ADSORPTION AND KINETICS OF ADSORPTION BY FLYASH IN SOLUTION

by

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ABSTRACT

Title of Thesis	: Adsorption and Kinetics of Adsorption by Flyash in Solution.
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The phenomena of adsorption is extremely important in water/wastewater treatment process. A process which uses flyash as the sorbent for removing organic compounds from aqueous solutions has been investigated. Also, the rate at which this process occurs, i.e., the kinetics of adsorption, has been studied. Single solute systems were examined and the samples were analyzed using a Flame Ionization Detector Gas Chromatograph. The potentialities of adsorption on flyash as a method of renovation of water have not been realized fully, because little knowledge is available regarding the effective application of the method for this purpose.

Flyash has been known to exhibit adsorptive and ion exchange capabilities. This is essentially due to its carbon content. Furthermore, it is an inexpensive and easily obtainable material.

The results of this investigation indicates that adsorption of organic compounds onto flyash is feasible. The time taken for adsorption is high when compared to that of activated carbon. The efficiency of the process depends upon the characteristics of flyash, the system condition and the properties of the organic compounds present in the system.

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I.A. INTRODUCTION AND OBJECTIVES :

Industrialization has led to the use of many chemicals for industrial, domestic and agricultural purposes. Most of these compounds exhibit toxic properties and can have an negative effect on man and the environment when exposed. Millions of tons of waste are disposed of in land as ocean dumping is banned. This type of disposal in a landfill has created a problem by contaminating the soil, water (both ground and surface) and air due to the many reactions taking place in the landfill.

Various methods have been tried to dispose of solid waste produced by these many activities in a way that it won't affect the soil, water and air. Soil is contaminated because it interacts with water to form an integrated system with most of the contaminants adhering to the particles. Surface and ground water are contaminated due to the flow, precipitation and percolation of water via the wastes. Air is contaminated because of the production of gas and particulate matter which gives bad odor and material that is hazardous.

When precipitaion takes place the water moves through the solid waste and carries with it the heavy metals and other materials which are hazardous to man and environment, into the ground water or into the surface streams. This phenomenon is known as leaching. The complex which is formed out of water and materials in the waste like heavy metals and inorganic anions forms what is known as leacheate. The passing of the leacheate into the ground water is highly undesirable because of the adverse effects it has on man and environment.

Flyash is byproduct of combustion of coal/oil. Large quantities of flyash are being produced every year. There is a need to dispose of the flyash in an effective and controlled manner. Codisposal of flyash and the toxic and hazardous substances in the leacheate can be possible as flyash can act as an adsorbent and these substances can be made to adsorb onto flyash.

Adsorption is the process of collecting soluble substances that are in solution on a suitable interface. It is an effective means for removing quantities of numerous biochemically resistant organic compounds from aqueous solution. The process can be pictured as one in which molecules leave solution and are held on the solid surface by chemical and physical bonding. This process involves the preferential accumulation or concentration of one or more components of a liquid mixture or concentration of substances at the surface or interface of the solid.

This phenomenon forms the basis for many industrial operations, including separation and purification of chemical products, treatment of wastewater and others. This process can occur at an interface between any two phases - liquid, gas and solid interphases. The material being concentrated or adsorbed is the adsorbate and the adsorbing phase is the adsorbent.

Synthetic organic compounds present acute problems for wastewater treatment and/or for reuse of water. The adsorption process is being used extensively in wastewater purification, but demands for a better quality of treated wastewater effluent have led to an intensive examination and use of the process of adsorption. These compounds have been sucessfully removed from solution by the process of adsorption using Activated Carbon by large. In this paper an alternative - Flyash - is being used to investigate the adsorptive properties and the rate at which adsorption occurs (Kinetic Study).

I.B. LITERATURE REVIEW :

Research concerned with the removal of both biologically resistant and biologically inert material from the leachate generated in a landfill has been emphasized. The mobility of hazardous leachate from landfill into the surrounding ground or its proliferation into ground water can be retarded by using some clay soils as liners, because of their low permeability. This means that this material can be used to adsorb the pollutants. Illite, vermiculite, kaolinite and Ottowa sand are being investigated because these soils have been found to exhibit either a strong cationic or anionic exchange capability.

With the large scale construction of utility-owned coal/oil fired power plants, large quantities of a solid combustion byproducts have been generated. Commonly designated as flyash, this byproduct has created a serious disposal problem for many power generating industries which have not, as yet, been solved. Studies by many researchers have shown that flyash, clay and other waste products can be used to a greater extent for co-disposal along with leachate and other hazardous wastes encountered in waste streams.

Baker and Luh [1] (1971) studied adsorption of pyridine from aqueous solution onto sodium kaolinite and sodiuk montmorillonite. The batch study data revealed that the extent of sorption is from acidic solutions with maxima occuring from sodium kaolinite at approximately pH 5.5 and for sodium monmorillonite at approximately pH 4.0. The sorption was described by the Freundlich Isotherm. They also explored the desorption of pyridine-clay in aqueous solution which showed that the desorption is a direct function of pH and the number of stages [2] (1971). At a comparable pH and clay to organic ratio they showed that Pyridine desorption was slower than desorption.

Clay was used to remove phenols from aqueous solutions and this process was developed by Rios [3](1960). He showed that clay adsorbents ordinarily used for purification of organic substances and which have been regenerated by combustion have a good adsorbent power for phenolic substances in solution.

The adsorption and mobility of polychlorinated biphenyls (PCBs), polybrominated biphenyls (PPBs), hexachlorobenzene (HCB) and other halogenated hydrocarbons using earth materials was studied by Griffin et.al. [4](1980). They predicted that the adsorption of the halogenated compounds can be described by the Freundlich Isotherm. They found a direct correlation between the total organic carbon content of the soils and the amount sorbed.

Zachara et.al. [5](1987) studied single and binary solute sorption of pyridine, quinoline and acridine on low organic carbon subsurface material when saturated with water. Single solute sorption for all compounds is higher in the acidic soil as compared to alkaline soil. Also competitive sorption occurs more in acidic soil compared to the alkaline soil.

Natural clay when suitably treated can be used as an adsorbent for treatment of organic compounds. Wolfe [6]

(1986) has developed this when he treated montmorillonite with amines.

Griffin et.al. [7] (1976) examined the removal of heavy metals by kaolinite and montmorillonite and concluded that both cationic and anionic adsorption on these clays were significant.

Preferential sorption characteristics for clays for removing lead, cadmium and calcium was studied by Bittell and Miller [8](1974) and they found that cations exhibited consistent preferential characteristics.

In a test done in University of Cincinnati, it was found that flyash demonstrated capabilities in removing refractory organics from wastewater in both batch and column study. This indicates that the removal of chemical oxygen demand (COD) by adsorption is logarithmically related to time of mixing, initial COD and, concentration of flyash [9](Deb, et.al. 1966).

Ballance et.al. [10](1969) reported that flyash has certain properties which enhances chemical coagulation and settling of turbid water, when flyash is used as a coagulant aid in water treatment.

Chan et.al. [11](1978) used a combinations of acidic and basic (illite/flyash/zeolite) sorbents and reported that it is most efficient for the removal of heavy metals and fluoride ions from petroleum sludge leachate.

The effectiveness of adsorption for concentration of acidic range of different types of refractory organic materials has been demonstrated. Synthetic organic waste materials that have been shown to be subject to removal from aqueous solutions or phenols in [12,13], alkylbenzenesulfonates and other synthetic detergent compounds [14,15], insecticides and fungicides [16], nitrochlorobenzenes [17], tetrachloroethane and trychloroethylene [18], synthetic dyes [12].

I.C. BACKGROUND :

Flyash is the particulate residue from flue gases which is collected by means of electrostatic precipitators when powdered coal and/or oil are burned. Coal contains non-combustible mineral matters. A large portion of this mineral matter is transformed into residual by-products during carbonization process. Flyash obtained from thermal power plants as a byproduct creates problems regarding its storage and disposal. An inexpensive management technology in handling/disposal/utilization of flyash is needed. Flyash was used in this study to investigate the effectiveness as an adsorptive material.

The exact chemical composition of flyash is dictated by both the composition of the fuel fired and the degree of burning. As the efficiency of burning increases, the carbon content of the flyash decreases. In addition, the type of combustion equipment used also has a bearing on the chemical composition of flyash.

The physical characteristics of flyash used for the study is given in Table 1, in appendix A (Liskowitz, et.al.[19], 1982).

Also, the literature that was studied revealed that flyash has been used in a variety of different applications, including the construction of roads, ice control, dams and bridges, the making of concrete and cinder blocks, and as soil conditioners.

Flyash was selected as an sorbent because of the following reasons :

1. Flyash is a by-product material.
2. Flyash is one of the cheapest materials.
3. Flyash has certain properties which enhance chemical coagulation and settling characteristics of the pollutants.
4. Flyash is capable of removing appreciable quantities of BOD and COD.
5. Combinations of Illite/flyash/Zeolite are very efficient for the removal of heavy metals and fluride ions from petroleum sludge leachate.
6. Flyash has been found to have good sorption capacity for Mercury (II).
7. Very little work has been done to treat hazardous organics using flyash.

II. THEORY OF ADSORPTION :

II.A. TYPES OF ADSORPTION :

Adsorption can occur from solution onto a solid as a result of the characteristic properties for a given solute-solvent-solid system or a combination thereof. High affinity of the solute for a particular solid or a dislike of the solute for the solvent (hydrophobic) are the two major forces.

In the design of processes used for treatment, two main aspects, kinetics and ultimate capacity for adsorption are the main creteria. This is regardless of the physical state of the adsorbent and the process in which it is being used. The forces that govern the uptake kinetics of the organic solutes from dilute solutions are quite different from those which govern the ultimate capacity [20](Weber et.al.,1964).

Adsorption of materials from solution by porous adsorbents like flyash and activated carbon takes place by essentially three rate limiting steps.

1. Film Diffusion : This is the transport of adsorbate through the surface film to the exterior of the adsorbent.
2. Pore Diffusion : This is the diffusion of the adsorbates within the pores of the adsorbent and,

3. Chemisorption : This is the adsorption of the solute on the interior surfaces bounding the pore and capillary spaces of the adsorbent.

During adsorption the molecules leave solution and are held on the solid surface by chemical and physical bonding. The molecules are called the adsorbate and the solid is called the adsorbent. If the bonds that form between the adsorbate and the adsorbent are very strong, the process is almost always irreversible, and chemical adsorption or chemisorption is said to have occured. Otherwise, if the bonds that are formed are very weak, as is characteristic of bonds formed by van der Waals forces, physical adsorption is said to have occured. The forces involved in physical adsorption include both van der Waals - London (Dispersion) Forces and electrostatic interactions comprising mainly polarizability and dipole interactions [20][22](London, 1930 a and b). The molecules adsorbed by this means are easily removed, or desorbed, by a change in the solution concentration of the adsorbate and the process is said to be reversible.

The van der Waals - London interaction is comprised of three interactions:

1. dipole - dipole interaction,
2. dipole -induced dipole interaction and
3. induced dipole - induced dipole interaction.

The most significant factor is the dispersion due to the interaction of induced dipole - induced dipole. This is present between all atoms and molecules in close proximity. The electrons move in their orbits and the force is originated from their oscillating motion. This force results in a dipole and this can induce a dipole in other atom or molecule near it by interaction.

Chemisorption occurs within the pores of the adsorbent. The characteristics of chemisorptive forces are high heat of adsorption, highly specific, monolayer only, may involve dissociation possibly over a wide range of temperature, slow and irreversible process, and electron transfer leading to bond formation (usually covalent) between sorbate and sorbent's surfaces [23](Atkins, 1978). This is an exothermic process as it produces large heat of adsorption. It can take place at extremely low sorbate concentration and still produce sorbent site saturation [24](Hamaker et.al., 1972).

II.B. FACTORS INFLUENCING ADSORPTION :

Adsorption is influenced by various factors - both physical and chemical. The surface area of the adsorbent, the nature of the adsorbate, dipole moment, pH, temperature and the type of the solutes influence the rate of adsorption.

Sorbent Characteristics : The surface area, the pore size distribution, heterogenity and composition are some of the characteristics which influence adsorption.

Specific surface area can be defined as that portion of the total surface area that is available for adsorption. Thus the amount of adsorption accomplished per unit weight of the solid adsorbent is greater the more finely divided and the more porous the solid [17] (Weber, 1964.) The surface reaction will vary with available surface area and hence the adsorption rate should exhibit a monotonic increase with some function of the inverse of the diameter of the adsorbent particles. Also, the adsorption capacity of a nonporous adsorbent should vary as the inverse of the particle diameter;that for a highly porous adsorbent should be relatively independent of particle diameter. Both the rate and extent of adsorption by particles of a fixed size should vary approximately linearly with the dosage of adsorbent over a range of doses that do not result in great differences in the concentration of the solute remaining in bulk solution phase [17,25] (Weber and Morris, 1963a,b;1964a).

Nature of the adsorbate : The controlling factor for adsorption equilibria to a large extent depends upon the solubility of the solute. According to Lundelius' rule an inverse relationship can be anticipated between the extent of adsorption of a solute and its solubility in the solvent from which adsorption occurs. Adsorption of an aliphatic series of organic acids on carbon from aqueous solution increases in the order formic-acetic-propionic-butyric, whereas the order is reverseed for adsorption from toluene [26](Holmes and McKelvey, 1928).

In general, the solubility of any organic compound in water decreases with increasing chain length, because the compound becomes more hydrocarbon like as the number of carbon atoms become greater. This is the Traube's rule.

Under appropriate conditions of pH a few materials have the property to ionize, for example fatty acids. Activated carbon commonly carries a net negative surface charge [27](Bean et.al., 1964) which is believed to be of significance for adsorption; further many of the physical and chemical properties of certain compounds undergo drastic changes upon ionization. As compounds become more complex, the effect of ionization becomes of decreasing importance [20](Weber,1964).

For adsorption purposes the effect of solute polarity on adsorption is that a polar solute will prefer the phase which is more polar [17] (Weber,1963).

Effect of pH : pH governs the degree of ionization. In adsorption process the hydrogen and hydroxide ions are adsorbed quite strongly, and the adsorption of other ions is influenced by the pH of the solution. Investigations of Snoeyink and Weber (1963) [17] of the reaction of the hydrated proton with active carbon have revealed that from a phenomenological point of view, both hydronium ion and the conjugate anion of the acid added are removed stoichiometrically.

Temperature : The extent of adsorption generally increases with decreasing temperature as adsorption reactions are generally exothermic. Small change in temperature tend not to alter the adsorption process to a significant extent.

Adsorption of mixed solutes : A mixture of many compounds are encountered during the adsorption process for purification of water/wastewater. These compounds may act relatively independently, mutually enhance adsorption or may interfere with one another.

Nature of the adsorbent: Mattson et.al.(1969, 1969a,b, 1970)[28, 29] provided a detailed examination of the character of functional groups formed on active carbon under different conditions of activation, using the internal reflectance spectroscopy as means of charecterizing surface functional group. To characterize the surface character of other potential adsorbents is difficult, but this information is very important because the physicochemical nature of adsorbent can have profound effects on the rate and the capacity for adsorption.

III. ADSORPTION ISOTHERM :

III.A. GENERAL DESCRIPTION :

The extent to which the full surface area of an adsorbent can be used for adsorption depends on the concentration of solute in the solution in which the adsorbent is mixed. The specific relationship between the concentration of the solute and the degree of removal from solution by an adsorbent at constant temperature defines adsorbtion isotherm [20] (Weber et.al., 1964).

Equilibrium should be reached between the concentration of solute remaining in solution to that of the concentration of solute at the surface of the adsorbent for adsorbtion to take place. This is positive adsorption in a solid-liquid system. At this equilibruium there is a defined distribution of solute between the liquid and the solid phases. This distribution ratio measures the position of equilibrium. This depends on the concentration of the solute, presence of other solutes, the type of system, temperature and various other factors.

The quantity of adsorbate that can be taken up by an adsorbent is a function of the concentration of the adsorbate, surface area of the sorbent, pressure and the temperature of the system. Generally, the amount of material adsorbed is determined as a function of the concentration of the sorbate at a constant temperature, and the resulting function is called the adsorption isotherm. Commonly, the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but is not directly proportional.

The adsorption of an organic solute from solution can be represented by the following equation

$$X + S_v + H_2O = S_x + H_2O \quad \ldots\ldots\ldots\ldots\ldots(1)$$

where X is the adsorbate molecule, S_v represents a vacant adsorption site and S_x is the sorbate-sorbent complex.

The equilibrium constant K for the equation (1) is given by

$$K = aS_x / (a_x)(aS_v) \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where aS_x, a_x, and aS_v are the activities of the complex, the solute and the sorbent respectively.

For a very dilute solution the vacant adsorption site is the same as the pure solid phase and it is defined as equal to one. Hence the the sorbate - sorbent complex formed due to adsorption and the liquid phase concentration of the solute are directly proportional to each other. This can be represented as

$$K = (r_{sx}) \ (C_{sx})/(r_x)(C_x) \quad \ldots\ldots\ldots\ldots\ldots(3)$$

where r_{sx} is the is the activity coefficient of the complex, r_x is the activity coefficient of the organic compound, C_{sx} is the concentration of the complex and C_x is the concentration of the solute.

As the activity coefficient is very small for dilute solutions it can be neglected and the above equation can be reduced to

$$K = C_{sx} / C_x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

K is called the equilibrium adsorption coefficient which tells the adsorption capacity.

III.B. LANGMUIR ISOTHERM :

The Langmuir adsorption model is valid for single layer adsorption. This equation is limited by the assumption of uniform adsorption on the surface. Both the Langmuir and the BET isotherms may be deduced from either kinetic considerations or the thermodynamics of adsorption [30,31,33] (Langmuir, 1918; Brunauer et.al., 1938; Adamson, 1960).

The Langmuir isotherm is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface and that the energy of adsorption is constant. Also, there is no transmigration of adsorbate in the plane of the surface.

