Sorption and desorption of organic compounds by flyash

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New Jersey Institute of Technology, 1988

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SORPTION AND DESORPTION OF ORGANIC COMPOUNDS

BY FLYASH

by

Kashinath Banerjee

Dissertation submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
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APPROVAL OF DISSERTATION

SORPTION AND DESORPTION OF ORGANIC
COMPOUNDS BY FLYASH

By

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for
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and Environmental Engineering

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Title of Thesis: Sorption and Desorption of Organic
                    Compounds by Flyash

Kashinath Banerjee, Doctor of Engineering Science, 1988

Thesis directed by: Professor Paul N. Cheremisinoff

ABSTRACT

A sorbent treatment process has been developed which uses flyash as sorbent in the treatment of highly toxic and hazardous chemicals; these include: Alcohols, Aldehydes, Ketones and Aromatics. Batch, as well as dynamic, studies were performed, in different phases, during the investigation. Single and multiple solute systems were examined separately. The samples were analyzed using a Flame Ionization Detector Gas Chromatograph.

The result of this study demonstrates that isolation/ immobilization of the organic pollutants is technologically feasible by adsorbing the contaminants onto flyash. The residual carbon content of the flyash plays a very significant role during the treatment process. The sorption of the organic compounds onto flyash is believed to occur principally via the weak induction forces of London or dispersion forces which are the characteristics of the physical adsorption. The treatment efficiency depends on the characteristics of the solute, the sorbent and the solution. The existance of interaction and competition among the solutes, for adsorption sites, is clear in the case of a multiple solute system.

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[1] "Total Hydrocarbon Pollutants from a Non-Vented Radient Kerosene Heater", Int'l. Journal Env. Studies, Vol. 32, 1988, pp. 75-83.

[2] "Sorption of Selected Organic Pollutants by Flyash", 43rd Annual Purdue Industrial Waste Conference, May 10-12, 1988.

[3] "Sorbate Characteristics of Flyash", Int'l Physico-Chemical and Biological Detoxification Hazardous Waste Conf., Atlantic City, May 3-5, 1988.

[4] "Granular Activated Carbon in Water Treatment", Civil Engg. Practice, Vol. 5, Eds. P.N. Cheremisinoff, N.P. Cheremisinoff, and S.L. Cheng, Technomic Publishers, 1988.

[5] "Volatile Organic Pollutant Levels in Indoor Environments from the Use of Kerosene Heaters", Masters Thesis, New Jersey Institute of Technology, N.J., USA, May, 1984.

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SECTION I

1.1 INTRODUCTION

Development of sophisticated industrial societies has led to the proliferation of a vast number and variety of complex chemicals for industrial, agricultural and domestic use. Many of these compounds exhibit toxic, carcinogenic, mutagenic or teratogenic properties, and many have insidious effects on man and his environment in uncontrolled exposure situations. Industrial processes produce millions of tons of non-radioactive sludges and solid wastes. Generally, these wastes are disposed of in the upper layers of the earth's crust in landfills or by ocean dumping. Ocean dumping has become legally and environmentally unacceptable for this type of waste according to the Water Pollution Control Acts. Consequently, disposal of such wastes on land has increased but, under growing pressure, more stringent control has been effected.

One of the goals of federal hazardous waste management programs is to reduce dependence on land disposal. The Hazardous and Solid Waste Amendments of 1984 (HSWA) mandated that EPA must evaluate all hazardous waste streams and ascertain which should be restricted from land disposal. The disposal of huge volumes of solid waste in landfills is complex due to various interacting variables, and such disposal methods have created risk/hazard to human health and environmental concerns and problems.

Soil is composed of gas, water, microorganisms, and

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minerals which make up the solid matrix. As the solid waste
is disposed of on the land, the soil interacts with the
waste to form an air integrated system. This waste may
change the physical, chemical and biological processes of
in-situ soil systems. These processes become more complex
when infiltrated precipitation or groundwater comes in
contact with solid waste which often contains hazardous
substances. Thus, the potential for leaching exists. Water
dissolves organic and inorganic substances out of the solid
wastes and generates a leachate which usually contains a
high content of heavy metals, and inorganic anions. This
leachate can move out of the organic matter fill into the
surroundings and subsequently reach the groundwater supplies
or nearby aquifers. Economic alternatives to current
practices as well as their improvements is much desired.

Increased reliance on coal as an energy source has lead
to significant by-product management problems related to
storage or disposal of flyash generated as a result of
combustion. There is at present very few commercial uses
for utilization of large quantities of flyash. Therefore, a
need exists for an inexpensive management technology for the
environmentally safe disposal or storage until such uses are
developed. This study affords possibilities in techniques
of waste immobilization utilizing a by-product of combustion
as well as the opportunity to study the adsorption process.

Most of the problems caused by hazardous wastes result
from their uncontrolled release into the environment.
Destruction of the wastes or irreversible transformation to

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nonhazardous forms are means by which these releases can be avoided. For wastes of which neither destruction nor transformation is currently practical, isolation is often a suitable alternative control strategy. One means for isolating wastes is by adsorption onto a stable material, such that the solid mixture can then be disposed of. A second method for incorporating wastes into a stable solid mixture is to cause the solid to form around the waste. This is variously referred to (depending in part on the process used) as fixation, solidification and encapsulation.

1.2 LITERATURE REVIEW

Studies have indicated that some clay soils can be used as liners to retard the mobility of hazardous leachate from landfill because of their low permeability, or can be used as a sorbent material to adsorb the pollutants from the waste stream. Because of their dynamic and heterogeneous nature, the clay soils have the property of reacting with certain anions and cations and retaining them in an exchangeable state. By these reactions, the clay soils may serve as a medium for either waste storage or for ultimate waste disposal. With these backgrounds, many investigators have shown that leachate and waste streams containing organics, pesticides, herbicides, or heavy metals can be attenuated by clay minerals, soils and power plant products (fly ash). According to the literature, very little work has been done to treat hazardous organics using flyash.

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Rios [1](1960) has developed a process for removing phenols from aqueous solutions using clay. He showed that clay adsorbents ordinarily used for purification of organic substances of various types and which have been regenerated by combustion have good adsorbent power for phenolic substances in aqueous solutions.

Baker and Luh [2](1971) studied adsorption of pyridine from aqueous solution onto sodium kaolinite and sodium montmorillonite. The batch study data revealed that the extent of sorption is from acidic solutions with maxima occuring for sodium kaolinite at approximately pH 5.5 and for sodium montmorillonite at approximately pH 4.0. Sorption does not take place at a pH higher than 7. Equilibria were achieved within 24 hours with significant adsorption. They described the sorption process by the empirical Freundlich relationship.

