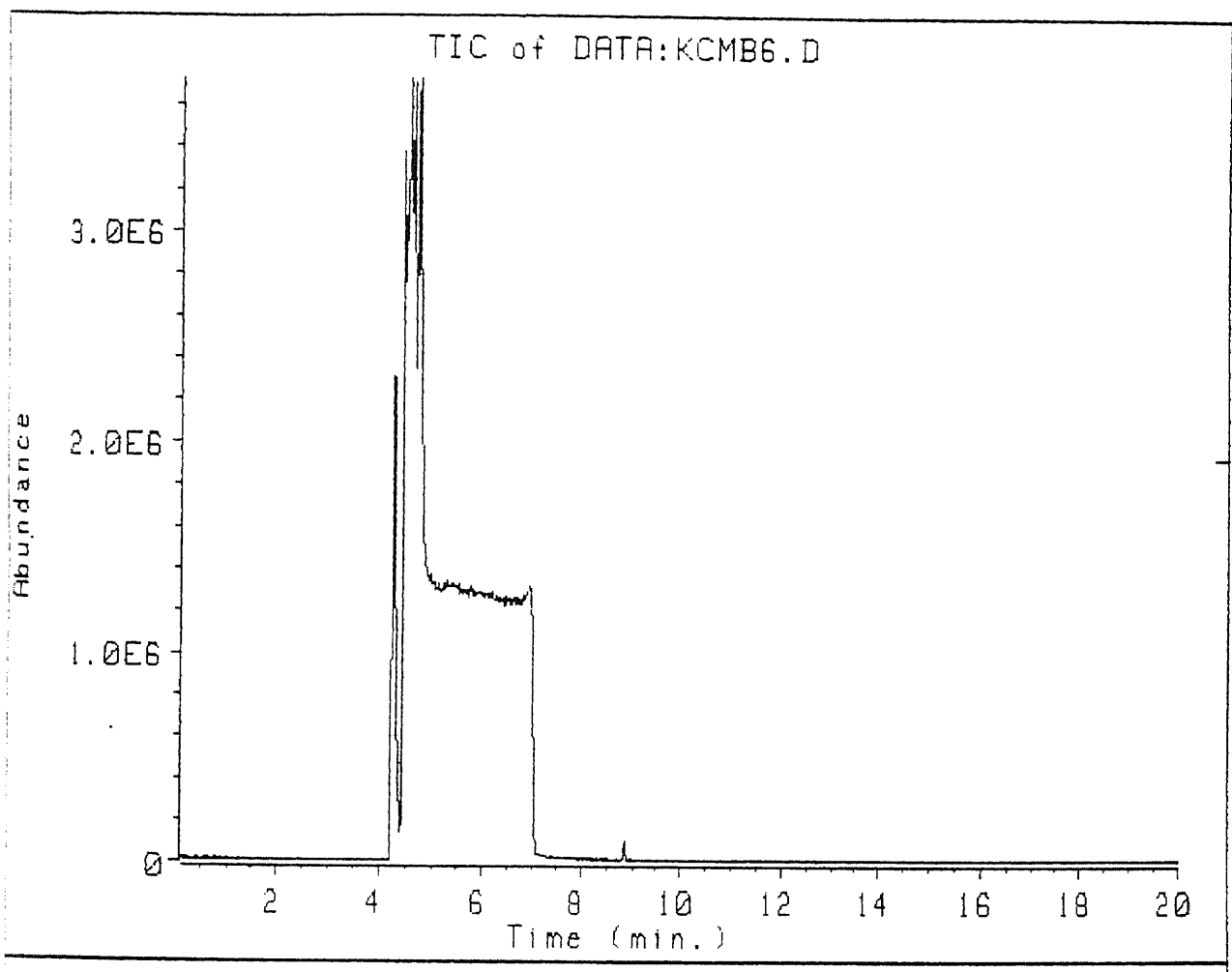