The Langmuir Isotherm has the general form

$$q_e = Q^o b C_e / (1 + b C_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where q_e is the amount adsorbed per unit weight of adsorbent

Q^o,b are empirical constants

C_e is the equilibrium concentration of adsorbate in solution after adsorption.

Actually Q^o is the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface and b is a constant related to the energy or net enthalpy by the equation

$b \quad e^{-\ H/RT}$

where H is the energy or net enthalpy

R is the gas constant and,

T is the temperature.

Two convenient linear forms of the Langmuir equation are

$C/q_e = 1/bQ^o + C/Q^o$ .... (6)

or

$1/q_e = 1/Q^o + (1/bQ^o)(1/C)$ ....(7)

Either of these forms may be used for linearization of data that accord with the Langmuir equation.

For very small amounts of adsorption the specific adsorption is proportional to the final concentration of adsorbate in solution, yielding a linear adsorption relationship

$q_e = Q^o bC$ .... (8)

For large amounts

$q_e = Q^o$

When adsorption is in accordance with the Langmuir isotherm, the total capacity of the adsorbent for an adsorbate is given by the limiting value of q_e as C approaches C and is equal to the value of Q^o. Assumption of a value for the surface area covered per molecule then allows computation of the active specific surface area of the adsorbent. The specific area can be determined by the relationship

$$_{s} = Q^{o} N_{Av} \; {}^{o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

in which ^{o} is the area per molecule, N_{Av} is Avogadro's Number, and Q^{o} is expressed in moles of adsorbate per unit weight of adsorbent.

A program written in Pascal language to solve the Adsorption Isotherm is given in appendix A.

III.C. Brunauer, Emmett, Teller (BET) Isotherm :

The Brunauer, Emmett, Teller (BET) Isotherm reflects multilayer adsorption. The assumptions in this Isotherm are that for a given layer need not complete formation prior to the initialization of subsequent layers and hence the equilibrium conditions will therefore involve several types of surfaces in the sense of number of layers of molecules on each surface site.

BET equation takes the form as shown below for adsorption from solution with the additional assumption that layers beyond the first have equal energies of adsorption.

$$q_e = BCQ^{o} /\{(C_s - C)[1 + (B - 1)(C/C_s)]\} \quad \ldots . (10)$$

in which C_s is the saturation concentration of the solute, C is the measured concentration in solution at equilibrium, Q^{o} is the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface, q_e is the number of moles of solute adsorbed per unit weight at concentration C, and B is a constant expressive of the energy of interaction with the surface. This equation in linear form can be rearranged as

$$C/(C_s - C)q_e = 1/BQ_o + \{(B-1/BQ)(C/C_s)\} \quad \ldots.(11)$$

A plot of the left hand term of the above equation against C/C_s gives a straight line of slope $(B - 1)/BQ^o$ and intercept $1/BQ^o$.

III.D. Freundlich Isotherm :

The Freundlich or the van Bemmelen equation has been used widely in adsorption processess. This isotherm applies for heterogenous surface energies in which the term, b, in the Langmuir Equation varies as a function of surface coverage, q_e , strictly due to variations in heat of adsorption (Adamson, 1967)[32].

The Freundlich equation has the general form

$$q_e = K_F C^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(12)$$

where K_F and n are constants, and $n > 1$

K_F is the capacity parameter related to the energy distribution and,

1/n is the intensity of adsorption.

The Freundlich Isotherm is basically empirical. Datas are found fitted to the logarithmic form of the equation

$$\log q_e = \log K_F + 1/n \log C \quad \ldots\ldots\ldots.(13)$$

which gives a straight line with a slope of 1/n and an intercept equal to the value of log K_F for C = 1.

The Freundlich Isotherm generally agrees quite well with Langmuir Isotherm and experimental data over moderate ranges of concentration.

IV. MATERIALS AND METHODOLOGY :

The materials used in this study are flyash, activated carbon and organics. This section describes the experimental and analytical techniques that are used to conduct these tests.

IV. A. Adsorbate Characteristics :

Organic compounds from three different functional groups, commonly found in industrial wastes were selected as the target species. They are as follows;

Alcohols - iso-Propanol and sec-Butanol;
Ketones - Methyl ethyl Ketone (MEK) and Acetone;
Aldehydes - Formaldehyde and Acetaldehyde.

All the above compounds used were laboratory reagent grade 99.99 % pure obtained from Fischer Scientific Company, Springfield, New Jersey. The Physical Properties of the compounds which were used are shown on table 1 to 4.

IV. B. Adsorbent Characteristics :

Flyash was used as the adsorbent. This material is described as the particulate residue from flue gases which is collected from burning of coal and/or oil. It is collected by means of electrostatic precipitators before they escape from the stacks. The constituents of flyash vary according to the type of coal used and the degree of combustion. In general, flyash is a fine, sandy material, dark grey in color. The individual particle size of this material ranges from 0.5 to 100 microns.

Militant, Conemough, Wellmore Cactus, Upshore, Keystone, Blender and Deep Hollow were the different types of flyash that was used for the experiments. They get their names depending upon the coal mines from which they originated. Characteristics, composition and fusion temperature of flyashes are described on table 5(Appendix B).

Activated carbon has been used as control because it is a well established adsorbent. Witco grade 718, petroleum hydrocarbon based activated carbon was used. The surface area = 1050 m /g approximately, 12 x 30 mesh (Manufacturers information). Prior to its use the material was soaked overnight in distilled water and dried at 103 C for 12 hours in order to remove fine particulates and dust from the material. All the experimental procedures used for flyash was used for activated carbon also.

IV. C. Instrument Used :

Perkin Elmer (Model 900) Flame Ionization Detector (FID) Gas Chromatograph was used for analysis. The common technique of gas chromatography is the elution technique, in which a stream of inert gas, called carrier gas passes continuously through the Chromatographic column and the sample to be analyzed is introduced instantaneously at the beginning of the column. When it reaches the column, it is largely adsorbed, but an equilibrium is set up between the column and the gas in the interstices of the column so that a portion of the sample always remains in the gas phase. This portion moves a little further along the column in the carrier gas stream, where it again equilibriates with the column. At the same time, material already adsorbed in the column re-enters the gas phase so as to restore equilibrium with the clean carrier gas which follows up the zone of vapour. The equilibrium constant is called the partition coefficient, K, which is defined as

K = mass of vapor/unit vol. of stationary phase (column packing) divided by the mass of vapor/unit volume of mobile phase (carrier gas). This coefficient is related to the retardation factor, R_F , which is the major parameter in all kinds of chromatography by the equation;

$$K = a/b\ (1/R_F - 1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

where, a is the fraction of the area of the section of the column occupied by the mobile phase, b is fraction of the area of the section of the column occupied by the stationary phase,

R_F is the retardation factor and

K is the partition coefficient.

Hence, the solute which has been introduced must traverse the entire length of the column in a period of time that is related to its partition coefficient, K. This travel time is called the retention time. The other end of the column is connected to a device called the detector, which detects the components as they emerge.

The Flame Ionization Detector, In which carrier gas is burned in a flame which causes ionization, which gives the flame an electrical conductivity was used. The conductivity of hydrogen flame is very small [39] (Littlewood, 1970), but when an organic vapour enters the conductivity rises and this increament is measured, usually in terms of area and is recorded.

The flame ionization detector required three gas streams - carrier gas, in this study Helium, at the rate of 1 ml/min., Hydrogen at the rate of 30 ml/min. and air at the rate of 250 to 300 ml/min.. The column effluent mixes with the hydrogen and is burned in an atmosphere of air. When organic matter is burned in hydrogen flame, positive and negative ions are generated. An ionization potential is set up between the two electrodes and the flow of ions produces an electric current in proportion to the amount of material burned. The current usually in the pico-ampere range. is amplified by an electrometer which produces an output signal to be relayed to a chart recorder, integrator or computer.

IV. D. Methodology :

Flyash and/or activated carbon (adsorbent) were transferred into a glass media bottle after weighing the accurately. The glass bottles were provided with a rubber lined septum and plastic screw cap. The bottles were completely filled with the dilute solution of the target compound and were agitated by a shaker for 12 hours in order to achieve equilibrium condition. Each mixture was allowed to settle overnight. These samples were then analyzed using the Perkin-Elmer Model 900 Flame Ionization Detector Gas Chromatograph.

For the adsorption isotherm study, the weight of the adsorbent was maintained at a constant (20g), while concentration of the target compounds were made to vary in the range of 10 mg/L to 100 mg/L. After weighing accurately 20 grams of flyash it was transferred into a 750 ml. glass media bottle which was equipped with rubber lined septum and plastic screw cap. The glass media bottles were then filled with the test solutions of known concentration, No vapor space was left in the bottles in order to minimize loss due to evaporation. The sealed bottles were then agitated using a shaker for equilibrium concentration (this is usually between four and six hours). Ten ul. of the clear supernatent of each sample was then injected into the gas chromatograph for analysis.

V. ADSORBABILITY TESTS :

V.A. ADSORBABILITY EXPERIMENTS :

An study was performed to investigate the occurance of adsorbtion of organic compounds onto flyash. In the laboratory six organic compounds commonly found in the industrial waste streams, were selected. They are s-Butanol, Isopropanol, Acetaldehyde, MEK, Formaldehyde and Acetone. Militant Flyash was used as the sorbent.

The method used to prepare and analyze the target compounds is described in section IV.D.

Langmuir isotherm equation had been used to analyze and evaluate adsorptive characteristics of flyash. The equation in the linear form is given below

$$1/q_e = 1/Q^o + (1/bQ^o * 1/C) \quad \ldots\ldots\ldots\ldots (15)$$

where q_e is the loading of impurity on a unit weight of sorbent material, C is equilibrium concentration remaining in solution , Q^o is a constant equal to the Y intercept and b is a constant which is got from the slope of the line (slope = $1/bQ^o$).

Single solute isotherm data were fit into the Langmuir isotherm equation. The data points were transformed by taking the inverse of C (the concentration of organic remaining in solution) vs the inverse of q_e (the amount adsorbed per unit weight of the adsorbent). These values were fit into the isotherm. The values of the concentration (C) and the amount of organic adsorbed per unit weight of the adsorbent are given in tables 6 to 11 (Appendix B). The graphs are shown in figures 1 to 6(Appendix C).

From the analysis of the data it appears that all the target compounds can be adsorbed to some extent onto flyash. The value of b which is directly proportional to the energy of adsorption is positive in all the cases. This proves that adsorption is occuring. The values of q_e is positive and this shows that monolayer adsorption is occuring.

Comparisions can be made for the adsorption of organics depending upon the group they belong. Methyl ethyl Ketone (MEK) and Acetone belong to the Ketone group. The water octanol partition coefficient of Methyl Ethyl Ketone is 3.22 and that of Acetone is 0.58. Water octanol partition coefficient is inversely proportional to the solubility. Hence, MEK is less soluble and it has the tendency to adsorb more when compared to Acetone. A similar comparision can be made for s-Butanol and iso-Propanol. Both belong to the Alcohol group and iso-Propanol is more soluble in water and hence it has a lesser tendency for adsorption when compared to s-Butanol. This is the same case with the aldehyde group. A summary of the properties of organic compounds used in adsorption correlations is given in table 12 [34] (Weast, 1977/78).

V.B. CHARACTERISTICS EFFECTING ADSORPTION :

Solute characteristics, such as molecular weight, functional group, polarity and solubility have been found to affect the degree and amount of adsorption of organic compounds on flyash. These parameters act in one system at the same time and hence the effect is a combined one. Experiments were conducted by Kashi Banerjee, towards his doctoral dessertation, 1988 [35] to study the affect of these various parameters which effect adsorption. Some of them are discussed briefly in the following paragraphs.

Effect of flyash dosage on the adsorption of Phenol : As seen the adsorption increased with increasing flyash dose up to a certain value (20 g) and then there was no further change, indicating that the system had reached steady state condition. For the study of adsorbability 20 g. of flyash per 750 ml. of organic waste solution has been used. This was considered to be the optimum dosage in this adsorption process.

Effect of washing : Flyash was washed because results indicate that washed flyash has better adsorptive properties than unwashed. Flyash which was obtained from thermal power plants contains various water soluble materials and by washing it helps removal of these materials. Previous research [36] (Liskowitz, et.al., 1983) indicated that flyash obtained from thermal plants contained dust and fine particulate matter. These matter bloc the openings and hence the capacity for adsorption is reduced. According to Kashi Banerjee, 1988, [35] an examination of the organic removal using high fusion, low power Militant flyash showed that the removal of phenol waste by washed flyash is about one to two times more than that of unwashed flyash.

A batch kinetic study was conducted to evaluate the optimum contact time between the waste solution and the flyash. The results indicated that the optimum detention time for removal of target compounds is usually sixty to hundred and fifty minutes. The optimum contact time is higher for high water soluble compounds than that of the low water soluble compounds.

Also the effect of pH on adsorption was studied and it shows that the adsorption capacity of flyash increases with increase in pH to around 5.5 and then decreases. Maximum adsorption takes place in pH range of 4.5 to 5.5. The adsorption of organic compounds is highly pH sensitive. This can be accounted by the fact that acidic medium would lead to an increase in Hydrogen ion concentration which neutralizes the negatively charged residual carbon surface enhancing the adsorption of negatively charged organic species.

Experiments conducted in the laboratory for multi-component solutions show the competition of the target compounds with each other. This competition for adsorption sites occurs when a wide spectrum of contaminants are present in the solution. This is discussed in a greater detail below.

V.C. SIMPLIFIED COMPETITIVE ADSORPTION MODEL :

Simplified Competitive Adsorption Model had been used to verify the experimental data for multi-component system. The equation is given as

$$q_i = K'^{[(n'-1)/n']} * [\{K_i C_i^{(i/ni)}\}^{1/n'}]$$
$$* [\{(K_i/K') C_i^{1/n_i}\}^{1/n'}]^{n'-1} \text{ ....(16)}$$

where

q_i = solid-phase equilibrium concentration of solute i in multi-solute system,

C_i = liquid phase equilibrium concentration of the solute i in multi-component system.

K_i & n_i = Empirical Frendlich constant for solute i in single-solute system

n' = Average of n i.e., (n + n + n + ...n)/N

K' = Average value of K i.e., (K + K + K +.....K)/N

N = Number of components

Multi-component adsorptive behavior of the following combinations were examined by Kashi Banerjee 1988, [35].

1. o-Xylene and Butanol

2. o-Xylene and Butyraldehyde

3. o-Xylene, Butanol, Methyl isobutyl Ketone and Butyraldehyde.

For each case the experimental data was compared with the theoretical value.

The program written in Pascal for calculating the value of q for the given number of components is given in appendix A.

VI. Kinetics of Adsorption :

VI.A. Overview :

Weber and Morris, Eagle and Scott, Dryden and Kay[17][37][38] and many others worked on kinetics of adsorption using activated carbon as the sorbent. They have concluded that the rate at which dissolved organic substances are removed from dilute aqueous solutions by solid adsorbent is a highly signigicant factor for applications of this process for water quality control. The overall rate of adsorption appears to be controlled by the rate of diffusion of solutes within the pores of the adsorbent. It is therefore necessary to examine the rate (kinetics) of adsorption of organic compounds onto flyash.

VI.B. Calculation of Rate Constant :

Efficiency is an important characteristic in the adsorption process. The residence time of the sorption reaction is governed by the rate constant, i.e., the rate at which sorption is taking place.

When sorption is taking place from liquid phase (of organic compounds) to solid phase it can be considered as an reversible reaction with an equilibrium being established between the two phases. A first order kinetic reaction model can be expressed as

$$A \underset{K_2}{\overset{K_1}{\qquad}} B$$

If the model holds true then the rate equation is expressed as

$$dC_B/dt = -dC_A/dt = K_1C_A-K_2C_B= K(C_{AO}-C_{AO}X_A) - K_2(C_{BO}+ C_{AO}X_A) \quad ....(17)$$

where

C_{AO} = initial concentration of the target organic compound in the solution, (mg/L) at time, $t = 0$

C_{BO} = initial concentration of the target organic compound on the sorbent, (mg/L) at time, $t = 0$

C_A = concentration of the target organic compound in the solution at any time (t), (mg/L)

C_B = concentration of the target organic compound on the sorbent at any time (t), (mg/L)

X_A = fractional conversion, i.e., adsorption of the target organic compound

K_1 = first order adsorption rate constant (time)

K_2 = first order desorption rate constant (time)

At equilibrium conditions

$$dC_B /dt = -dC_A/dt = 0 \;\ldots\ldots\ldots\; (18)$$

and $$X_{AE} = (K_E - C_{BO} /C_{AO})/(K_C+1) \ldots (19)$$

in which X_{AE} is the fractional conversion at equilibrium condition and K_C is the equilibrium constant defined as

$$K_C = C_{BE}/C_{AE} = (C_{BO}-C_{AO}X_{AE})/(C_{AO}-C_{AO}X_{AE}) = K_1 /K_2 \ldots (20)$$

in which C_{BE} and C_{AE} are the equilibrium concentrations for the target organic compound on the sorbent and in the solution respectively. The differential form of the rate equation in terms of equilibrium conversion can be obtained from equation 17, 19 AND 20.

$$dX_A /dt = (K_1 + K_2) (X_{AE} - X_A) \;\ldots (21)$$

Integration of equation 21 and substituting for K from equation 20 gives,

$$-\ln \{1 - (X_A /X_{AC})\} = K_1 \{1 + (1/K_C)\} t \ldots (22)$$

or $$\ln \{1 -(X_A /X_{AC})\} = -K't \;\ldots\ldots\ldots\ldots (23)$$

where K' = overall rate constant (Time^{-1})

and $$K' = K_1 \{1 + (1/K_C)\} = K_1 + K_1 /K_C$$

$$K' = K_1 + K_2 \;\ldots\ldots\ldots\ldots (24)$$

The slope of equation 23 denotes the overall rate constant (K') value of the system.