Luh and Baker [3](1971) also explored the desorption of pyridine - clay in aqueous solution which showed that the desorption is a direct function of pH and number of stages. Maximum sodium ion was released at pH = 1 not at the pH = pKa = 5.25 where pyridine sorption was maximum. Minimal desorption occurs at pH > 7. Pyridine desorption was much slower than adsorption at a comparable pH and clay:organic ratio.

Griffin et.al. [4](1980) did work on the attenuation of halogenated hydrocarbon wastes by earth materials. They studied the adsorption and mobility of polychlorinated

biphenyls (PCBs), polybrominated biphenyls (PBBs), hexa-
chlorobenzene (HCB) and hexachlorocyclopentadiene (C-56)
under laboratory conditions and predicted that the adsorp-
tion of the above mentioned compounds can be described by
the Freundlich adsorption isotherm equation. They found a
high direct correlation between the total organic carbon
content of the soils and the amount adsorbed. They con-
cluded that the above compounds would not migrate readily
through earth materials leached with water; however, it was
noted that reaction products of C-56 with water leached from
soil columns, and that these compounds may cause problems in
natural environments rather than C-56 itself.

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. They found that single solute sorption for all
compounds is higher in the acidic soil as compared to the
basic soil. Binary sorption experiments revealed that
competitive sorption occurs more in acidic sub soil rather
than basic sub soil.

Wolfe [6](1986) studied adsorption isotherms for eleven
organic compounds using treated (with amines) montmorillon-
ite which indicates that natural clay when suitably treated
is an effective adsorbent.

Griffin et.al. [7,8,9] (1976 & 1977) examined the
removal of heavy metals by kaolinite and montmorillonite and
concluded that both cationic and anionic adsorption on these
two clays were significant.

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Bittell and Miller [10](1974) investigated the removal of lead, cadmium and calcium and found that the cations exhibited consistent preferential sorption characteristics for clays.

The literature that was studied revealed that flyash has been used in a variety of different applications, including construction of roads, dams and bridges [11](Roy, et.al.,1981), making of concrete and cinder blocks, etc. Flyash was successfully used to recover phenol from an industrial wastewater by mixing the flyash with the waste-water and then lagooning the mixture [12](Wolfson, 1977). In Czechoslovakia, flyash was successfully used as an adsorbent to remove TNT (Tri nitro toluene) from solution. Flyash has also been used and has shown excellent results as a soil conditioner. It contains many trace elements which accelerate plant growth and has some fertilizer value when mixed with the sewage sludge [13](Chang, 1977).

In a test done at the University of Cincinnati, the findings indicated that flyash demonstrated capabilities in removing refractory organics from wastewater in both batch and continuous flow systems. The conclusion of this study indicated that the removal of chemical oxygen demand (COD) by adsorption is logarithmically related to three para-meters, (1) time of mixing, (2) initial COD, and (3) concentration of flyash [14](Deb, et.al. 1966).

Nelson and Guarino [15](1969) both reported that flyash can be used to remove appreciable quantities of COD and BOD.

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The investigations of Eye and Basu [16](1970) led to the following findings:

1. Flyash is capable of reducing COD of a secondary effluent by about 30% (much higher removal is possible when the initial COD is greater).

2. Removal of suspended solids using flyash by coagulation with lime is highly efficient.

3. Flyash is a useful agent in conditioning sludge prior to vacuum filtration.

Ballance et.al. [17](1969) used flyash as a coagulant aid in water treatment, reporting that flyash has certain properties which enhances chemical coagulation and settling of turbid water.

Chan et.al. [18,19](1978)(1980) reported that a combination of acidic and basic sorbents (illite/flyash/zeolite) is most efficient for the removal of heavy metals and fluoride ions from petroleum sludge leachate.

ADSORPTION THEORY AND FUNDAMENTALS RELEVANT TO THIS RESEARCH

2.1 SINGLE SOLUTE EQUILIBRIUM MODELS

Perhaps the most useful way to present equilibrium adsorption data is via an adsorption isotherm. An adsorption isotherm is an expression of the equilibrium distribution between the concentration of a species on the adsorbent surface and the concentration in solution, at constant temperature. According to Giles [20](1970), equilibrium adsorption data plotted as isotherms can potentially yield lots of information including: the nature of the adsorption reaction, the heat, free energy and entropy of the reaction, the specific surface of the solid and the sorptive property of the adsorbent.

By the early part of this century, a great deal of isotherm data (specially on gas-solid adsorption systems) had been generated, and interest was mounting to develop an adsorption theory/model to explain and "fit" these data. Several theories/models have been derived or proposed since that time, but none was specifically applicable to liquid-solid adsorption systems. Each theory/model has its utility, and each has its shortcomings. The major theories and models for adsorption from solution have been "borrowed" from those which were originally derived for adsorption of gases onto solids. For example, the Langmuir [21](1918) adsorption model was developed for the adsorption of gases onto nonporous solids (such as glass, platinum and mica),

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and makes the following assumptions:

1) The energy of adsorption is the same at each site and is independent of surface coverage (i.e., the surface is energetically homogenous),

2) Adsorption occurs only on localized sites and there is no interaction between adsorbate molecules, and

3) A molecule can only be adsorbed by a vacant site. (In other words, a monomolecular layer represents the maximum amount that can be adsorbed onto the solid.)

A relationship between adsorbate and adsorbent can be derived by considering the kinetics of condensation and evaporation of gas molecules at a solid surface. The surface is assumed to consist of a certain number of sites S, of which S_1 are occupied and $S_0 = S - S_1$ are free. The rate of evaporation is taken to be proportional to S_1, or equal to K_1S_1 and the rate of condensation is proportional to the bare surface (free surface) S_0 and to the gas pressure P, i.e., equal to K_2PS_0 ('K' is the proportionality constant) at equilibrium, yielding:

$$K_1S_1 = K_2PS_0 = K_2P(S - S_1) \tag{1}$$

Letting $\theta = S_1/S$, the fraction of the complete monolayer coverage, equation (1) becomes,

$$\theta = \frac{K_2P}{K_1 + K_2P} = \frac{b \cdot P}{1 + bP} \tag{2}$$

The adsorption coefficient, $b = K_2/K_1$, is related to the enthalpy (or heat) of adsorption (ΔH) by

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$$b = b_0 \exp \left(-\frac{-\Delta H}{RT} \right) \qquad (3)$$

where b_0 is constant of proportionality [22][23](Weber, 1972, Weber and van Vliet, 1980).