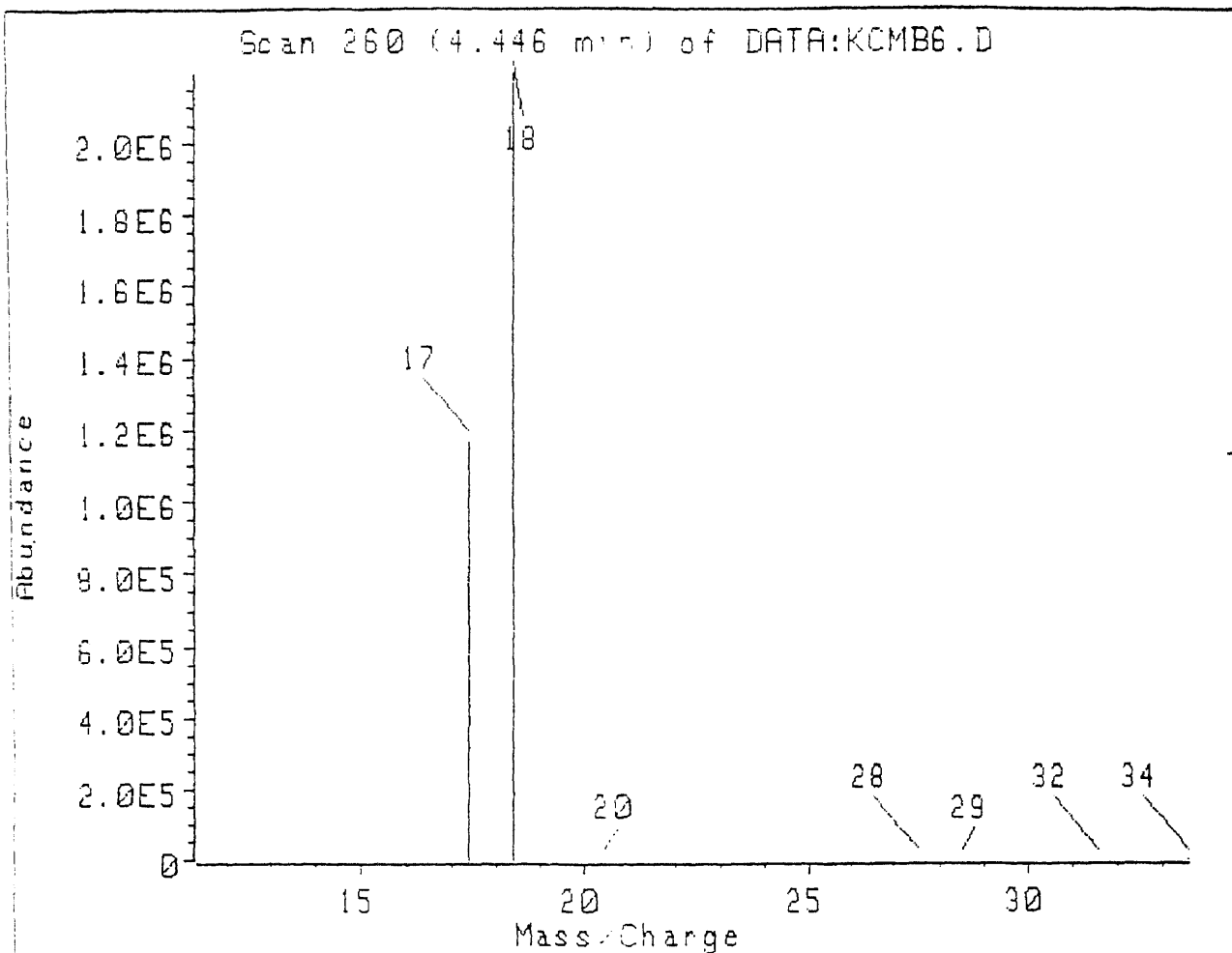