Three different sized particles of High Fusion, Low Power Militant flyash were used as sorbent materials in this phase of experiment. The grain size analysis was performed as per ASTM D421 an D422 (Mechanical as well as Hydrometer Method). Dilute solution of o-Xylene was used as the target compound. The overall rate constant value (-K′) has been calculated from the plot of ln $\{1 - (X_A / X_{AC})\}$ versus t as per equation 23. It was observed that the overall rate constant value (-K′) increased with an increasing influent concentration until it reaches the steady state condition was achieved in this case at an influent concentration of 135 mg/L. Driving force does not have any effect on the rate constant after this value of influent concentration of 135 mg/L.

Data was plotted as per the equation 21 at an initial concentration of 150 mg/L of o-Xylene. A near straight line fit was observed in all cases (Figure 14), indicating that the sorption reaction can be approximated to first order reversible kinetics. The values for the constants K_1 , K' , and K_C were calculate using Equations 20 to 24 and are presented in tables 13 and 14(Appendix B). The average particle diameter of the flyash decreases, the overall uptake rate increases, i. e., the flyash particle size established an inverse functional relationship with the overall rate constant value.

The adsorption of o-Xylene onto activated carbon follows first order reversible kinetics because a near straight line fit is got when a plot of ln $\{1 - (X_A / X_{AC})\}$ versus time is made. In order to evaluate the optimum contact time between the aqueous solution of the target compounds and the flyash, samples at particular time intervals were collected and analyzed until the mixture reached the equilibrium condition. Adsorption is indicated by the decreasing concentration of solute remaining in the solution. Optimum contact time for removal of the target compounds is in the range of one to two hours. Generally, the optimum contact time is higher during the adsorption of high water soluble compounds onto flyash than that of low water soluble compounds.

Phenol, Aniline, m-Cresol and o-Xylene were adsorbed onto Militant Flyash and Activated carbon. As seen in Figures 12 to 19 (Appendix C), the plateau was reached in about 40 minutes for activated carbon, whereas for flyash it was in between one to two hours.

VI.C. Effect of Residual Carbon Content of Flyash on Rates of Adsorption :

Studies were performed using an aqueous solution of Aniline onto different types of flyashes to see the effect of residual carbon on adsoprtion. The following flyashes were used - Wellmore Cactus, Conemough, Blender, Keystone, Militant and Upshore.

A constant influent concentration (275 mg/L) was maintained in each of the case. The concentration of Aniline remaining vs time using these different types of flyash are given in figures 7 to 13(Appendix C). It is clear from the figures that the rate of uptake of Aniline is a direct function of residual content of flyash. For flyashes the maximum K value was obtained during the adsorption of Aniline onto Wellmore Cactus flyash, which contains maximum percentage of the residual carbon among all the other flyashes studied. The rate parameter K established a strong linear correlation (R = 0.95) with the residual carbon content of the flyash.

For comparision purposes Aniline was made to adsorb onto Activated Carbon. The maximum adsorption onto activated carbon was acheived in thirty minutes where as for the flyash it took from sixty to 150 minutes.

VI. D. Effect of Flyash Particle Size on the rate of Adsorption :

The rate of heterogenous reaction such as adsorption onto a solid surface will vary with the particle size for a constant mass of sorbent (Weber) This rate should then exhibit a monotonic increase with some function of the inverse of the diameter of the sorbent (Helfferich).

The experiment was conducted using different sized particles of Conemough flyash on the aqueous solution of Aniline. The particle diameters are average of the mesh sizes for the sieves passing and retaining the particles. The concentration of Aniline remaining vs time was plotted for different particle sizes from the data. Figures 20 to 23(Appendix C), show the effect of size distribution. Results indicate that the relative rates of adsorption, i.e., the rate parameter, k, increases as the particle diameter of the Conemough flyash decreases. For example, the average particle diameter of the Conemough flyash used in this experiment to adsorb Aniline was 0.211 mm, 0.15 mm, 0.075 mm, and less than 0.075 mm and the corresponding rate parameters obtained are 0.375 mg/g(min) , 0.51 mg/g(min) , 0.73 mg/g(min) , and 1.38 mg/g(min) respectively. This confirms well to the hypothesis that the rate of adsorption is an inverse function of the sorbent's particle diameter.

VII. Conclusions and Summary :

The results of the study of adsorption and kinetics of adsorption of organic compounds on flyash may be summarized as follows

Uptake from dilute solutions proceeds slowly when compared to that of activated carbon. The time taken for adsorption onto flyash is about thirty to one hundred times more than that of activated carbon and this depends upon the carbon content of the flyash. The adsorption onto flyash follow the same pattern in terms of the effect of pH, temperature, and other physical and chemical factors, to that of activated carbon.

The effect of particle size of adsorbent have been observed to exert an influence on the capacity of carbon for adsorption. Capacity has been observed to increase with decreasing particle size of the adsorbent. The effect is probably a result of the opening of tiny, effectively sealed channels in the flyash. The surfaces of these channels become available for adsorption; thus, the specific area of the carbon may be increased. Also the residual carbon content effects the adsorption capacity and the rate. This can be seen by the fact that Wellmore Cactus flyash adsorbs more concentrations of the organics compared to other types of flyash, when subjected to Phenol at the same influent concentration.

These findings helps us to arrive at the conclusion that the adsorption mechanisms and the forces that take place during the adsorption of organic compounds onto flyash are identical to that of activated carbon. This theory can be used for treatment and disposal of organic material, where a cheap and available adsorbent is required.

Landfilling is an engineered method of disposal that involves collection, transportation, treatment and disposal of solid and semisolid wastes in the land. This should be done in a manner that it would not pose a threat to man and environment. One of the main problems of a landfill is the leachate, which may contaminate the groundwater and surface water. This problem can be overcome by providing the landfills with a liner surrounding the wastes in the fill so that contamination does not occur. Today many types of liners like low permeability clay and other rubber liners. This creates drianage problem. Tiles or perforated corrugated metal pipe installed at the bottom of the landfill can help collection of the leachate produced. The leachate collected needs treatment for disposal and this can be done using flyash. This depends upon the availability and the extent of treatment required for final disposal of the leachate.

Flyash can also be used for on site groundwater reclamation as time is not the main factor and adsorption can occur onto flyash. It can also be used in biological treatment processes as an alternative to air stripping or activated carbon. However, further investigation is necessary to apply this theory of adsorption onto flyash.

A lot of research can be done to explore the physical and chemical properties of flyash and increase the capacity and rate of adsorption. Addition of salts to the flyash to enhance the sorptive property or to use the combination of activated carbon and flyash for cost reduction in the process can be explored. The velocity and direction of the solution to be treated to get optimum adsorption capacity can be studied. Also the leaching charecteristics should be examined if flyash is to be used in landfills.

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APPENDICIES

```
(***********************************************************)
(                  Program for Langmuir Isotherm            )
(***********************************************************)

program qvalue (input, output);

const
     MAXNUM=10;

var
     Sum,num,denom,Q,b0,b,c,ci,qi   : real;
     I,N,j,j1                       : integer;
     outfile                        : text;
     filename                       : string[10];

begin
     writeln('Enter the output filename ');
     readln(filename);
     filename := filename+'.dat';
     assign(outfile,filename);
     rewrite(outfile);
     sum := 0.0;
     writeln ('enter the value of N     ');
     readln  (N);
     writeln ('enter the value of Q     ');
     readln  (Q);
     writeln ('enter the value of b0    ');
     readln  (b0);
     writeln(outfile,'         CI                    QI');
     writeln(outfile);
     writeln(' enter number of iterations :');
     readln(j);
     for i := 1 to N do
         begin
              writeln ('enter the value of b',i);
              readln (b);
              sum := sum + (b);
         end;
         for j1:=1 to j do
         begin
            writeln('enter the value of c:');
            readln(c);
            denom := 1 + sum*c;
            num := Q*b0*c;
            qi  := num/denom;
            writeln (outfile,'   ',c:4:5,'          ',
qi:4:5);
         end;
    close(outfile);
end.
************************************************************
```

```
(**********************************************************)
(* Program for multi-solute adsorption                    *)
(**********************************************************)
program th;

var
  q,k,c,n,k1,n1              : real;
  a1,a2,a3,po,l2,iter        : integer;
  ni,ki,ci                   : array  [1..40] of real;
  qi                         : array [1..4,1..40] of real;
  ans,ans1                   : char;

(*********************************************************)
     procedure input;

     begin
          clrscr;
          ans := 'y';
          while (ans = 'y')
            begin
               write('Select The Type Of The System ');
               writeln('And Then Give The');
               writeln('Values For The Parameters ');
               writeln('N and K.');
               writeln;
               writeln('Give The Type Of The System :');
               writeln;
               writeln(' 1.  System I.');
               writeln(' 2.  System II.');
               writeln(' 3.  System III.');
               writeln(' 4.  System IV.');
               write(' Type Response  :  ');
               readln(a1);
               po := a1;
               ans := 'n';
               writeln;
               if (a1 = 1) then
                  begin
                    write('For Butyral : ');
                    readln(ni[2],ki[2]);
                    a1 := 2;
                  end
               else if (a1 = 2) then
                  begin
                    write('For Butanol : ');
                    readln(ni[2],ki[2]);
                  end
               else if (a1 = 3) then
                  begin
                    write('For Aniline : ');
                    readln(ni[2],ki[2]);
                    writeln;
                    write('For Phenol : ');
                    readln(ni[3],ki[3]);
```

```
                  end
               else if (a1 = 4) then
                  begin
                    write('For Butyrald : ');
                    readln(ni[2],ki[2]);
                    writeln;
                    write('For MIBK : ');
                    readln(ni[3],ki[3]);
                    writeln;
                    write('For Butanol : ');
                    readln(ni[4],ki[4]);
                  end
               else
                  begin
                    ans := 'y';
                    writeln;
                    writeln('Type Correct Response !');
                    writeln;writeln;
                  end;
          end;
          writeln;
          write('For O-XY : ');
          readln(ni[1],ki[1]);
          writeln;
          write('Give N'' And K'' : ');
          readln(n1,k1);
          writeln;
          write('Give The Number Of Iterations : ');
          readln(iter);

     end; (* input *)


(*********************************************************)
     procedure calculate;

     var

          temp1,temp2,temp3,temp4,temp5,sum,sum1 : real;
          i,j,k : integer;

     begin
          sum := 0.0;
          for i := 1 to a1 do
             begin
               temp4 := ki[i] * exp((ni[i])*ln(ci[12]));
               temp5 := exp((1/n1)*ln(temp4/k1));
               sum := sum + temp5;
             end;
          sum1 := exp((n1-1)*ln(sum));
          for j := 1 to a1 do
             begin
               temp1 := exp(((n1-1)/n1) * ln(k1));
               temp2 := ki[j] * exp((ni[j]) * ln(ci[12]));
```

```
               temp3 := exp((1/n1) * ln(temp2));
               qi[j][l2] := temp1 * temp3 * sum1;
             end;
     end; (* Calculate *)


(***********************************************************)
     procedure output;

     var
          i,j,k : integer;

     begin
          clrscr;
          if po = 1 then
             begin
               write('Single Solute (O-XY ');
               writeln('and Butyral) :');
               writeln;
               writeln('Ci     Qi      Cj         Qj');
               writeln;
               for i := 1 to iter do
               write(ci[i]:3:3,'  ',qi[1][i]:4:3);
               writeln('  ' , ci[i]:3:3,'  ',qi[2][i]:4:3);
             end
          else if po = 2 then
             begin
               writeln('Two Component (O-XY and Butanol):');
               writeln;
               writeln('Ci     Qi      Cj        Qj');
               writeln;
               for i := 1 to iter do
               write(ci[i]:3:3,'  ',qi[1][i]:4:3);
               writeln(' ',ci[i]:3:3,'  ',qi[2][i]:4:3);
             end
          else if po = 3 then
             begin
               write('Three Component (O-XY, Aniline');
               writeln(' and Phenol) :');
               writeln;
               write('Ci     Qi      Cj        Qj');
               writeln('     Ck     Qk');
               writeln;
               for i := 1 to iter do
               write(ci[i]:3:3,'  ',qi[1][i]:4:3,' ');
               write(ci[i]:3:3,' ',qi[2][i]:4:3,'  ');
               writeln(ci[i]:3:3,'  ',qi[3][i]:4:3);
               end
          else if po = 4 then
             begin
               writeln('Four Component (Butyraldehyde
                          ,MIBK,Butanol,and o-Xylene)  :');
               writeln;
               writeln('Ci   Qi   Cj    Qj   Ck    Qk
```

```
                        Cl    Ql');
               writeln;
               for i := 1 to iter do
                  begin
                    write(ci[i]:3:3,'  ',qi[1][i]:4:3,
                    ' ',ci[i]:3:3,'  ',qi[2][i]:4:3,' '
                    ,ci[i]:3:3);
                    writeln('  ',qi[3][i]:4:3,' ',
                    ci[i]:3:3,'  ',qi[4][i]:4:3);
                  end;
          end;
          writeln;
          writeln;writeln('Press any key to continue...');
     repeat until keypressed;
     end; (* output *)


(**********************************************************)
begin (* main *)

     ans1 := 'y';
     repeat
          input;
          for l2 := 1 to iter do
             begin
               writeln;
               write('Give Concentration : ');
               readln(ci[l2]);
               calculate;
             end;
          output;
          writeln;
          write(' Do You Want To Perform Another Calculation
               y/n  : ');
          readln(ans1);
          writeln
     until ans1 = 'n';
end. (* end*)
```

```
(**********************************************************)
(*                Program to calculate slope              *)
(**********************************************************)

Program mvalue (input, output);

var
   x,y,m : array  [1..1000] of real;
   i     : integer;
   fvar  : text;

procedure input;
begin
     Assign (fvar, 'dataoxac');
     rewrite (fvar);
     writeln (fvar, '   ortho-Xylene/Act. Carbon');
     writeln (fvar, '   Influent Concentration = 100 mg/L');
     writeln;
     writeln(fvar);
          for  i := 1 to 17 do
          begin
          writeln ('Enter x');
          readln (x[i]);
          writeln ('Enter y');
          readln (y[i]);
          m[i] := (ln(y[i])/ln(x[i]));
          end;
            writeln (fvar,'Time',' Eff. Conc.','Slope ');
            writeln;
            writeln (fvar,'0.0000 ',' 100.0000 ','0.0000');
            for i := 1 to 17 do
             begin
             writeln (fvar,' ', x[i]:4:4, '',y[i]:4:4, '
                      m[i]:4:4, '   ');
             end;
             close (fvar);
end.

*************************************************************
```

TABLE 1:
Summary of properties of Organic compounds (Alcohol group) [34] (Weast,77/78)

Property	Methonol	Butonol	Isopropanol	Sec-Butonal
Molecular weight (m, g/mol)	32.04	74.10	60.09	74.12
Dipole moment (, [Debyel]	1.70	1.67	1.67	1.67
Electronic polarizibility (, 10^{-24} cm^3)	41.0	110.30	87.80	109.64
Molar volume (v, cm^3/Mol)	40.49	91.50	76.53	91.73
Parachor (p, cm^3, $dynes^{1/4}$/mol,$cm^{1/4}$)	88.29	203.78	165.18	200.89
Density (g/cm^3) at 20°c	0.7914	0.8908	0.7851	0.8080
Refractive index n_d at 20°c	1.3288	1.3992	1.3776	1.3954
Surface tension /dynes/cm at 20°c	22.61	24.60	21.70	23.00

TABLE 2:
Summary of properties of Organic compounds (Ketone group) [34](Weast,77/78)

Property	Acetone	MEK	MIBK	Cyclohexanone
Molecular weight (m, g/mol)	58.10	72.10	100.2	98.20
Dipole moment (u, [Debye])	2.89	2.89	3.08	3.25
Electronic polarizibility (,10^{-24},cm^3)	80.52	103.62	150.0	132.30
Molar volume (v, cm^3/mol)	73.47	89.52	125.10	98.41
Porachar (p, cm3, $dynes^{1/4}$/mol,$cm^{1/4}$)	162.10	199.34	282.50	221.36
Density (g/cm^3) at 20^{o}c	0.7908	0.8054	0.801	0.9978
Refrective index n_D at 20^{o}c	1.3588	1.3814 at 15^{o}c	1.396	1.4522
Surface tension /dynes/cm at 20^{o}c	23.70	24.60	26.0	25.6

TABLE 3:
Summary of Properties of Organic compounds (Aldehyde group)
[34](weast,77/78)

Property	Formaldehyde	Acetaldehyde	Butvaraldehyde
Molecular weight (m, g/mol)	30.0	44.10	72.10
Dipole moment (u, [Debye])	2.27	2.72	2.72
Electronic polarizibility (,10^{-24},cm^3)	42.46	57.45	102.84
Molar volume (v, cm^3/mol)	36.81	56.29	88.25
Porachar (p, cm3, dynes$^{1/4}$/mol,cm$^{1/4}$)	83.29	120.80	199.28
Density (g/cm^3) at 20°c	0.815	0.7834	0.817
Refrective index n_D at 20°c	1.3799	1.3316	1.3843
Surface tension /dynes/cm at 20°c	26.20	21.20	26.00

TABLE 4:
Summary of properties of Organic compounds (aromatic group)
[34](weast,77/78)

Property	O-xylene	Phenol	M-cresol	Ethyl benzene
Molecular weight (m, g/mol)	106.16	94.11	108.13	106.16
Dipole moment (u, [Debye])	0.62	1.45	1.30	0.59
Electronic polarizibility (,10^{-24},cm^3)	175.11	139.46	163.43	178.10
Molar volume (v, cm^3/mol)	118.37	87.77	104.61	122.41
Porachar (p, cm3, $dynes^{1/4}$/mol,$cm^{1/4}$)	277.25	221.96	261.42	284.56
Density (g/cm^3) at 20°c	0.8968	1.0722	1.0336	0.8672
Refrective index n_D at 20°c	1.5058	1.5509	1.5398	1.4959
Surface tension /dynes/cm at 20°c	30.10	40.90	39.0	29.20

TABLE 5:

Physical charecteristics of Flyash
[63](Liskowitz,et.el.,1982)

Coalmine	militant	Conemough	Wellmore Cactus	Deep Hollow (Back hopper)
Location	Clearfield Co.,PA	Conemough FA.	Buchanan Co.,VA.	preston Co.,W.Va
Boiler Temp.(F) Flame	n/a	2700	3150	1600
Coal Ash Fusion Temp.(F)	2555	2125	2155	2575
Leachats pH	3.6 - 7	7 - 8.5	8 - 9	3.9 - 7
Carbon Contents	1.52%	2.5%	3.73%	N/A
Sulphur Contents	0.95%	0.5%	0.53%	N/A

N/A = Not Available

TABLE 6:

Adsorption Isotherm
Acetone onto Militant flyash

Effluent concentration	X/M (g/g)
19.20	68.30
27.89	85.45
39.82	105.8
66.93	144.48
96.92	180.42

$b = 0.017$
$q = 0.273$

Table 7:

Adsorption Isotherm
MEK onto Militant Flyash

Effluent concentration	X/M (g/g)
19.73	68.30
30.00	104.78
49.82	142.78
69.20	174.47
174.47	218.70

b = 0.0159
q = 0.334

TABLE 8:

Adsorption Isotherm
Acetaldehyde onto Militant Flyash

Effluent concentration	X/M (g/g)
12.43	143.94
27.93	226.52
39.92	276.67
57.99	341.00
96.98	454.59

b = 0.0277
q = 0.552

TABLE 9:

Adsorption Isotherm
Formaldehyde onto militant flyash

Effluent concentration	X/M (g/g)
15.12	86.75
26.39	118.78
39.90	149.72
63.55	194.31
89.97	236.07

$b = 0.0240$
$q = 0.319$

TABLE 10:

Adsorption Isotherm
s-Butanol onto militant flyash

Effluent concentration	X/M (g/g)
19.23	99.12
29.20	133.35
47.26	187.77
58.32	217.92
79.32	271.10

b = 0.0112
q = 0.551

TABLE 11:

Adsorption Isotherm
Isopropanol onto militant flyash

Effluent concentration	X/m (g/g)
13.69	38.71
26.92	62.15
37.91	78.98
53.62	100.67
73.98	126.11

b = 0.0152
q = 0.222

Table 12. Summary of properties of Organic Compounds used in Adsorption Correlations [34] (Weast, 1977,78).