In the aqueous solution, when $\theta = q_e/Q^0$ where q_e is the weight of solute adsorbed per unit weight of sorbent at equilibrium concentration C_e. Q^0 is the weight of solute adsorbed per unit weight of sorbent in forming a complete monolayer on the surface.

The Langmuir isotherm can be written as,

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \qquad (4)$$

Rearrangement of equation (4) to a linear form gives:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \left(\frac{1}{bQ^0} \right) \frac{1}{C_e} \qquad (5)$$

Data are generally plotted according to equation (5) and the constants b and Q^0 are calculated from the best fitting straight line.

Another equation that is much more widely used to describe liquid-solid adsorption data is the Freundlich or exponential, empirical equation [24](1926). It is a concise analytical expression of the experimental facts, rather than a picture of the adsorption mechanism. In the last seven decades, numerous attempts have been made to give a theoretical meaning to the equation. Kipling [25](1965) cited the work of Henry [26](1922) which recognized the Freundlich equation as a special case of the Gibbs relationship. A general derivation of the Freundlich equation can

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be shown from the site energy distributions [27](Clark, 1970; [28]Sheindorf, 1981; [29] Sheindorf, 1982; [30] Adamson, 1967). When an exponential distribution of adsorption energies is assumed [31](Sips, 1948), the following isotherm equation is obtained,

$$N(Q) = \alpha \exp(-Q/nRT) \tag{6}$$

where, $N(Q)$ is the number of sites having adsorption energy Q, and α, n are constant. It is assumed, further, that for each energy level, the coverage θ follows the Langmuir isotherm (equation 4), and the adsorption coefficient b depends on the adsorption energy in equation (3), but with $\Delta H = Q$.

The fraction of adsorption sites having an energy of adsorption between Q and $Q + dQ$ occupied by adsorbate is

$$d\theta_T(Q) = \theta(Q) \, N(Q)dQ \tag{7}$$

The total coverage by the adsorbate is obtained by integrating equation (7) over the whole range of adsorption energies, i.e., between the limits $-\alpha$ and $+\alpha$. The integral, after substitution of (Q) and N(Q) from equations (4), (6) and (7), is

$$\theta_T = \frac{b_0 \exp\left(Q/RT\right) C_e}{1 + b_0 \exp\left(Q/RT\right) C_e} \times \alpha \exp(-Q/nRT)dQ \tag{8}$$

which yields

$$\theta_T = \alpha \, RT \, b_0^{1/n} \, C_e^{1/n} = A'C_e^{1/n} \tag{9}$$

where A' is the constant under isothermal conditions. If the adsorption is expressed in terms of weight of adsorbate

per unit weight of adsorbent q_e, then the Freundlich isotherm is written in the form

$$q_e = K_F C_e^{1/n} \qquad (10)$$

where $K_F = Q^o A'$.

The Freundlich equation is used to fit the data to the logarithmic form of the equation -

$$\log q_e = \log K_F + 1/n \log C_e \qquad (11)$$

The intercept is roughly an indicator of sorption capacity and the slope, $1/n$, indicates adsorption intensity. The major drawbacks of the Freundlich equation are:

a)   It does not reduce to a "Henry's Law" relationship as the system approaches infinite dilution, except for the rare case where n exactly equals to c.

b)   It predicts that adsorption increases indefinitely with the solute concentration, and therefore, could never be applicable to the case of monolayer adsorption (since there are only a finite number of adsorption sites, which would eventually become saturated).

Therefore, use of the Freundlich equation should be restricted to the region of the isotherm between "Henry's Law" regime and the start of site saturation (for the case of monolayer coverage). This restriction very often limits the Freundlich model to represent only a narrow range of the isotherm curve.

The simplest possible isotherm is the one in which the adsorption capacity (q_e) is directly proportional to the equilibrium solution concentration (C_e).

$$q_e = K C_e \qquad\qquad (12)$$

where K is the constant of proportionality called the capacity parameter.

Equation (12) is frequently referred to as Henry's Law (for adsorption), since it is analogous to Henry's law in gas-liquid equilibria (i.e., the solubility of a gas in a liquid is directly proportional to its vapor pressure). All adsorption equations (or models) must reduce to this linear (Henry's law) isotherm as infinite dilution is approached, in order to be valid from a theoretical standpoint. The Langmuir equation obeys this boundary condition (for infinite dilution $C = 0$ and the denominator of equation 4 becomes 1, leaving $q_e = Q_o b\, C_e$ where $Q_o b$ is constant), but the Freundlich isotherm does not, except for the trivial case in which the exponent is equal to one. Although other isotherm models exist, those described above are the ones principally used in this dissertation. Therefore, the discussion herein has been limited to these models.

2.2 ADSORPTION FORCES AND MECHANISMS

Adsorption involves the accumulation of substances at a surface or interface, and occurs largely as the result of forces active within surface boundaries. Generally speaking, there are two types of adsorptive forces that manifest themselves between an adsorbent surface and adsorbate, as well as solvent molecules of a given system, including physical adsorption, involving only relatively weak inter-

molecular forces, and chemisorption which involves, essentially, the formation of a chemical bond. The general features which distinguish physical adsorption from chemical adsorption are as follows:

Physical Adsorption - Low heat of adsorption (2 to 3 times less than latent heat of vaporization), monolayer or multi-layer, no dissociation of adsorbed species, only significant at relatively low temperature, rapid and reversible [32] (Ruthven, 1984).

The forces involved in physical adsorption include both van der Waals - London (Dispersion) forces and electrostatic interactions comprising mainly polarizability and dipole interactions [33][34]] (London, 1930a and 1930b).

Van der Waals - London Forces

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

a)   dipole - dipole interaction

b)   dipole - induced dipole interaction

c)   induced dipole - induced dipole interaction.

The last interaction, i.e., induced dipole - induced dipole, is known as the London or "dispersion" force, and turns out to be the most significant of the three.

The London interaction is present between all atoms and molecules in close proximity. The force originates from the oscillating motion of electrons in their orbitals around atoms/molecules, which results in an instantaneous dipole. This instantaneous dipole of one molecule/atom will induce a synchronous dipole in a nearby molecule/ atom, and an

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attractive energy will result. This energy E(r), between

two different atoms is given by the following expression:

$$E(r) = -\frac{(3/2)\,\alpha_1\,\alpha_2}{r^6\left[\frac{1}{h\nu_1} + \frac{1}{h\nu_2}\right]}$$ (13)

where:

α = polarizability of atoms 1 and 2, respectively

r = distance between the two atoms

ν = oscillating frequency of the electron-nucleus system
   for atoms 1 and 2, respectively

h = plank constant.