Figure-8.8 TIC of decomposition of adsorbed methylene blue
in water

Figure-8.9 Mass spectra of decomposition products of Saturated GAC with Water



LIBRARY SEARCH RESULTS

Scan 260 (4.446 min) of DATA:KCMB6.D
SAT.GAC AND WATER 20ML IN MW

Library file: DATA:NBS_REVE.L
Library name: NBS MASS SPECTRAL DATABASE

	CAS #	Library Index #	Match Quality
1: Water (8C19C1)	7732185	4	9609
2: Ethanol, 2-nitro- (8C19C1)	625489	823	9510
3: Pentanedial (9C1)	111308	1244	9438
4: Butanedial (9C1)	638379	607	9381
5: Ethanedial (9C1)	107222	90	9274
6: 2-Propanol, 1-amino- (8C19C1)	78966	328	9247
7: 1-Butanol, 2-amino- (8C19C1)	96208	770	9245
8: 1,1-Ethanedial, 2,2,2-trichloro- (9C1)	302170	9659	9218
9: Ethanedimidic acid, dihydrazide (9C1)	3457372	2536	9085
10: 2-Propanol, 1,3-bis(dimethylamino)- (8C)	5966518	6581	8883

Figure-9. NBS Library Search results for Figure-7.9

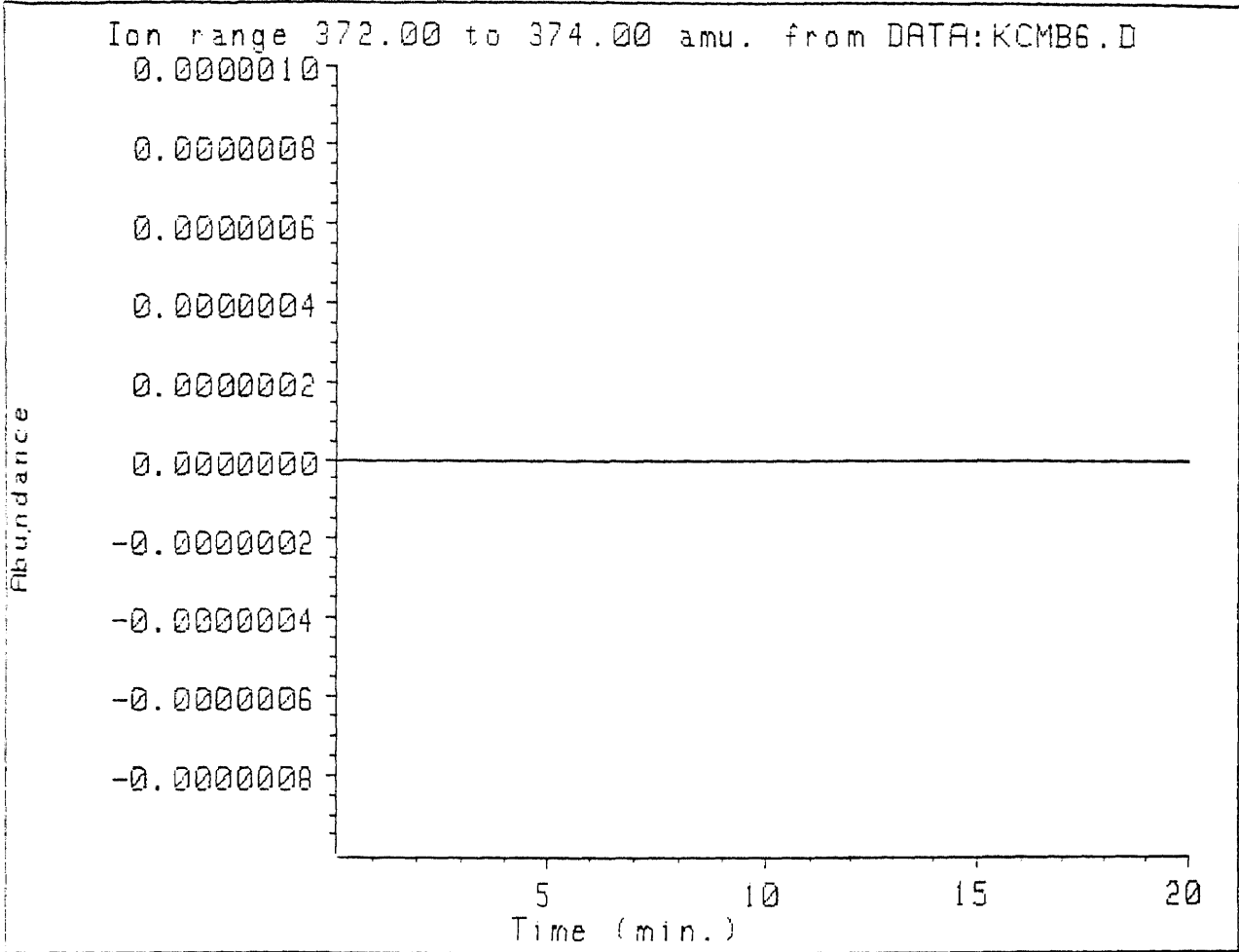