Property	Acetone	MEK	iso-Propanol	s-Butanol	Form-Aldehy.	Al
Molecular Weight (M, g/mol)	58.10	72.10	60.09	74.12	30.10	44.10
Dipole Moment (u, Debyel)	2.89	2.72	1.67	1.67	2.27	2.72
Electronic Polarizibility (,10 cm)	80.52	103.62	87.8	109.64	42.46	57.45
Molar Volume (v, cm /Mol.)	73.47	89.52	76.53	91.73	36.81	56.29
Parachor (P, cm ,dynes Mol,cm)	162.1	199.34	165.18	200.89	83.29	120.8
Density (g/cm ,at 20 C)	.7908	.8054	.7851	.808	.815	.7834
Refractive Index (n at 20 C)	1.3588	1.3814 at 15 C	1.3776	1.3954	1.3799	1.3316
Surface Tension (dynes/cm at 20 C)	23.7	24.6	21.7	23.0	26.2	21.2

TABLE 13:

Adsorption kinetics of o-Xylene onto high fusio Militant FLyash

Average particle diameter, (mm)	k per min.	k_1 per min.	k_2 per min.
0.150 mm (-70 to +100 mesh)	0.058	0.032	0.026
0.075 mm (-100 tO +200 mesh)	0.162	0.119	0.043
less than 0.075 mm (less than 200 mesh)	0.200	0.168	0.032

where:

k = overall rate constant (per min)
k_1 = rate of adsorption (per min)
k_3 = rate of desorption (per min)

TABLE 14 :

Adsorption kinetics of o-Xylene onto Activated carb

Average particle diameter, (mm)	k per min.	k_1 per min.	k_2 per min.
0.273 mm (-50 to 60 mesh)	6.16	5.749	0.411

where:

k = overall rate constant (per min)
k_1 = rate of adsorption (per min)
k_2 = rate of desorption (per min)

Figure 1. Adsorption Isotherm

s-Butanol onto Militant Flyash

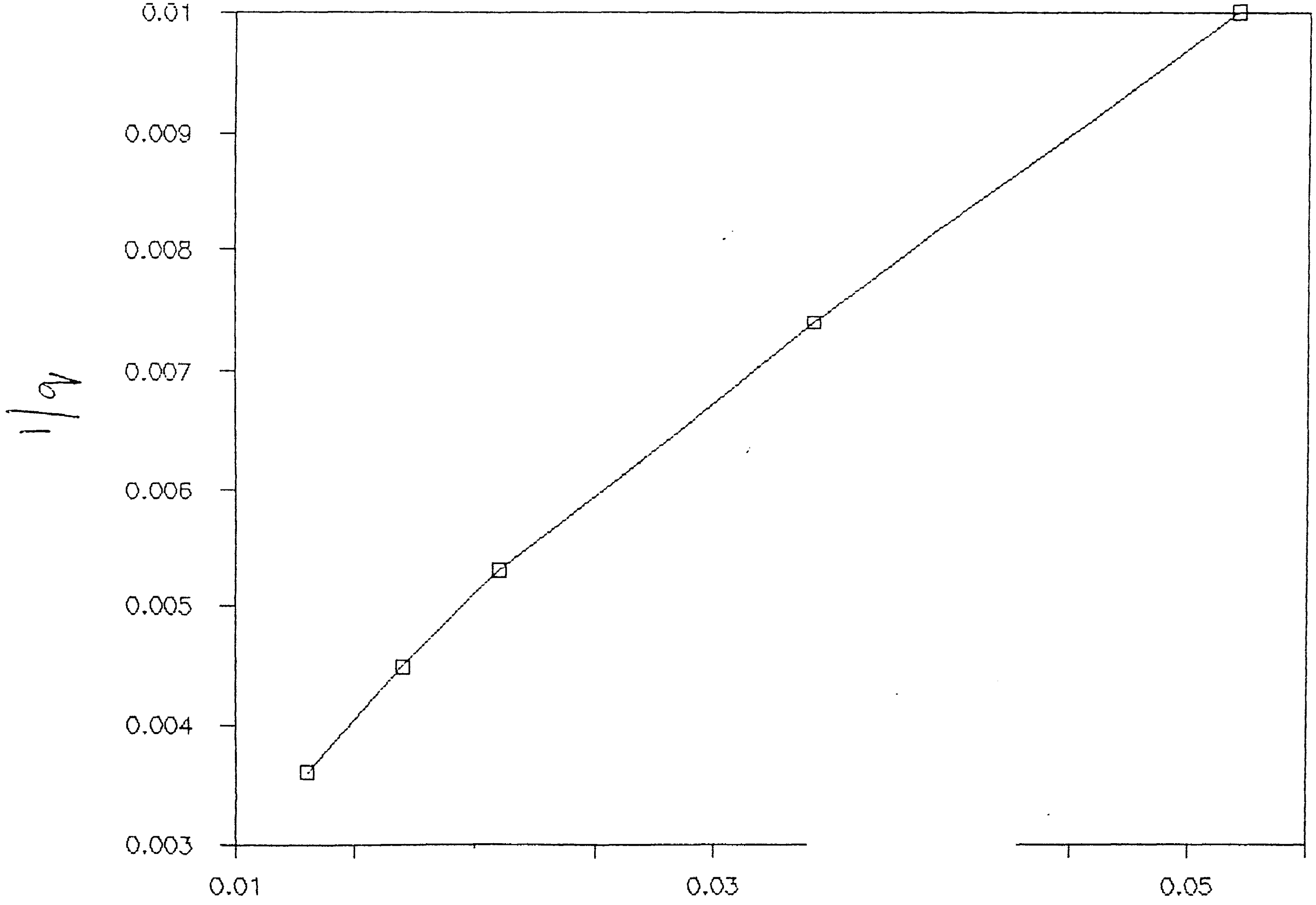
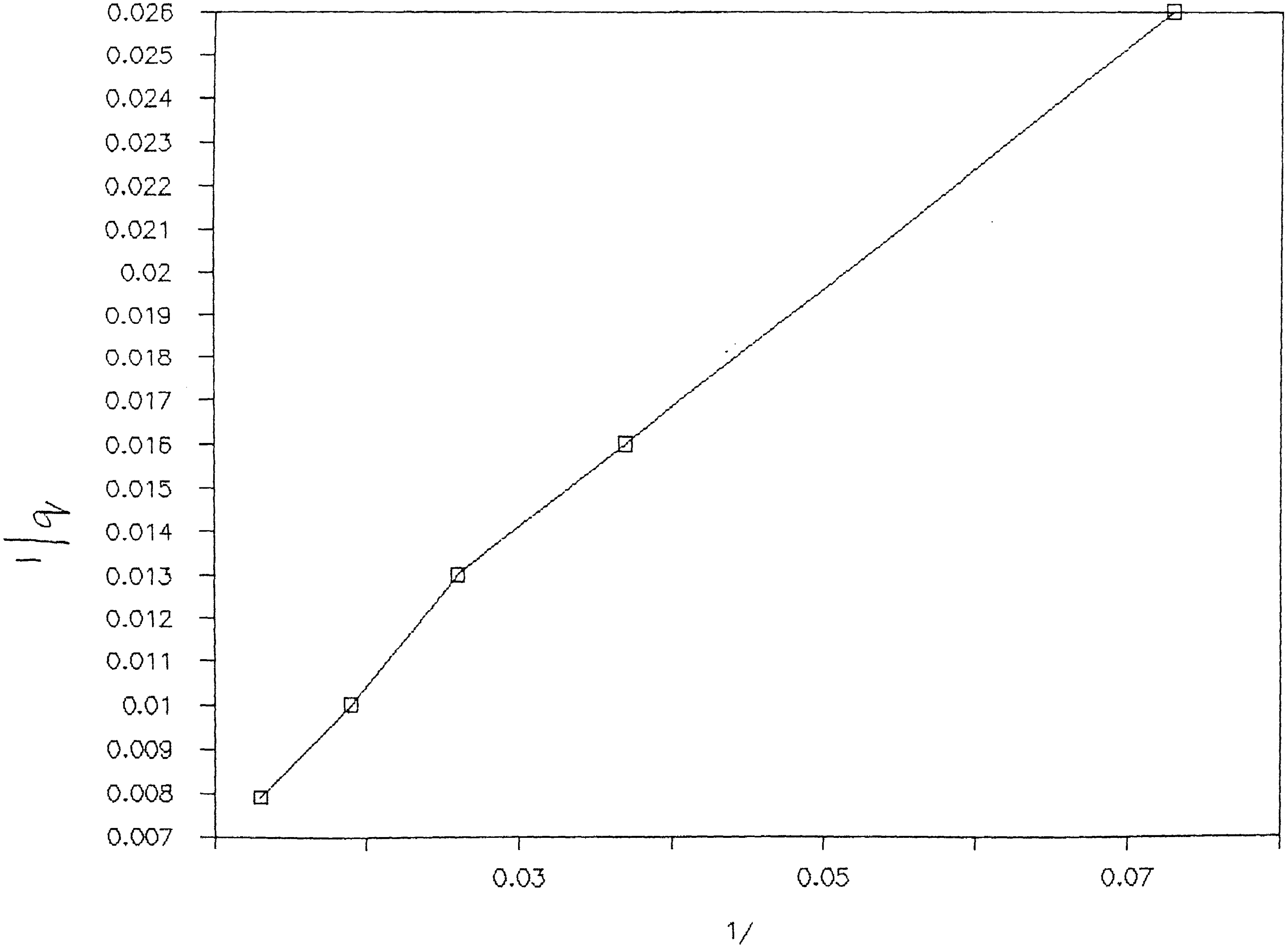