An atom's polarizability is a measure of how "loosely"

the nucleus controls its electron distribution under the

influence of an applied electric field. Mathematically, it

is the proportionality constant, α , in the following

equation.

$$u_{induced} = \alpha\ E$$

where, $u_{induced}$ is the dipole induced by the applied

electric field, E.

The London force generally predominates over the other

forces in the case of non-polar surfaces, e.g., carbon and

graphite [27](Clark, 1970)- [22](Weber, 1972).

The dipole-dipole attractive interaction results when

two polar molecules approach each other. The average

dipole-dipole attractive interaction energy between two

molecules is given by the following equation:

$$E(r) = -\frac{\mu_1^2\,\mu_2^2}{24\,\pi^2\,\epsilon_0^2\,\epsilon^2\,K_B\,T\,r^6}$$ (14)

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where,

u_1, u_2 = dipole moment of molecules 1 and 2, respectively

ϵ_0 = permittivity in a vacuum

ϵ = permittivity of the medium

K_B = Boltzmann constant

T = Temperature

r = distance between the two molecules.

The dipole - induced dipole interaction results when a molecule with a permanent dipole moment is in the vicinity of another molecule (which may itself be polar or nonpolar), the first molecule will induce a dipole in the second, and an attractive force will result, whose average interaction energy is:

$$E(r) = - \frac{2 \mu_1^2 \alpha_2}{16 \pi^2 \epsilon_0 \epsilon r^6} \tag{15}$$

where the symbols have the same meaning as given previously.

Generally, dipole - induced dipole energy is quite small relative to the total interactional potential; and that the dispersion energy is the most significant [35](Laidler and Meiser, 1982). The differential heat of adsorption ($-\Delta H$) for the van der Waals - London interactions are generally on the order of 1 to 2 KCal/Mol for atoms and small molecules [36](Hamaker and Thompson, 1972). However, values of 5 to 15 KCal/mol were calculated by Kiselev [37][38](1969 and 1970) for gas phase adsorption and by McGuire and Suffet [39](1980) for liquid phase adsorption of alcohols, ketones, hydrocarbons and CO_2, onto graphitized

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carbon back and activated carbon, respectively.

b) <u>Ion-Dipole</u> <u>and</u> <u>Ion-Induced</u> <u>Dipole</u> <u>Forces</u>

The electric field surrounding an ion will cause an attractive force towards a polar molecule with an interaction potential given by:

$$E(r) = - \frac{ze \mu \cos \theta}{4\pi \epsilon_0 \epsilon r^2} \qquad (16)$$

where,

z = ion valance

e = electron charge

θ = angle between the dipole moment and an imaginary line connecting the ion with the polar molecule.

(The remaining terms have previously been defined.)

An ion can also induce a dipole moment in a molecule which has no permanent dipole. The energy of this interaction is:

$$E(r) = - \frac{\alpha (ze)^2}{8\pi \epsilon_0 \epsilon r^4} \qquad (17)$$

where all the symbols are as previously defined.

Chemisorption – The characteristics of the chemisorptive forces are high heat of adsorption (at least 2 to 3 times higher than latent heat of vaporization), 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 covalant) between sorbate and sorbent's surfaces [40](Atkins, 1978).

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It is, therefore, an exothermic process which is
normally accompanied by a large heat of adsorption, typical-
ly in the range of 30 to 50 KCal/mol, and occasionally much
higher [30](Adamson, 1967). A molecule being chemisorbed
may actually undergo chemical reaction because of the high
adsorption energies involved, and thereby lose its identity
[40](Atkins, 1978). Another distinguishing feature of
chemisorption reported by Hamaker and Thompson [36](1972) is
that it can take place at extremely low sorbate concentra-
tion and still produce sorbent site saturation.

2.3   THERMODYNAMICS OF ADSORPTION

Adsorption, like all other natural phenomena, is a
thermodynamic process which occurs because the system
(comprised of solvent, solute and sorbent, in this case
water, an organic compound and flyash/ activated carbon)
always attempts to achieve its lowest possible free energy
state through equilibrium condition. Theoretically, adsorp-
tion equilibrium is a function of temperature, pressure,
sorbent surface area and the total amounts of the chemical
species (i.e., concentration of the sorbate) present in the
system. An adsorption isotherm experiment is usually
performed by holding all these variables constant except for
the sorbate concentration. Another alternative method is to
hold all these variables constant except for the sorbent
surface area (i.e., the amount of sorbent added). The
adsorption of an organic solute from aqueous solution (at

infinite dilution) can probably be best represented by the following equilibrium expression:

$$X + S_v + H_2O = Sx + H_2O \qquad (18)$$

where X is the adsorbate molecule, S_v represents a vacant adsorption site, and Sx is the sorbent-sorbate complex. The equilibrium constant, K, for reaction (18) is given by

$$K = \frac{a_{Sx}}{(a_x)(a_{S_v})} \qquad (19)$$

where a_{Sx}, a_x and a_{Sv} are the activities of the complex, the solute and the sorbent respectively. At infinite dilution, the activity of the "vacant site" is analogous to the activity of a pure solid phase, and is, therefore, defined as equal to one. This results in the following expression for K:

$$K = \frac{\gamma_{Sx} \, C_{Sx}}{\gamma_x \, C_x} \qquad (20)$$

where γ_{Sx} and γ_x are the activity coefficients of the complex (formed due to adsorption) and the organic compound respectively. C_{Sx} and C_x are the concentrations of the complex (solid phase concentration of the solute) and the solute (liquid phase concentration of the solute).

Usually, γ_{Sx} (activity coefficient for the sorbent-sorbate complex) is considered constant for all cases of adsorption from dilute solution [32](Ruthven, 1984). γ_x (activity coefficient of the organic compound) is very small for dilute solution, hence it can be neglected. Thus, equation (20) can be written as –

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$$K = \frac{c_{sx}}{c_x} \qquad (21)$$

K is called the equilibrium adsorption coefficient which is a measure of the adsorption strength, sometimes also called the adsorption "capacity" parameter. This coefficient (K) can be related to the standard differential Gibbs energy of adsorption (ΔG^O) by

$$\Delta G^O = - RT \ln K$$

where R is the universal gas constant (1.987 Cal/mol) and T is the temperature in ^{O}Kelvin.