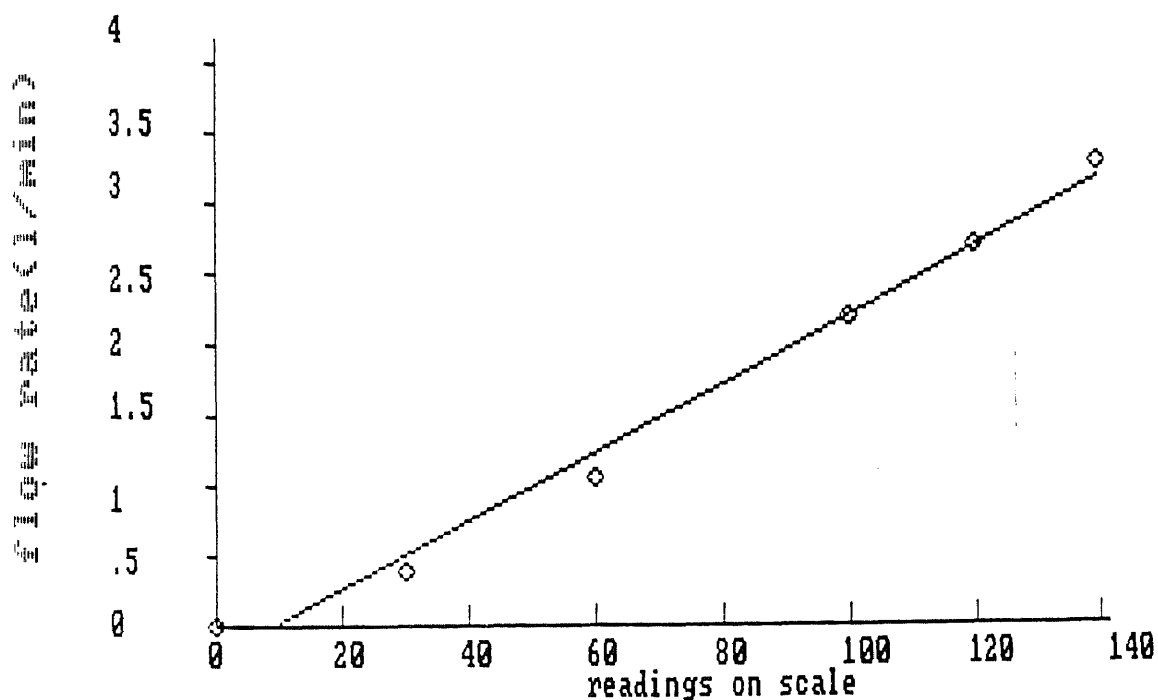


Figure-9.1 Ion chromatogram for Figure-7.8

Figure-9.2 Calibration curve for flow meter



Calibration of flow meter

POINT	X	Y
1	0	0
2	30	.38
3	60	1.05
4	100	2.2
5	120	2.7
6	140	3.28

Slope = $2.419322E-02$ +/- $1.365028E-03$

Intercept = $-.2128247$ +/- $.1657821$

Correlation = $.9936932$

Calculated on points 1 TO 6

ACQUISITION PARAMETER FILE

DATA:KCMB1.A

Miscellaneous

Description : STANDARD
 Operator :
 Date & time : 28 Feb 89 7:21 pm
 Inlet : GC
 Configuration file : DATA:TCETUNE.U
 Acquisition mode : Scan
 Electron Multiplier : -200.00
 EM absolute : FALSE

Temperature Zones

Initial temperature : 40.00
 Initial time : 0.00
 Equilibration time : 0.20

	Set Points	Soft Limits	Status
	-----	-----	-----
Oven	40	300	On
Inj Port A	0	250	Off
Inj Port B	185	250	On
Transfer Line	280	300	On
Ion Source	0	250	On
Mass Analyzer	0	300	On
Detector A	0	250	Off
Detector B	0	0	On