Figure 2. Adsorption Isotherm



Isopropanol onto Militant Flyash

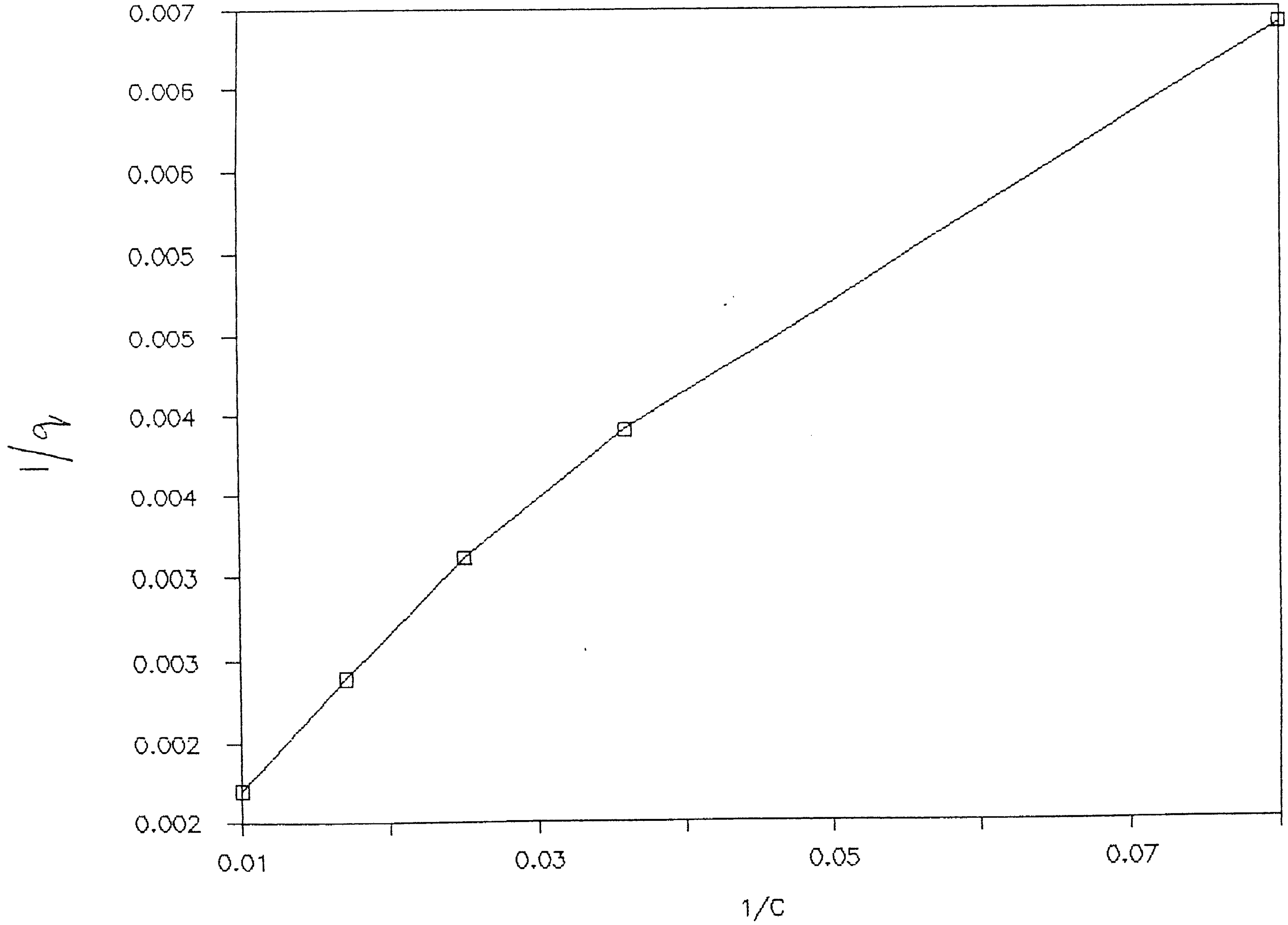


Figure 3. Adsorption Isotherm

Acetaldehyde onto Militant Flyash

Figure 4. Adsorption Isotherm

Formaldehyde onto Militant Flyash

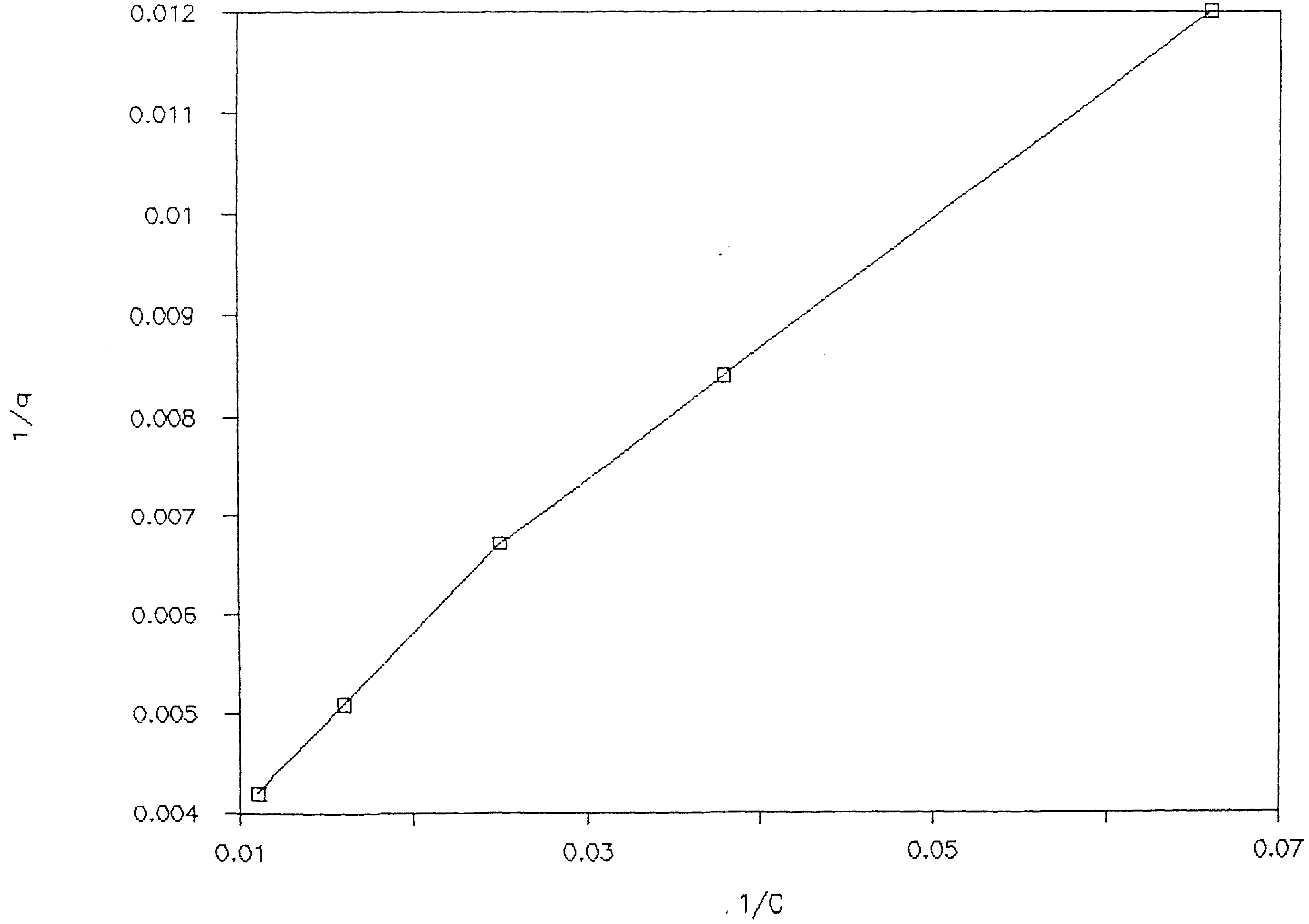


Figure 5. Adsorption Isotherm

Acetone onto Militant Flyash

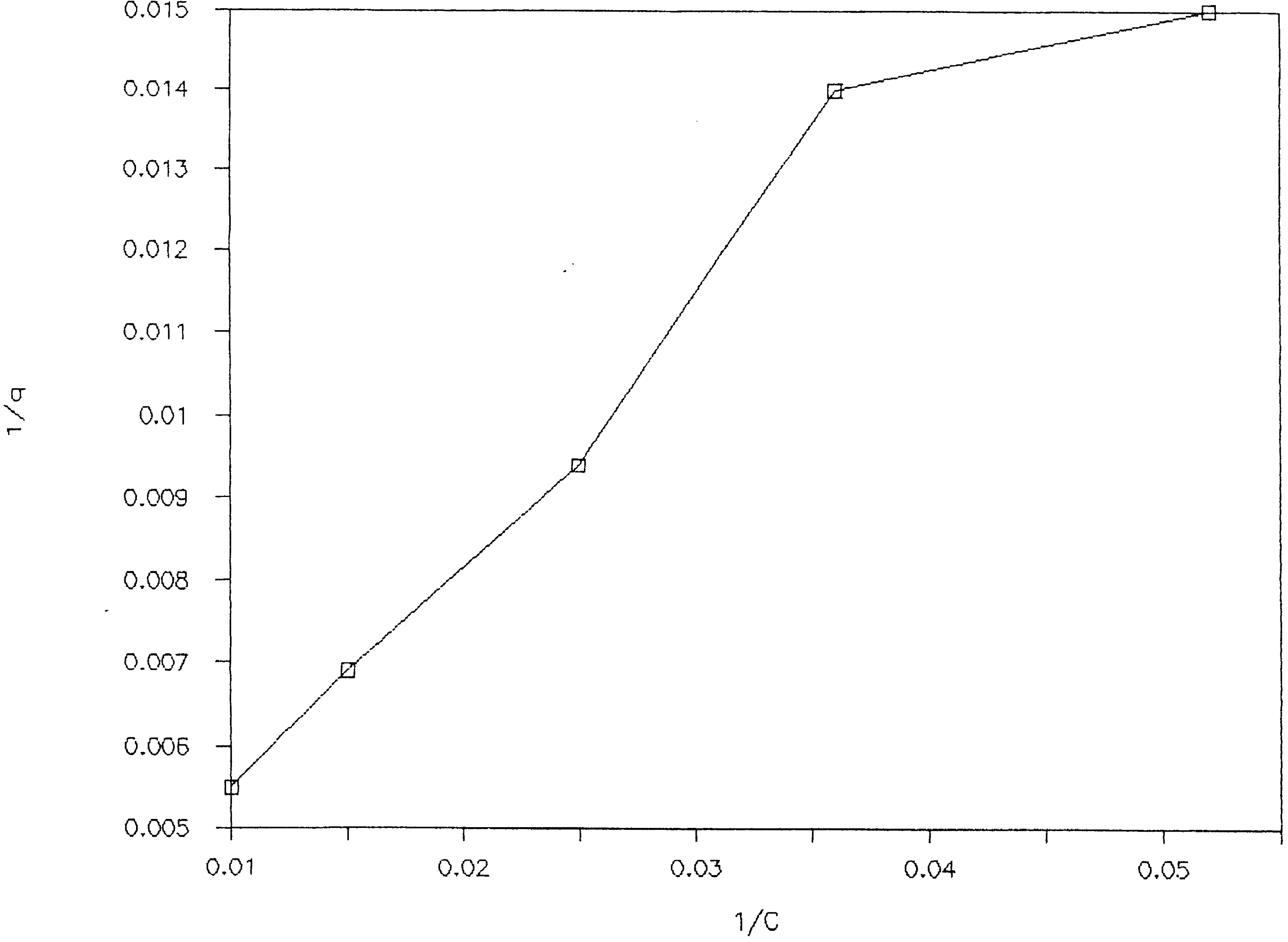


Figure 6. Adsorption Isotherm

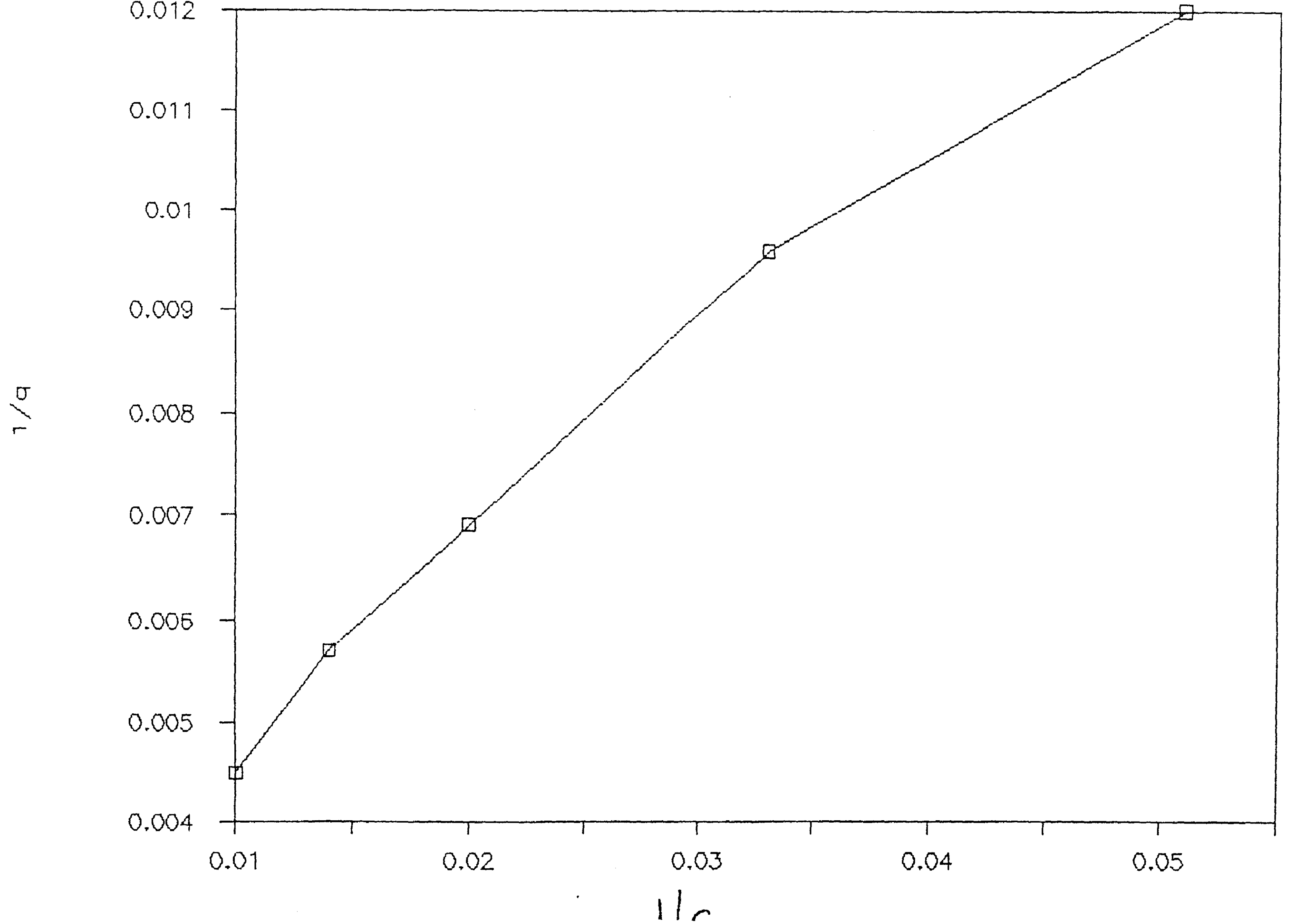

MEK onto Militant Flyash

Fig. 7 Kinetic Study

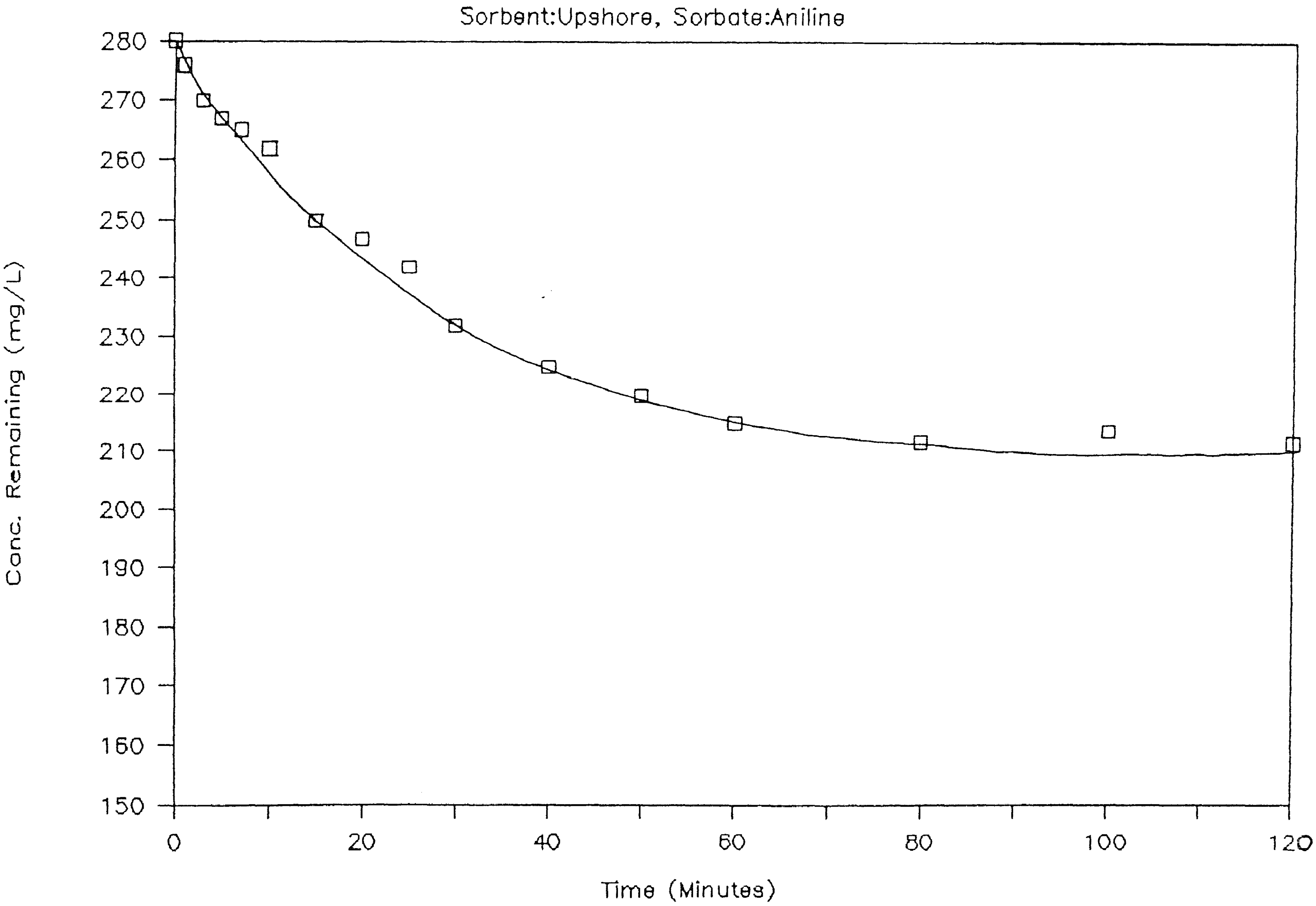