The standard differential enthalpy of adsorption (also called heat of adsorption) can be determined from the van't Hoff expression by:

$$\frac{d \ln K}{dt} = \frac{\Delta H^O}{RT^2} \qquad (22)$$

where ΔH^O is the differential heat of adsorption. The integral form of equation (22) is –

$$\ln \frac{K_1}{K_2} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \qquad (23)$$

ΔH^O can be calculated by determining adsorption capacity parameters (K_1 and K_2) at two different temperatures (T_1 and T_2).

Entropy of adsorption (ΔS^O) can be calculated using

$$\Delta G^O = \Delta H^O - T\Delta S^O \qquad (24)$$

A knowledge of the free energies, enthalpies and entropies of adsorption can provide clues to the types of adsorption mechanism(s) and force(s) involved.

2.4 Adsorption Equilibrium Models for Multi-component Systems

Several models have been developed to describe the competitive adsorption of organic contaminants in an aqueous solution. Competitive adsorption equilibria was first spurred by the work of Butler and Ockreut [41](1930) and Markham and Benton [42](1931), who explained the Langmuir equilibrium model into a general equation for multicomponent sorption equilibra. Hill [43](1946) described adaptation of the BET model to mixtures of gases. Redlich and Peterson [44](1959) examined an empirical three-parameter equation to include mixture of gases.

In the 1970's, the interest in the description of multicomponent equilibria based on thermodynamic condition became more pronounced. Radke and Prausnitz [45](1972a), [46](1972b) suggested an adaptation of the Gibbs adsorption equation in which solute spreading pressure equivalency at equilibrium was assumed to arrive at an "Ideal Adsorb Solution" (IAS) condition. Jain and Snoeyink [47](1973) modified the Langmuir competitive equilibrium model for certain types of two-component systems. DiGiano et.al. [48](1978), [49](1980) proposed a simplification of the IAS model for competitive adsorption equilibria (simplified Ideal Adsorb Theory) to avoid the tedious calculations associated with the IAS model. Calligaris and Tien [50](1982) calculated multicomponent adsorption on the basis of the IAS model by grouping adsorbates with similar adsorption properties.

Each model provides adequate description of multi-

component equilibrium, but under particular system conditions; they have been shown inadequate for other system conditions. Significant progress in the ability to predict multicomponent adsorption equilibria for dilute solution was made with the Ideal Adsorb Solution Theory (IAST), proposed by Radke and Prausnitz [45][46](1972). It is based upon the thermodynamic equivalence of the spreading pressure of each solute at equilibrium. The spreading pressure of a solute, π_i, is defined as the difference in interfacial tension between the pure solvent - solid (water - flyash) interface and the sorbate - solid (water + organic - flyash) interface. Mathematically, it can be defined as -

$$\pi = \gamma^0 - \gamma \tag{25}$$

where π is the spreading pressure,

γ^0 = surface tension of the pure solvent (water)

γ = surface tension created by the mixture of solvent and solute.

Single - solute isotherm data are required to compute the spreading pressure of each solute, i, according to

$$\pi_i(c_i) = \frac{RT}{A} \int_0^{c_i^*} \frac{q_i}{c_i} \, dc_i \tag{26}$$

where R is the universal gas constant, T is the temperature, and A the specific surface area of the sorbent. When single - solute isotherm data are described by an appropriate mathematical model, e.g., $[q_i = f(C_i)]$, equation (26) can be expressed, and spreading pressure calculated as follows:

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$$\pi_i(q_i) = \frac{RT}{A} \int_0^{q_i^*} \frac{d \log C_i}{d \log q_i} \, d q_i \tag{27}$$

In equation 26 and 27, C_i^* and q_i^* are, respectively, the liquid and solid phase concentration of species i in single solute systems which gives the same spreading pressure as that of the mixture; while c_i and q_i are the respective liquid and solid phase concentration of solute 'i' in the mixture. Other equations required for the IAST calculation are:

$$\pi_i = \pi \tag{28}$$

$$C_i = Z_i C_i^* \tag{29}$$

$$\sum_{i=1}^{N} Z_i = 1 \tag{30}$$

$$q_i = Z_i q_T \tag{31}$$

where 'Z_i' is the mole fraction of solute 'i' in the adsorbed phase, 'q_T' is the total quantity of material adsorbed from the mixture, 'N' is the total number of species. To obtain a solution, equation 27 must be integrated over the concentration range of interest (utilizing the single-solute equilibrium model) to calculate spreading pressure and accordingly the adsorption capacity (q_i). This model is very effective, but becomes increasingly difficult to use for an increasing number of solutes because of the tedious calculations. Based upon the IAS model and the Freundlich isotherm for single component systems, DiGiano et.al. [48][49](1978, 1980) established a

scheme called "Simplified Competitive Equilibrium Adsorption Model" which greatly reduces the computational effort required to implement Ideal Adsorb Solution Theory. This model has been used in this dissertation to correlate the experimental data along with the predicted value.

Simplified Competitive Adsorption Model

As mentioned before, that in order to avoid tedious calculations, DiGiano et.al. proposed a simplified competitive adsorption model. First, they assumed [48](1978) that the spreading pressure for multicomponent and the single solute system can be equal only if all the values of the equilibrium concentration of species 'i' in single solute system are identical for the special case of identical isotherms. If the total amount of species 'i' adsorbed in the mixture is equal to $q_{e,i}$ under these conditions, the following equation can be derived,

$$q_i = K_i C_i \left(\sum_{i=1}^{N} C_i^{n_i - 1} \right) \tag{32}$$

A further simplification of the model [49](1980) allows for dealing with the more realistic cases in which single solute isotherms are not identical. The simplified competitive adsorption model is described by -

$$q_i = K^{\left(\frac{n'-1}{n'}\right)} \left(K_i c_i \right)^{n_i'/n'} \left[\sum_{i=1}^{N} \left(\frac{K_i}{K} c_i \right)^{n_i'/n'} \right]^{(n'-1)} \tag{33}$$

where,

q_i = solid-phase equilibrium concentration of solute 'i' in multicomponent system

C_i = liquid-phase equilibrium concentration of solute 'i' in multicomponent system

K_i and n_i = Freundlich constant for solute 'i' in single solute system

n' = average value of n_i; i.e., $\dfrac{n_1 + n_2 + \cdots + n_n}{N}$

K' = average value of K_i; i.e., $\dfrac{K_1 + K_2 + \cdots + K_n}{N}$

N = number of components, 1,2,3,........ n.

2.5 EFFECT OF VARIOUS PARAMETERS ON ADSORPTION

From the previous discussion of thermodynamics, it is clear that the solute concentration, temperature, adsorbent surface area (or sorbent mass) can all affect the quantity of solute adsorbed. However, in addition to these variables, there are other characteristics and/or properties of the sorbent, sorbate and solution which can influence the strength of sorption. By fixing some of the parameters while changing a few of the remaining ones, adsorption on flyash has been studied systemically to some degree.

2.5.1 Sorbent Characteristics

The important physical characteristics of the sorbent (flyash) include pore-size distribution, surface heterogeneity, bulk and surface composition, and the boiler condition from where it was obtained.

2.5.2 Solution Condition

The effect of solution conditions on adsorption has also been a popular subject of study. For example, the effect of pH on the adsorption of organics on activated carbon has been investigated by several researchers (Snoeyink, et.al. [51] 1969; DiGiano and Weber, [52] 1969;

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Ward and Getzen, [53] 1970; Rosene and Manes, [54] 1977).

Each of them concluded that pH has tremendous effect on the

sorptive properties of activated carbon. The effect of

temperature on adsorption has been studied by Mattson, et.al

[55] (1969), and Weber and Morris [56] (1964). Generally,

the extent of adsorption decreases with an increase in

temperature, a phenomenon dictated by thermodynamics.

Sorbate concentration always influences the amount adsorbed.

As the sorbate concentration increases, the amount adsorbed

increases (but there is not necessarily a linear correspon-

dence), until the sorbent becomes "saturated" with the

sorbate. Beyond this point, increasing sorbate concentra-

tion will not further increase the quantity sorbed, and the

isotherm should become flat.

2.5.3 Sorbate Properties

The effect of physical properties of different

adsorbates on the extent of adsorption have been studied

most extensively. Various workers have related differences

in adsorptive behavior of different substrates to molecular

weight (Weber and Morris, [56](1964); Weber and Keinath,

[57](1967); Giusti et.al. [58](1974); Al-Bahrani and Martin,

[59](1976); and Martin and Al-Bahrani, [60](1977). The

effect of aqueous solubilities and octanol-water partition

coefficient has been studied by Lambert and Hance

[61](1967). They found that the adsorption capacity of the

soil increases as the solubility of the compound in water

decreases. The inverse relationship between the extent of

adsorption on activated carbon and aqueous solubility for various organic compounds has been observed by a number of researchers (Mattson and Mark, [62](1971); Adamson, [30](1967), and Weber, [22](1972).

Until now, no information has been available in the literature regarding the influence of the above parameters, during the adsorption of organic compounds onto flyash. In this dissertation a special emphasis has been given to examine the influence of sorbent (flyash), solution and solute properties on the adsorption process. Furthermore, an attempt has been made to correlate sorption processes with the more fundamental sorbate properties such as polarizability, dipole moment, Parachor, and molecular volume.

SECTION III

OBJECTIVES AND SCHEME OF WORK

The literature review given in the previous section clearly demonstrates how scanty our knowledge is regarding the sorptive behavior of flyash. In the light of the above shortcomings, the following research objectives have been formulated for this study.

It was intended to examine the adsorption of organic compounds that are of environmental concern as hazardous and/or toxic materials. The research has focused on the use of flyash which is a by-product of coal.

3.1 PRIMARY OBJECTIVES

a) To identify flyash as an alternative treatment source.

b) To identify the optimum treatment conditions by determining the influence (if any) of the following factors upon the sorption process: kinetic effect, pH condition, sorbent concentration (amount of sorbent used), pretreatment (washing) of the sorbent and size distribution.

c) To investigate the adsorption mechanism and the effect of various parameters (parameters related to sorbent as well as sorbate characteristics) that takes place during the adsorption process. The purpose is to measure, describe, explain and model/correlate the equilibrium sorption characteristics of the organic compounds with flyash. The emphasis has been given to

the relationship between sorption and fundamental molecular properties such as polarizability, dipole moment, molar volume, molecular weight, solubility, partition coefficient and so on. The effect of flyash composition on its sorptive characteristics has also been investigated.

d) To implicate the predominant sorption mechanism(s) and force(s) involved, based on the above results/correlations, and by determining three fundamental thermodynamic properties of the sorption process (free energy, enthalpy and entropy).

e) To examine the effect of interaction between the compounds (in a composite/complex system) during the sorption process.

3.2 SECONDARY OBJECTIVES

The secondary objective was to determine the expected contribution of this research to practical application.

3.3 SCHEME OF WORK

In order to achieve the above stated objectives, the following research program was pursued.

a) **Single dosage test** – a logical beginning of this research was to investigate whether or not adsorption of the organic compound occurs onto flyash. Single dosage batch tests were performed using flyash as

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sorbent material and various organic species as sorbate
(compounds from four different functional groups such
as Alcohols, Ketones, Aldehydes and Aromatics) were
selected. The selection was also based on the U.S. EPA
toxicity/hazard rating of the most "dangerous"
compounds. The output of this phase of experimentation
indicated rough estimations of adsorption of pollutants
onto flyash.

b) The influence of significant factors such as contact
time, pH, sorbent concentration, sorbent pretreatment
condition and other interferences were examined in this
phase of study which yielded optimum treatment condition.

c) **Isotherm study** - detailed isotherm experiments were
performed on the same compounds (except propional-
dehyde) that were used in the single dosage test.
Isotherm study results helped to explain the relation-
ship betwween sorption and fundamental molecular
properties.

d) **Thermodynamic study** - an attempt was made to determine
the thermodynamic properties of free energy, enthalpy
and entropy of sorption by performing isotherms at two
different temperatures using van't Hoff expression, the
differential heat of adsorption (ΔH°) has been
calculated which helped to find the possible adsorption
mechanism.

e) **Multi-component adsorption equilibria** - in this phase
of experiment, isotherm studies were conducted by
mixing two or more compounds (compounds from same

functional group, as well as compounds from different functional groups) together. The experimental data were correlated with the predictive model (Simplified Competitive Adsorption model). The result explained the effect of interaction that takes place among the compounds during the multi-component sorption process.

f) **Lysimeter (dynamic) study** - the output of the lysimeter/continuous column study provided information regarding the dynamic flow characteristics, continuing flow capacity and the exhaustion rate of the sorbent material, and established data on a larger scale above the test tube.

g) **Desorption/leaching study** - desorption experiments were performed in order to investigate the leaching characteristics of flyash.

h) An attempt was made to perform statistical analyses of all the experimental data with the knowledge of probability and statistics in order to establish various correlations. These correlations helped to establish adsorption mechanism(s)/model(s) for the utilization of flyash in immobilizing organic pollutants.

i) Activated carbon was used (as sorbent material) throughout the experiment as a comparison to state-of-the-art and control.