Fig.8 Kinetic Study

Sorbent:Conemough Flyash,Sorbate:Phenol

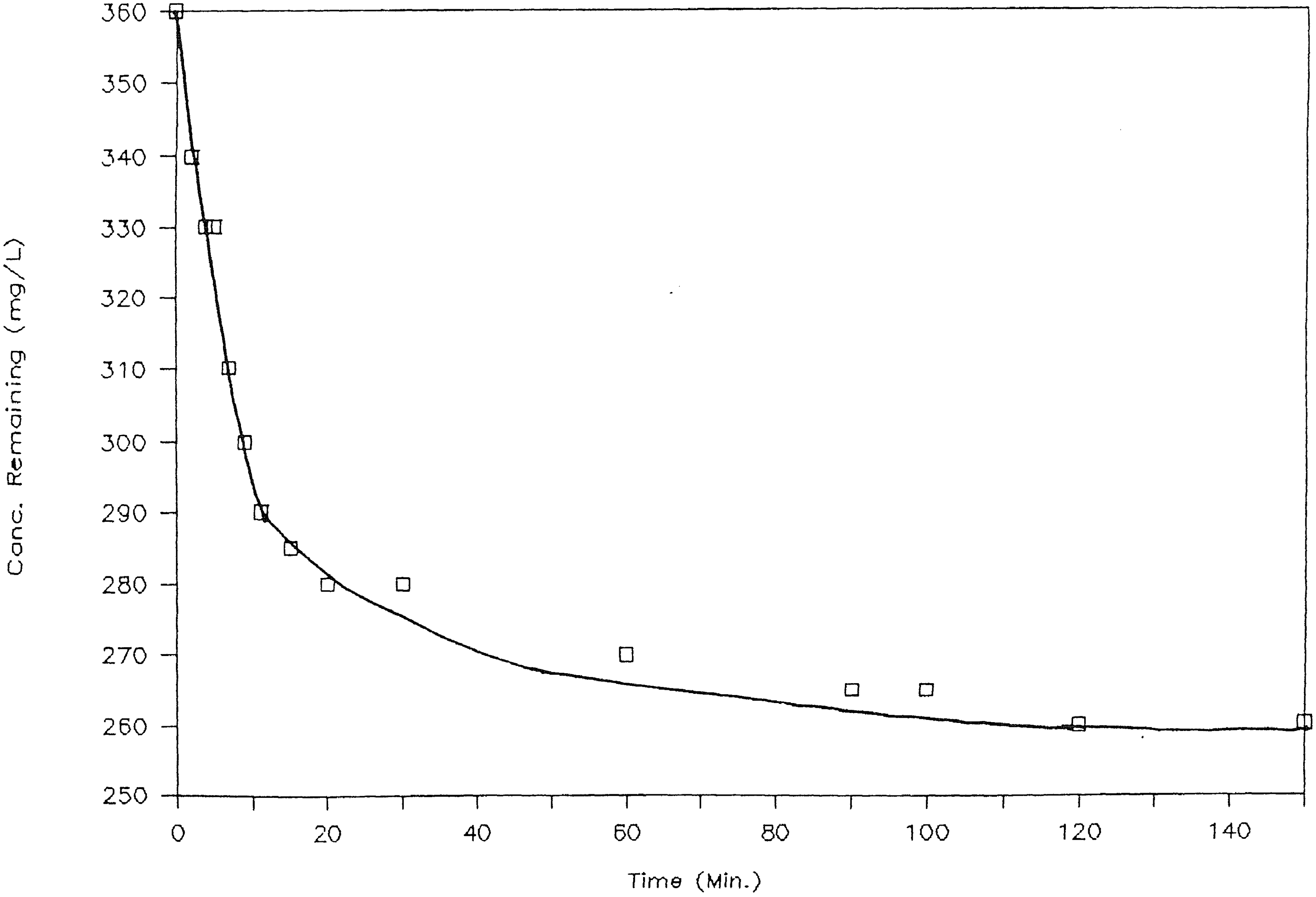


Fig. 9 Kinetic Study

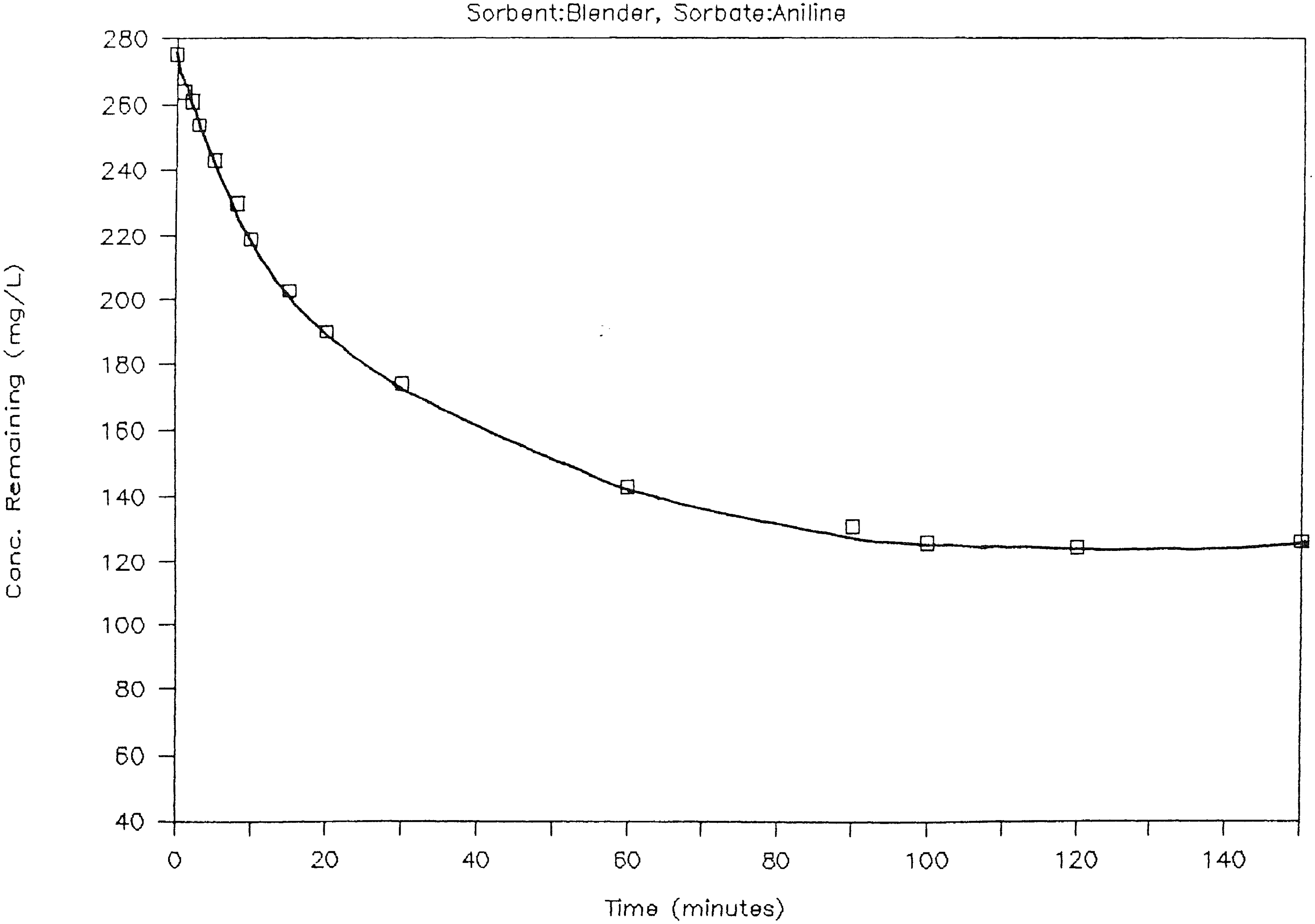


Fig.10 Kinetic Study

Sorbent:Conemou.,Sorbate:Aniline

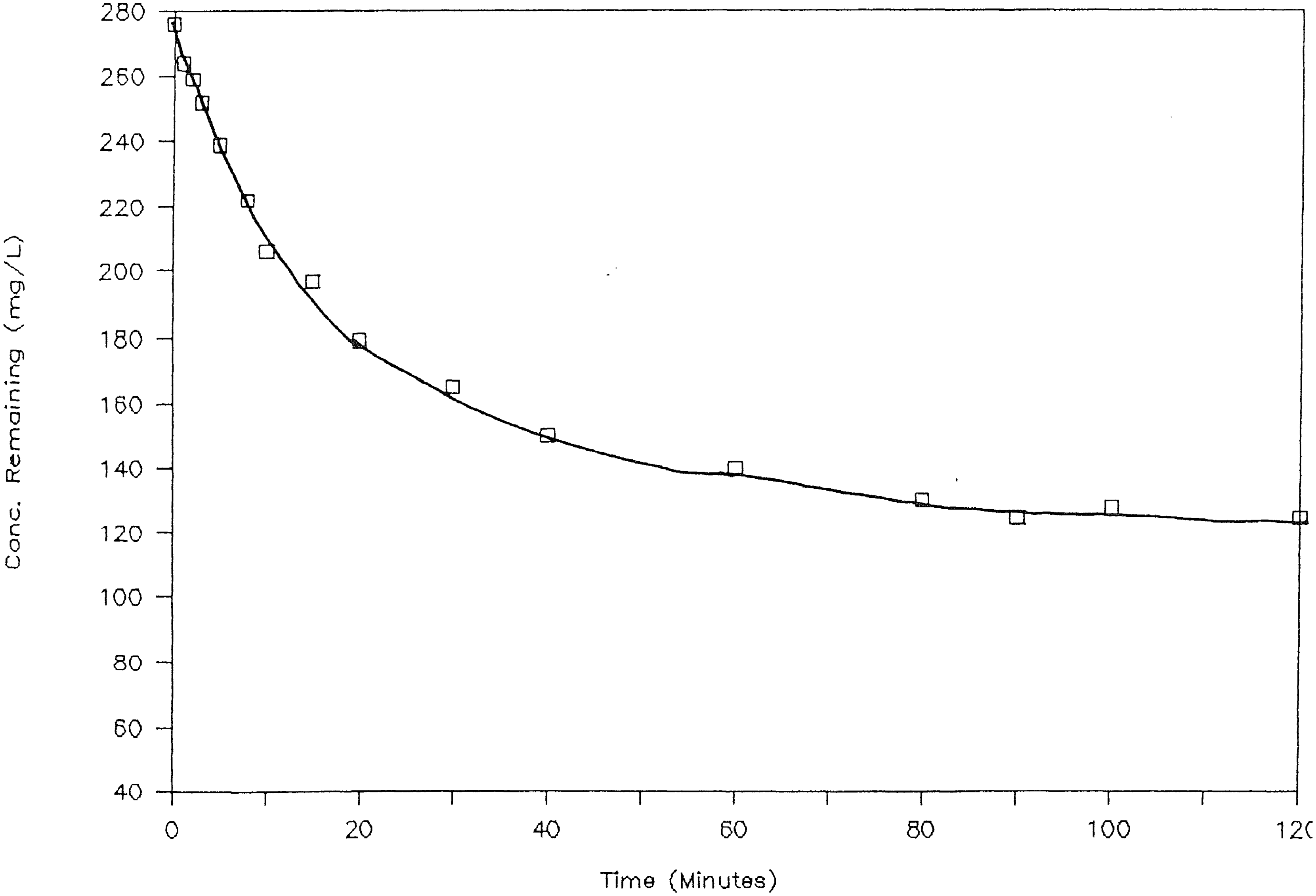


Fig. 11 Kinetic Study

Sorbent:Keystone,Sorbate:Aniline

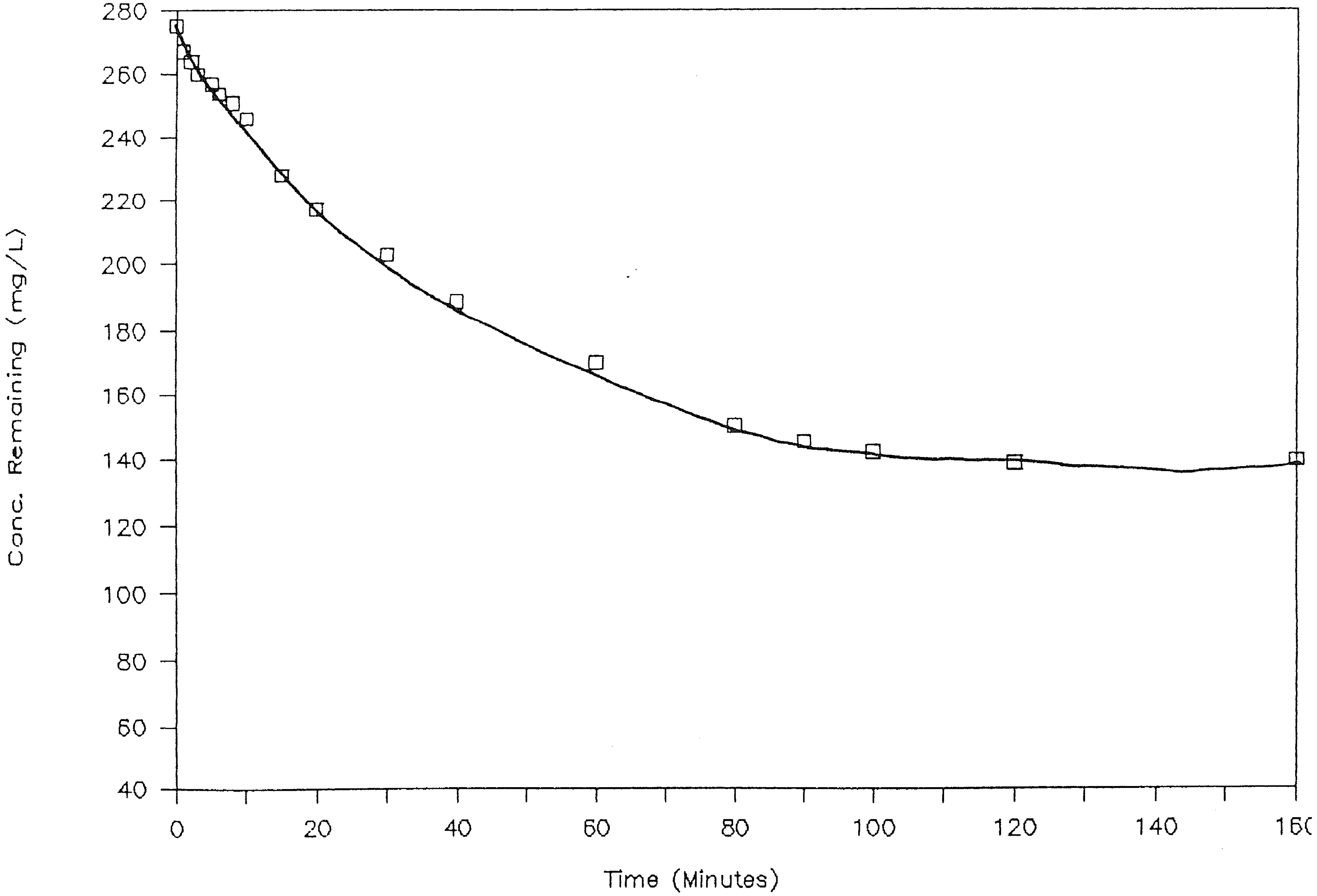


Figure 12 Kinetic Study

ortho-Xylene onto Militant Flyash

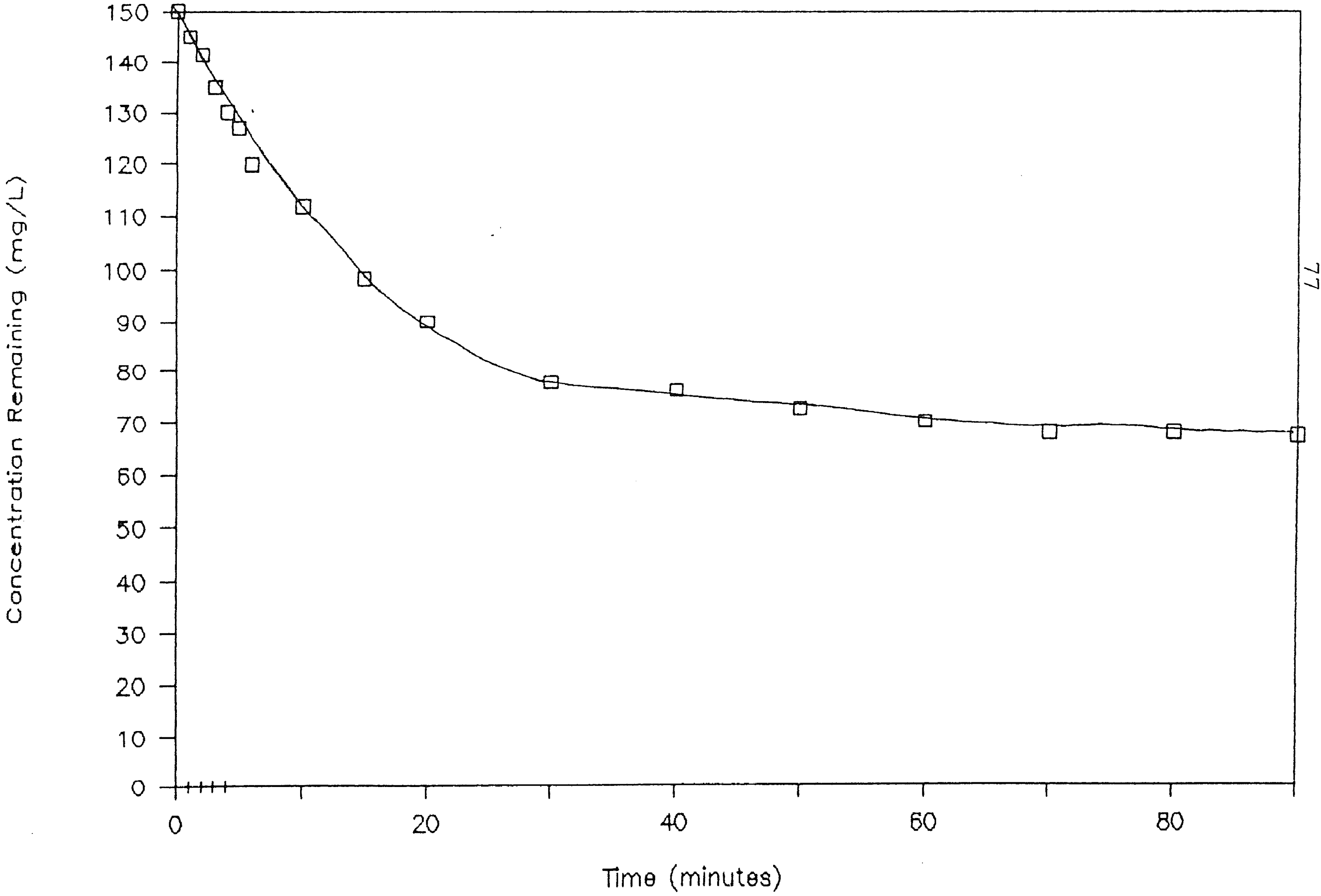


Figure 13 Kinetic Study

meta-Cresol onto Militant Flyash

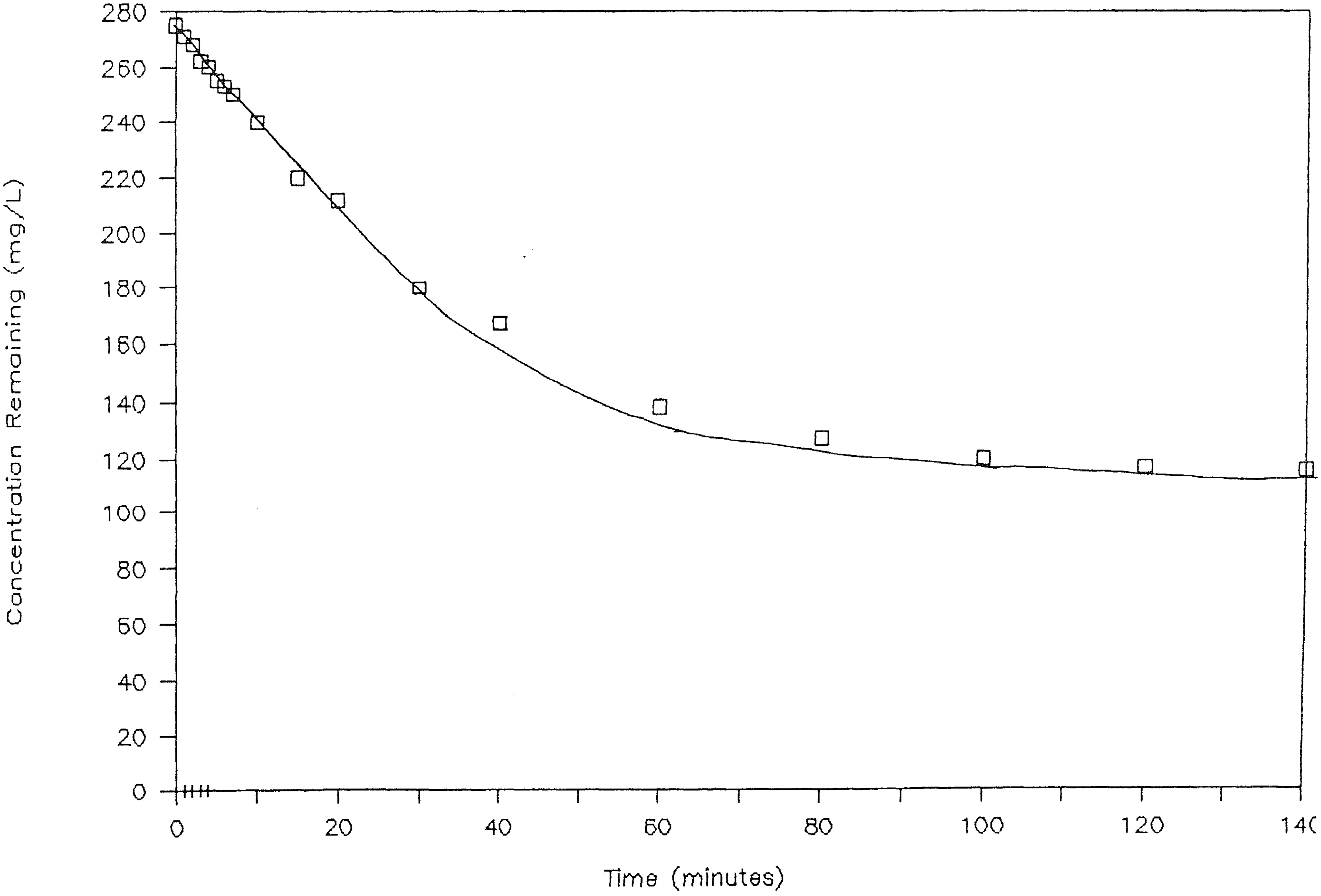


Figure 14 Kinetic Study

Phenol onto Militant Flyash

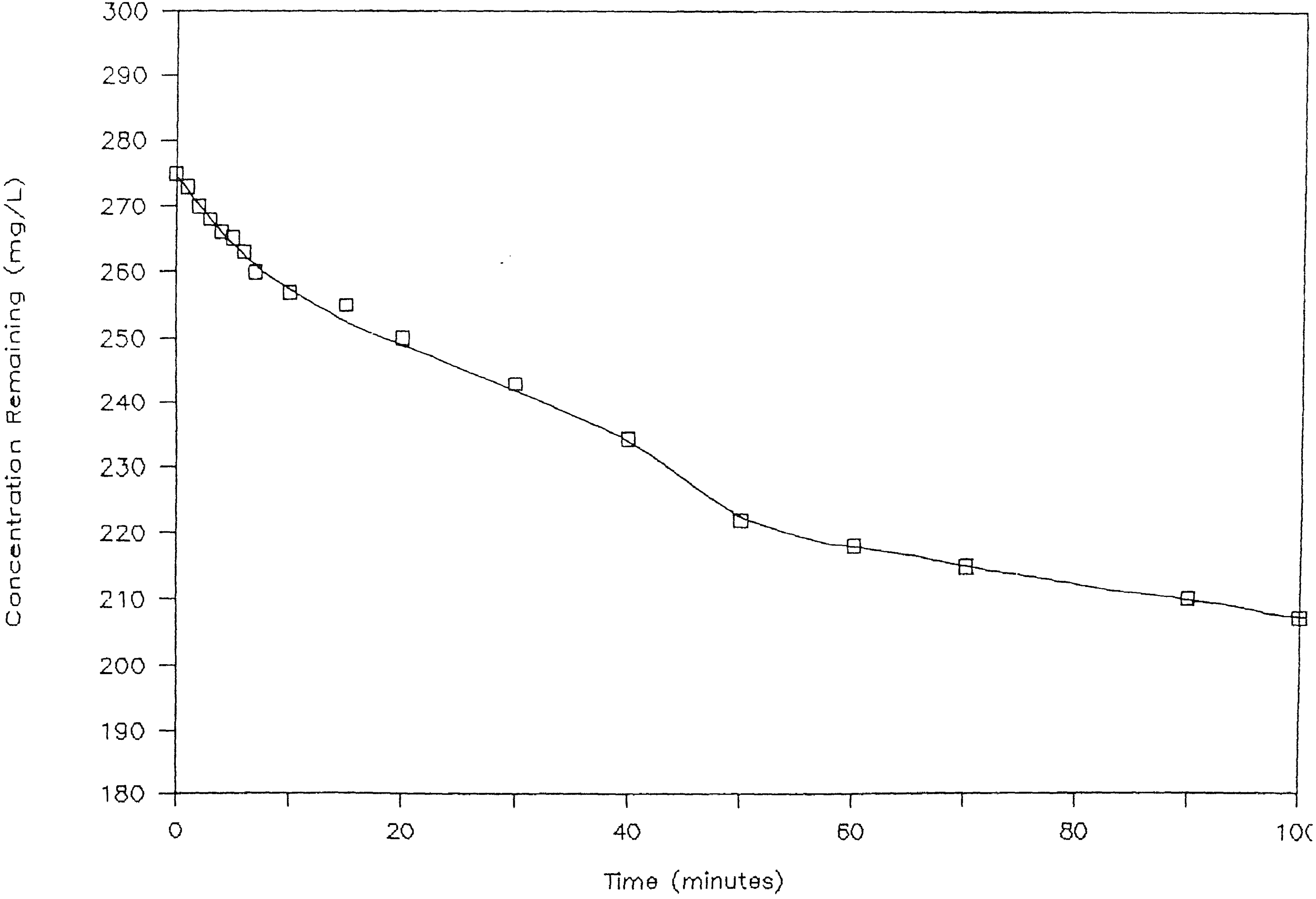


Fig. 15 Kinetic Study

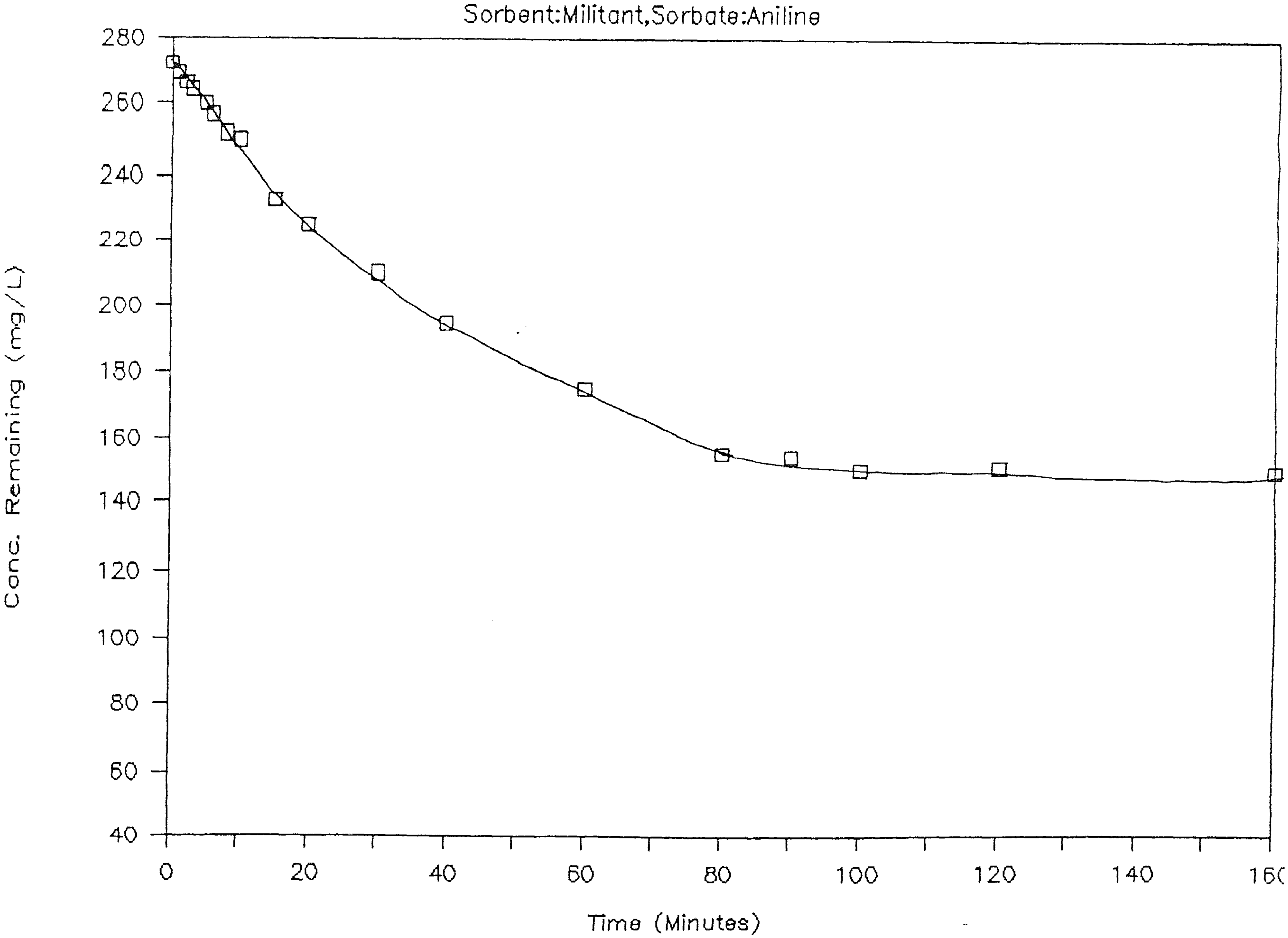


Fig. 16 Kinetic Study

Sorbent:Act. Carbon, Sorbate:0–Xylene

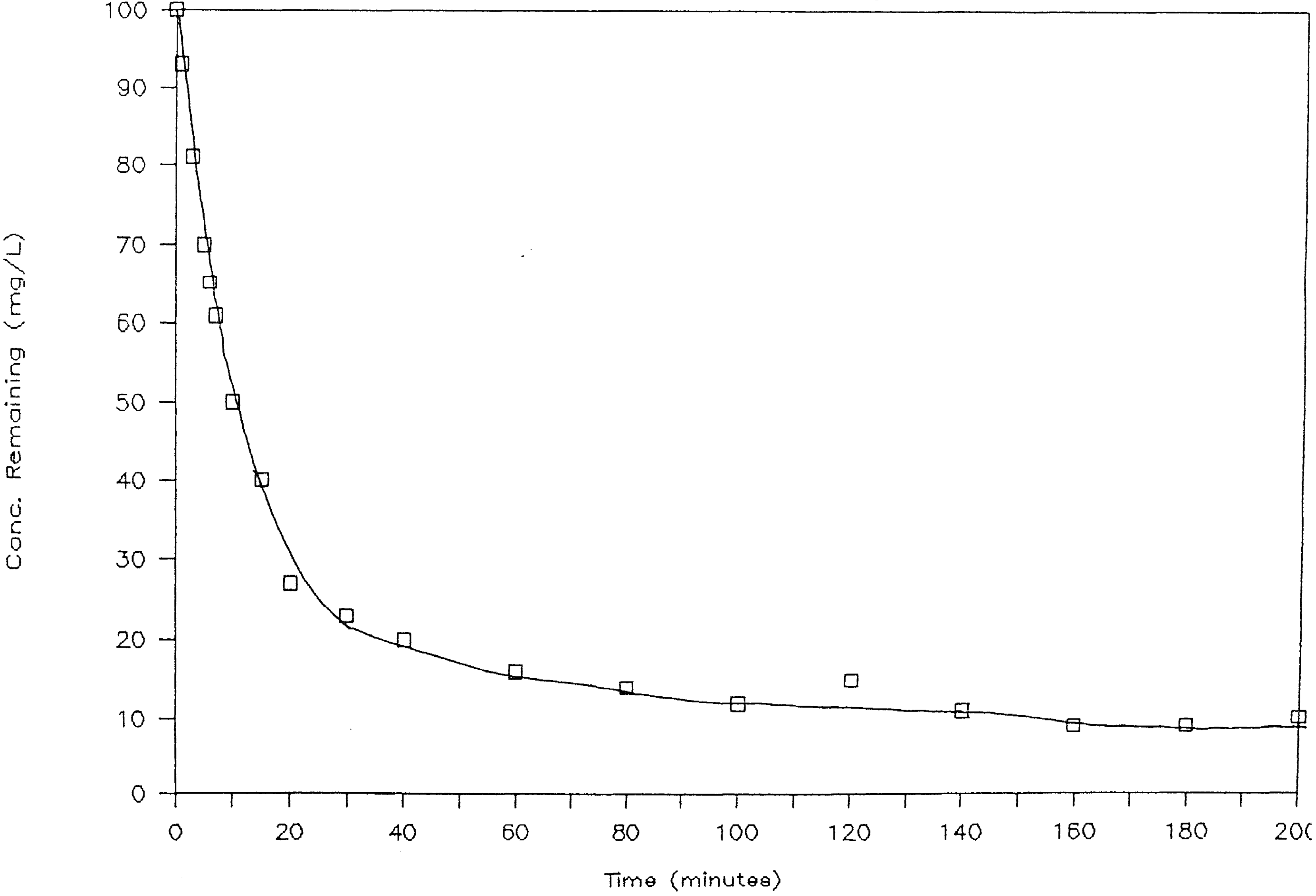


Fig. 17 Kinetic Study

Sorbent:Act. Carbon, Sorbate:m-Cresol

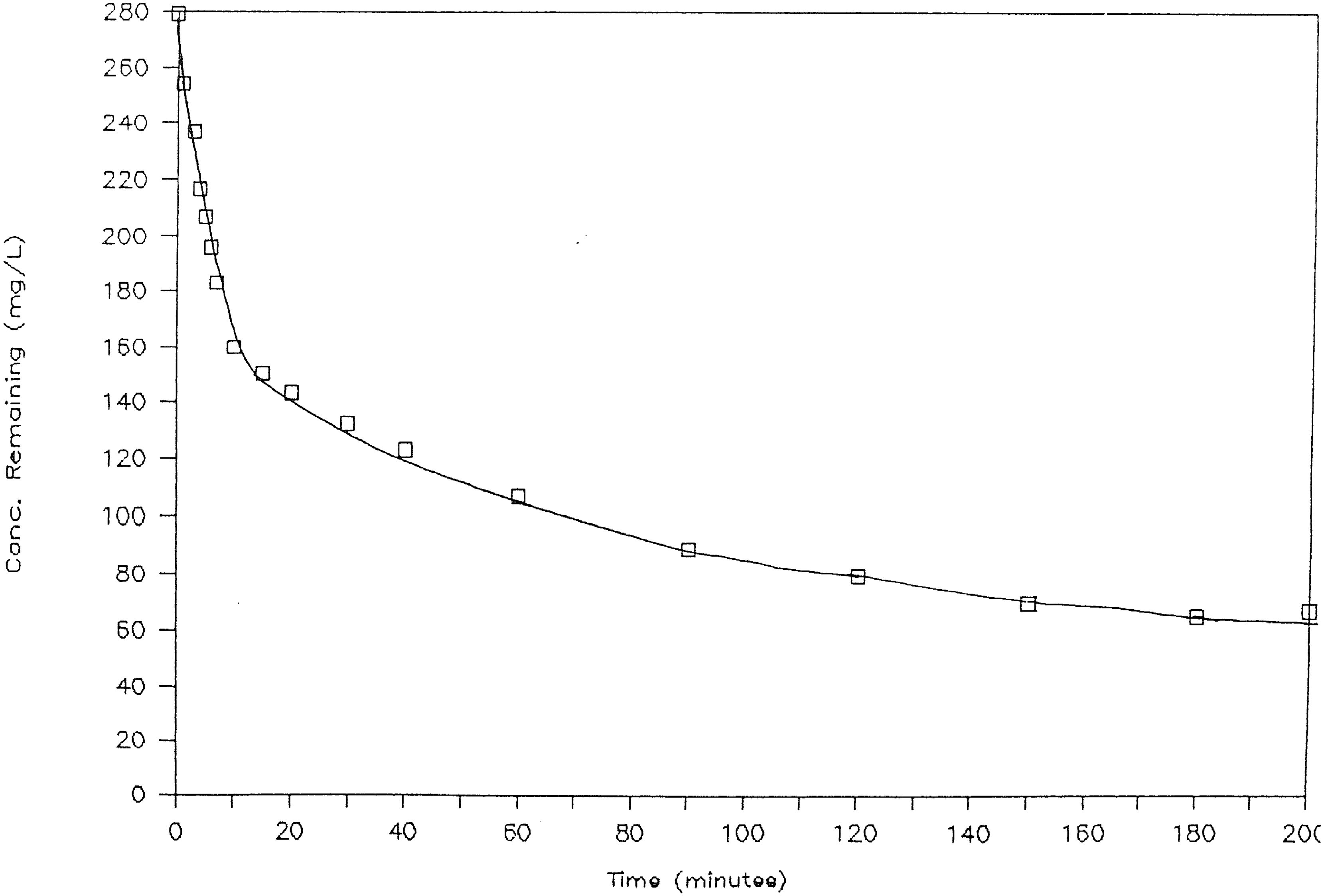


Fig. 18 Kinetic Study

Sorbent:Act. Carbon, Sorbate:Phenol

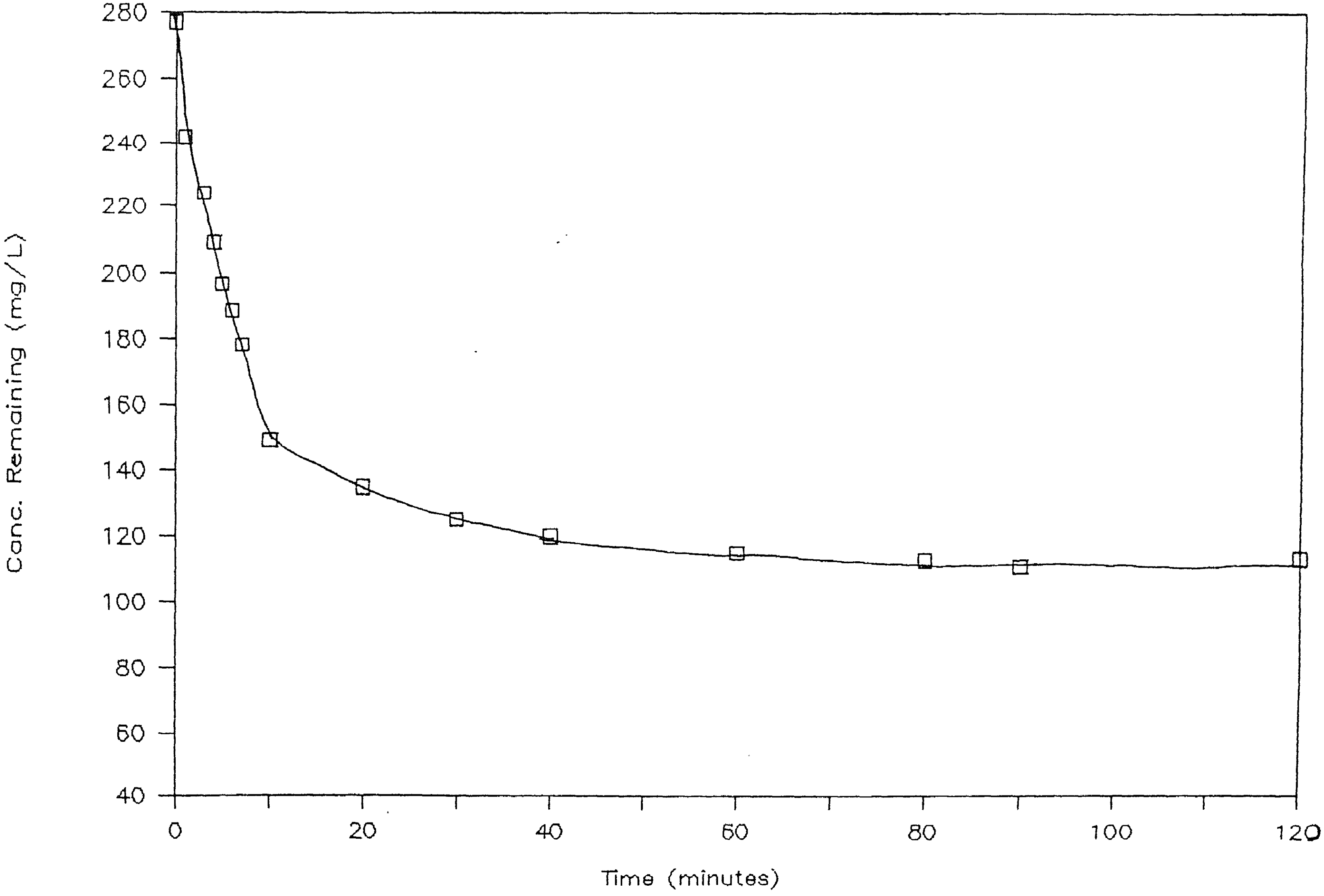