SECTION IV

MATERIALS AND METHODS

In this section, the experimental and analytical techniques that were used to conduct the experiments are described.

4.1   ADSORBENT CHARACTERISTICS

The adsorbent used in this research was flyash. This material is defined as the fine particulate matter escaping from chimney stacks. It is a byproduct of electric power generation using coal as fuel in combustion. It is usually collected by the electrostatic precipitators from the flue gas 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 gray in color. The individual particle size of this material ranges from 0.5 to 100 microns.

Seven different types of flyashes were used in this research. They include - Militant, Conemough, Wellmore Cactus, Upshore, Keystone, Blender and Deep Hollow. Flyashes are identified as per the name of their coal mines. The characteristics, composition and fusion temperature of flyashes are summarized in Table 1.

Activated carbon has been used as control throughout the study because it is a well established sorbent material. Activated carbon used in this research was "Witco Grade

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Table 1. Physical Characteristics of Flyash (Adapted from ... et al., 196?)

Coal Area	Midland	Concourch	Wellmore (plant) (outlet)	Deep Hollow (Back Hopper)	Pierce (outlet)	Keystone	Upshure
Location	Clearfield Co., Pa.	Concourch Pa.	Buchanan Co., Va.	Creston Co. W.Va.	Mixed flyash	Keystone Pa.	Upshure Co. W.Va.
Boiler Temp. (°F Fire)	n/a	2700	3150	1600	3160	2400	2470
Coal Ash Fusion Temp. (°F)	2555	2123	2155	2575	2188	2135	2700+
Leachate pH	7.60 to 7.90	7.60 to 8.50	8.00 to 9.00	7.60 to 7.90	7.00 to 7.90	6.90 to 7.90	7.90 to 8.50

n/a = not available

718", petroleum hydrocarbon based (surface area = 1050 m^2/g approximately, 12 x 30 mesh) [Manuf. information] material. 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 dusts from the material. All the experimental procedures, using activated carbon as sorbent material, were exactly identical as that which were followed during the flyash adsorption.

4.2 ADSORBATE PROPERTIES

Organic compounds from four different functional groups, commonly found in the industrial waste, were selected as "target" species in this research. They are as follows:

Alcohols – Methanol, Ethanol, Propanol, Butanol, iso-Propanol and sec-Butanol.

Ketones   – Acetone, Methyl ethyl Ketone (MEK), Methyl iso-butyl Ketone (MIBK), and Cyclohexanone.

Aldehydes – Formaldehyde, Acetaldehyde and Butyraldehyde.

Aromatics – Benzene, Aniline, o-Xylene, Phenol, m-Cresol and Ethylbenzene.

The above selection was based on U.S. EPA hazard rating [64] (Priority Pollutant's list). The physical properties of the compounds are presented in Section 5.8. All the above compounds used were laboratory reagent grade (99.99 % pure), obtained from Fisher Scientific Company, Springfield, N.J.

4.3 EXPERIMENTAL PROCEDURE

4.3.1 Selection of Optimum Sorbent Dosage

Accurately weighed (2.5 g, 5.0 g, 10.0 g, 15.0 g, 20.0 g, 25.0 g, 30.0 g, 35.0 g and 40.0 g) high fusion low power Militant flyash were taken into the glass media bottles, 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. The samples were then analyzed using a Perkin-Elmer Model 900 Flame Ionization Detector Gas Chromatograph.

4.3.2 Attainment of Equilibrium/Kinetic Study

The contact time required to reach equilibrium varies with the type and size of the sorbent used, the nature and concentration of the compound under study and the mixing condition. Kinetic studies were performed by adsorbing o-Xylene molecules, from its aqueous solution, onto different sized particles of high fusion, low power Militant flyash. The effect of sorbent paticle size on the rate of uptake of sorbate has been examined in this phase of experiment.

In each phase of experiment samples (20 g of sorbent per 750 ml. of dilute solution of the target compound) were taken at a particular time interval and were analyzed using Perkin-Elmer Gas Chromatograph. The experiments were continued until the samples reached to the steady state (equilibrium) condition.

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4.3.3 <u>Single</u> <u>Solute</u> <u>Adsorption</u> <u>Equilibria</u>

In order to carry out adsorption isotherm at room temperature (20°C approximately) weight of the sorbent was maintained at a constant while concentration of the sorbates (target organic compounds) were made to vary in the range of 10 mg/l to 100 mg/l. Accurately weighed 20 g. of flyash was placed into a 750 ml. glass media bottle (equipped with rubber lined septum and plastic screw cap). The glass media bottles were then filled with the test solutions. 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 until an equilibrium concentration was achieved (4 to 6 hours).

All the isotherm studies were performed at optimum pH condition. Most of the target organic compounds showed highest removal under slightly acidic conditions (pH 4.0 to 6.0). (The detailed procedure on pH effect has been described in Section 5.2.2). After 4 to 6 hours of agitation, samples were allowed to settle overnight. 10 ul. of the clear supernatant of each sample was then injected into the gas chromatograph for analysis. During the entire experiment a blank (solution only) has been used.

4.3.4 <u>Multi-Component</u> <u>Adsorption</u> <u>Equilibria</u>

The experimental procedure for studying adsorption in multi-component mixtures were very similar to those for the single-solute studies. Equal amounts (concentrations) of each sorbate were mixed together at various concentrations (range of concentration - 5 mg/l to 50 mg/l). Two binary

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systems (o-Xylene/ Butanol and o-Xylene/Butyraldehyde) and
two 4-component systems (o-Xylene/MIBK/Butyraldehyde/Butanol
and o-Xylene/Phenol/Aniline/m-Cresol) were investigated.
The suspensions were mixed and treated in the same manner as
in the single solute adsorption experiments.