Fig.19 Kinetic Study

Sorbent:Act. Carbon, Sorbate:Aniline

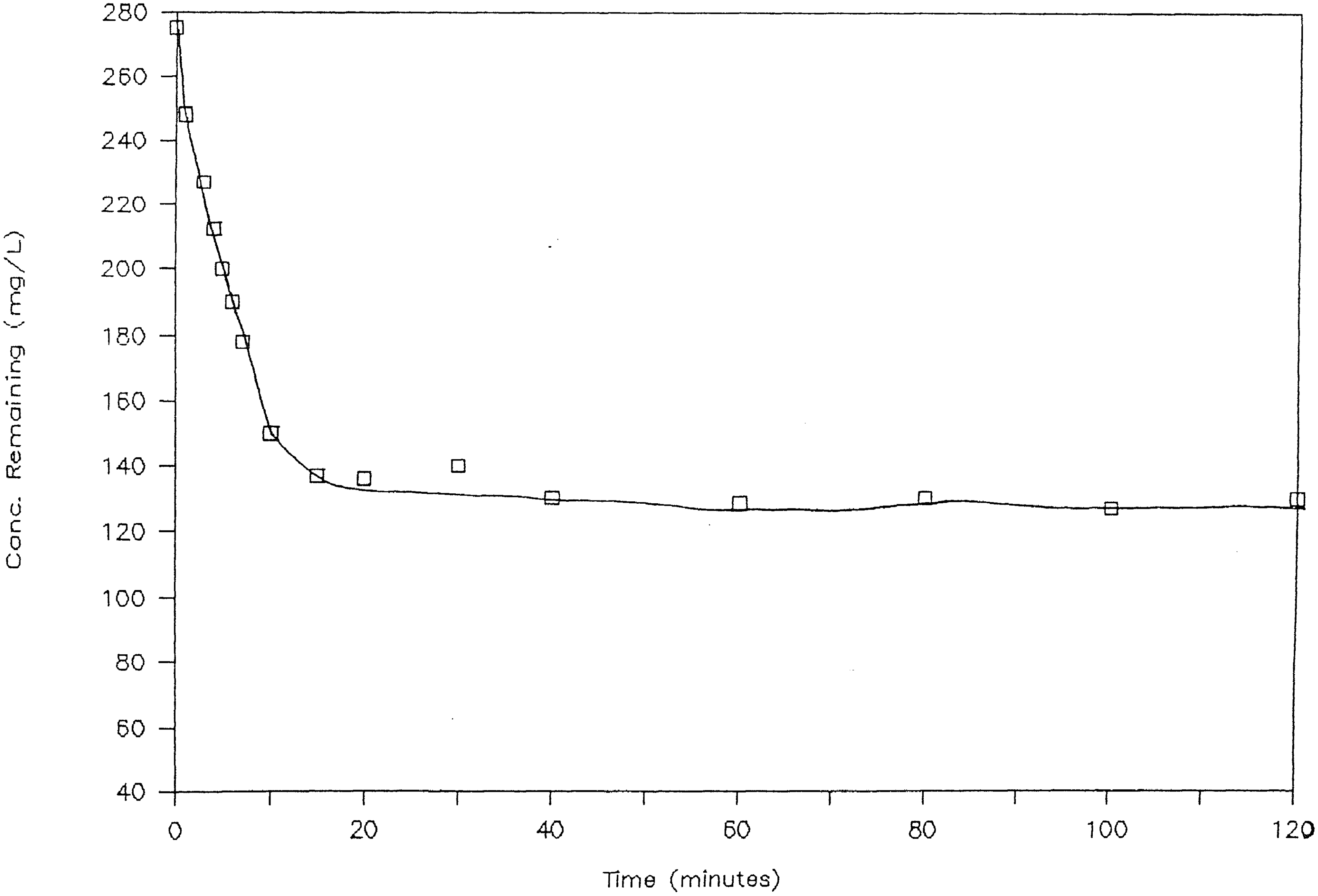
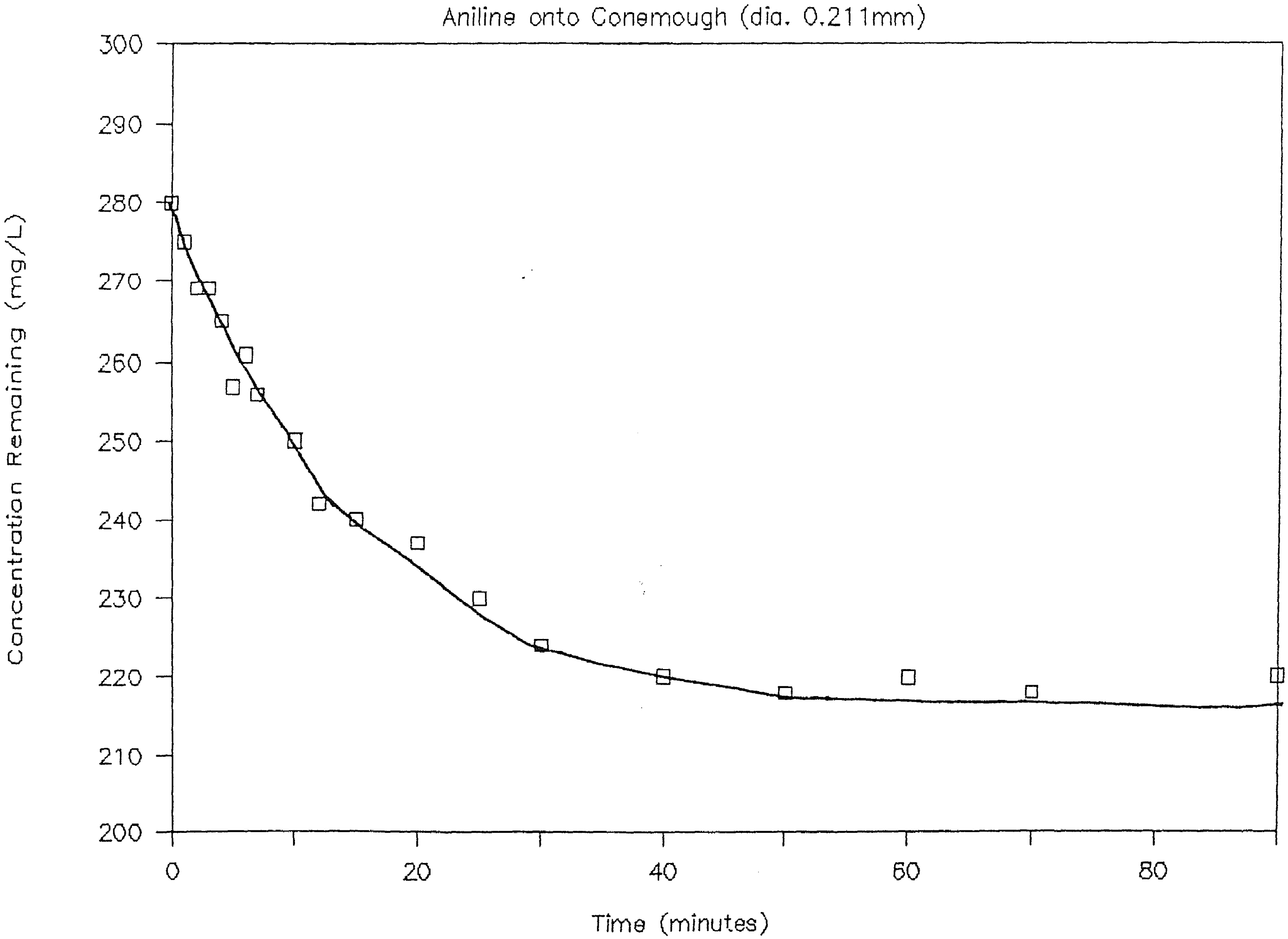


Figure 20 Effect of Size Distribution


Aniline onto Conemough (dia. 0.211mm)

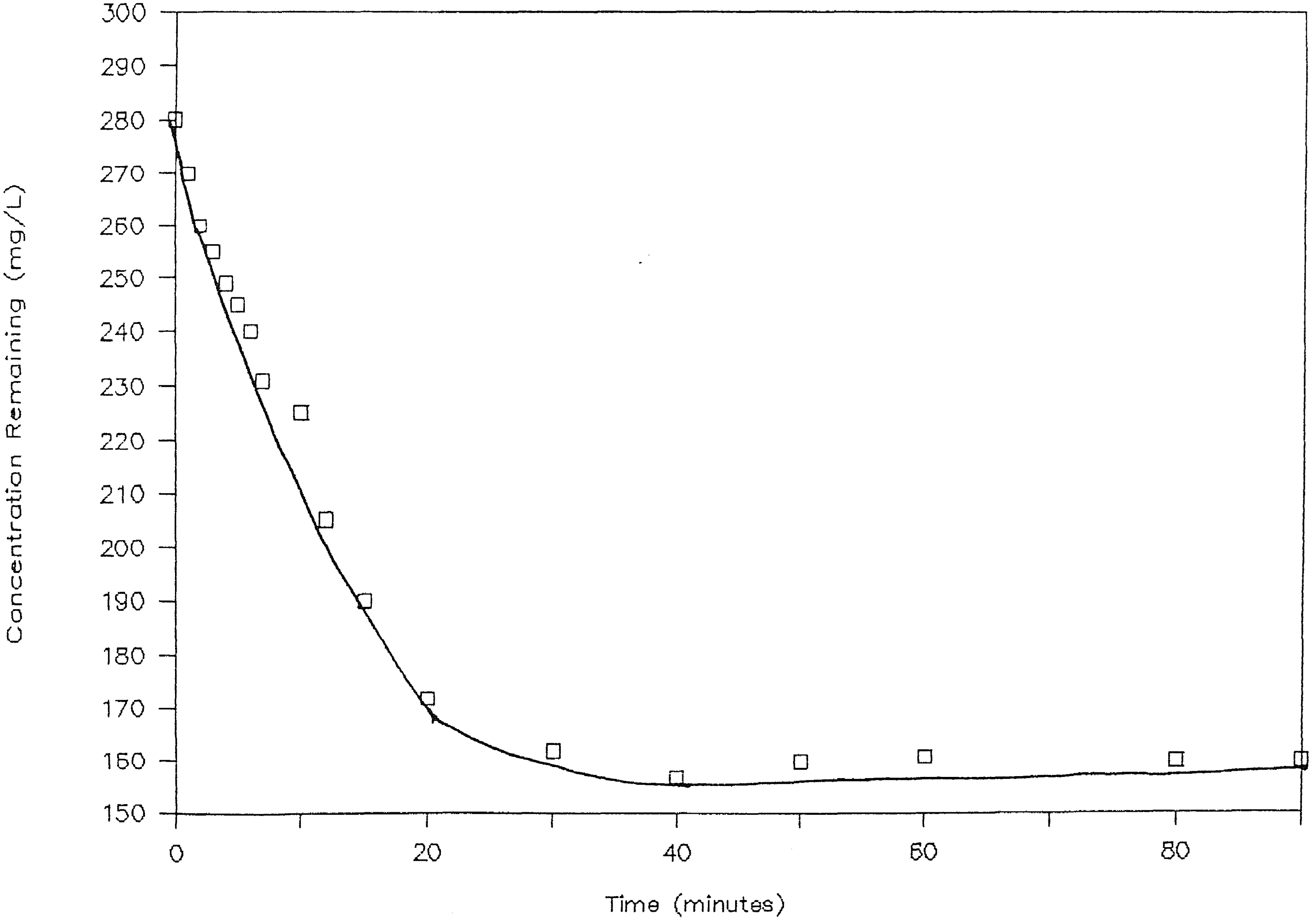


Figure 21 Effect of Size Distribution

Aniline onto Conemough (dia. 0.075mm)

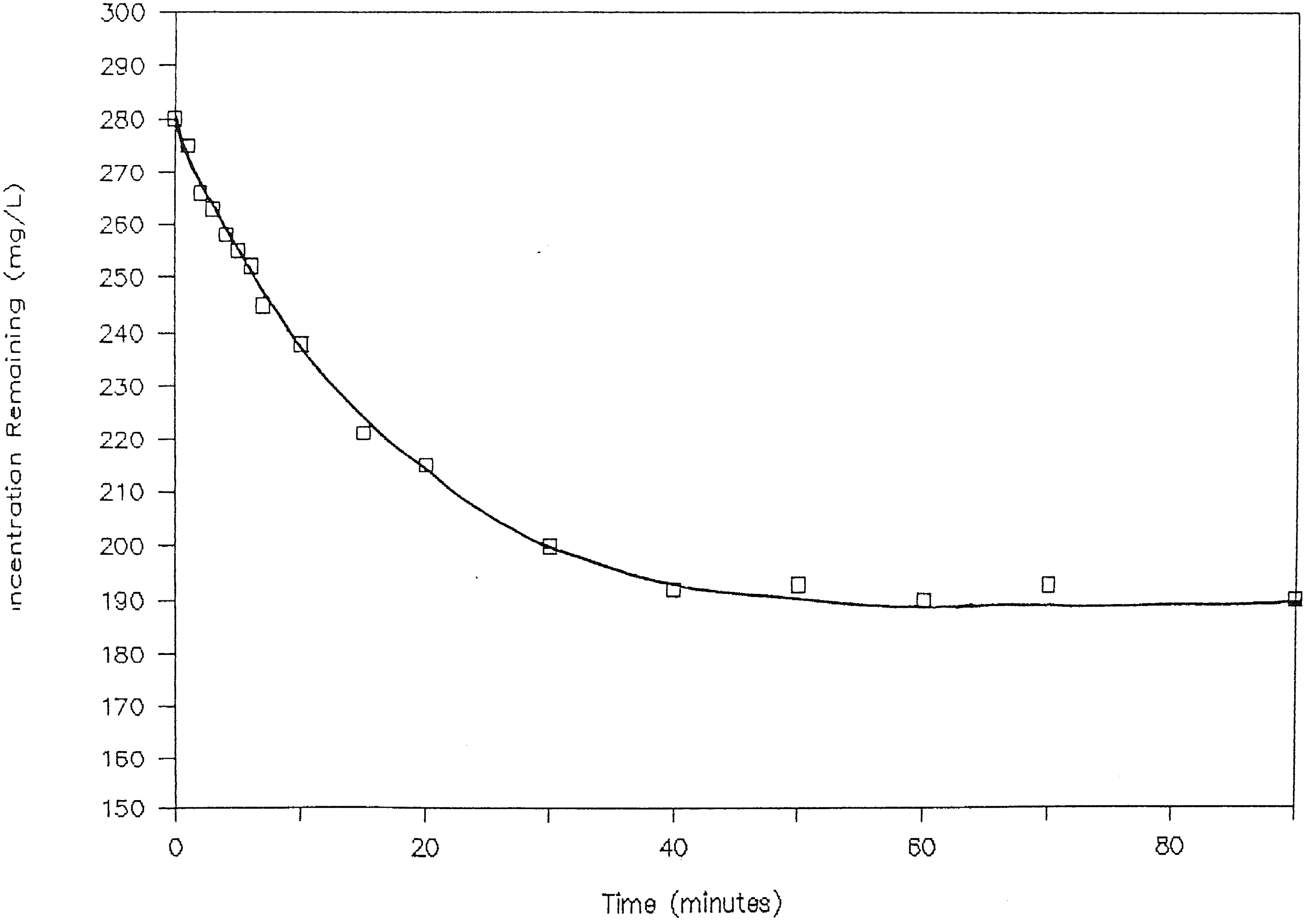


Figure 22 Effect of Size Distribution

Aniline onto Conemough (dia. 0.15mm)

Figure 23 Effect of Size Distribution

Aniline onto Conemough (dia. −200 mesh)