4.3.5 Dynamic Study

Columns used in the laboratory were constructed of
pyrex glass tubing (50 mm ID, 0.5 cm wall thickness, 120 cm
length) supported in a vertical position. A 164 micron pore
site corumdum disc was placed in each column directly over
the drain hole to prevent clogging of the outlet and also to
support the sorbent material. The column was packed with
the preweighed sorbent, with 3-4 cm of Ottawa sand below and
above the sorbent to prevent disturbing the geometry of the
sorbent during addition of organic solution. The packed
column was then slowly wetted with the organic solution to
allow total saturation and to force all entrapped air in the
flyash voids out of the column packing. After the satura-
tion period of at least 24 hours, the column was filled with
the solution to the level of an overflow drain that had been
tapped into the top side of the column in order to maintain
a constant head condition. Influent solution was fed to the
top of the column through a valve manifold that distributed
the solution to the different column. The volume of
effluent solution passing through the column was continuous-
ly monitored. Effluent samples were analyzed using the
Perkin-Elmer Model 900 Flame Ionization Detector Gas
Chromatograph and the LCI-100 Integrator.

4.4   ANALYTICAL PROCEDURE

The major instrument used to analyze the samples throughout the experiment was Perkin Elmer (Model 900) Flame Ionization Detector (FID) Gas Chromatograph. The central item of this apparatus is the chromatographic column, a long tube packed permeably with some adsorbent. The common technique of gas chromatography is the elution technique, in which a stream of inert gas, called carrier gas (Helium or Nitrogen) passes continuously through the column and the sample to be analyzed is introduced instantaneously at the beginning of the column; then it is swept by the carrier gas onto 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 vapor as shown in Figure 4.1. The equilibrium constant is called the partition coefficient, K, defined as -

$$K = \frac{\text{mass of vapor/unit vol. of stationary phase (column packing)}}{\text{mass of vapor/unit vol. of mobile phase (carrier gas)}}$$

The partition coefficient, K, is related to the retardation factor, R_F, which is the major parameter in all

kinds of chromatography by the equation,

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

where,

a = fraction of the area of the section of the column occupied by the mobile phase

b = fraction of the area of the section of the column occupied by the stationary phase

R_F = retardation factor

K = partition coefficient

It follows that the solute that 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. If another solute is introduced into the column (all chromatographic parameters being unchanged) which has a different partition coefficient from that of the first solute, it will traverse the column in a greater or lesser period of time. The other end of the column is connected to a device called a detector, the purpose of which is to detect the components/ solutes as they emerge one by one.

The detector used in this research was a Flame Ionization Detector, in which carrier gas is burned in a flame which causes ionization, thus giving the flame an electrical conductivity. The conductivity of hydrogen flame is very small [65] (Littlewood, 1970), but when an organic vapor enters into the flame the conductivity rises and this increment is measured, usually in terms of area, and recorded (Figure 4.2).

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Figure 4.1   Diagram of a Packed Column
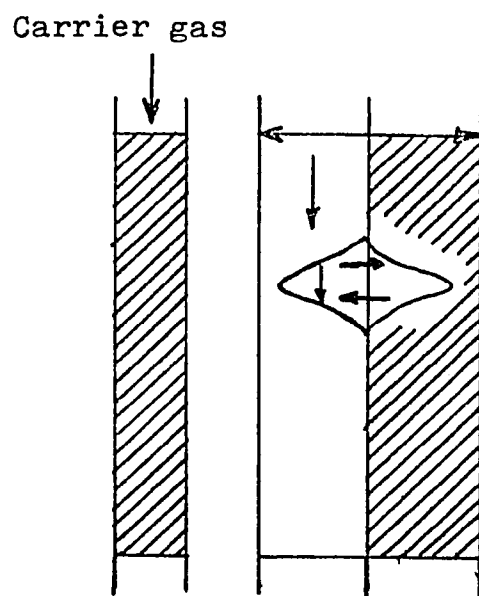
Carrier gas

Figure 4.2   Basic Circuit of a Flame Ionization
              Dector
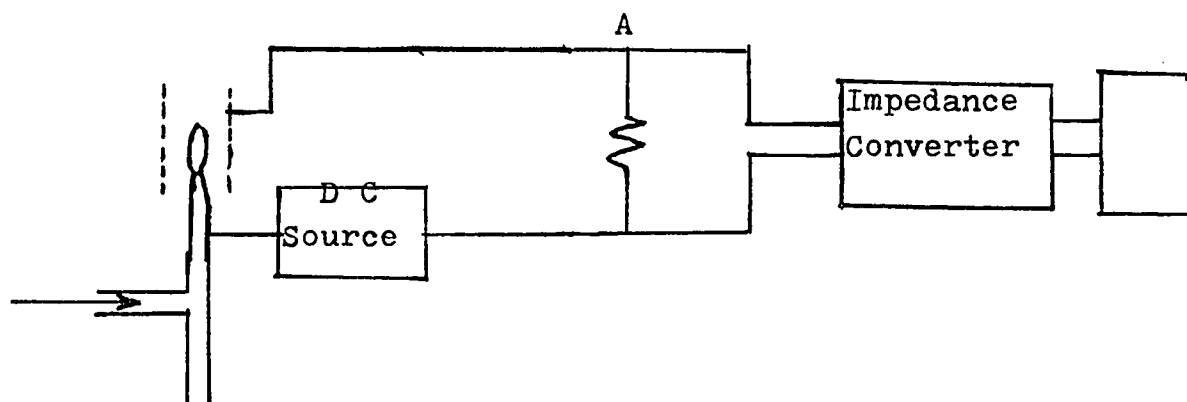
The flame ionization detector (FID) required three gas streams - carrier gas (Helium at the rate of 1 ml/min.), hydrogen (flow rate 30 ml/min.) and air (flow rate 250 - 300 ml/min.). The column effluent mixes with hydrogen and is burned in an atmosphere of air. When organic matter is burned in a hydrogen 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-amp. range, is amplified by an electrometer which produces an output signal to be relayed to a chart recorder, integrator or computer. The column used in this research to analyze the data had the following specifications:

"GP 80/100 Carbopack C:/0.1% SP-1000,
6ft x 2 mm ID glass column"

In the case of multi-component systems, the most efficient separation was obtained under the following temperature program -

Initial temperature - 30°C, hold for 1 min.

Rise   - 6°C/min. to 200°C

Final temperature   - 200°C, hold for 10 min.

Isothermal condition was used in the case of single-solute systems.

Initial temperature - 200°C

Final temperature   - 200°C

A typical chromatogram of a sample is shown in Figure 4.3.

Figure 4.3 Sample Chromatogram.

1. Methanol
2. Ethanol
3. Iso propanol
4. Sec.Butanol
5. Propanol
6. Butanol
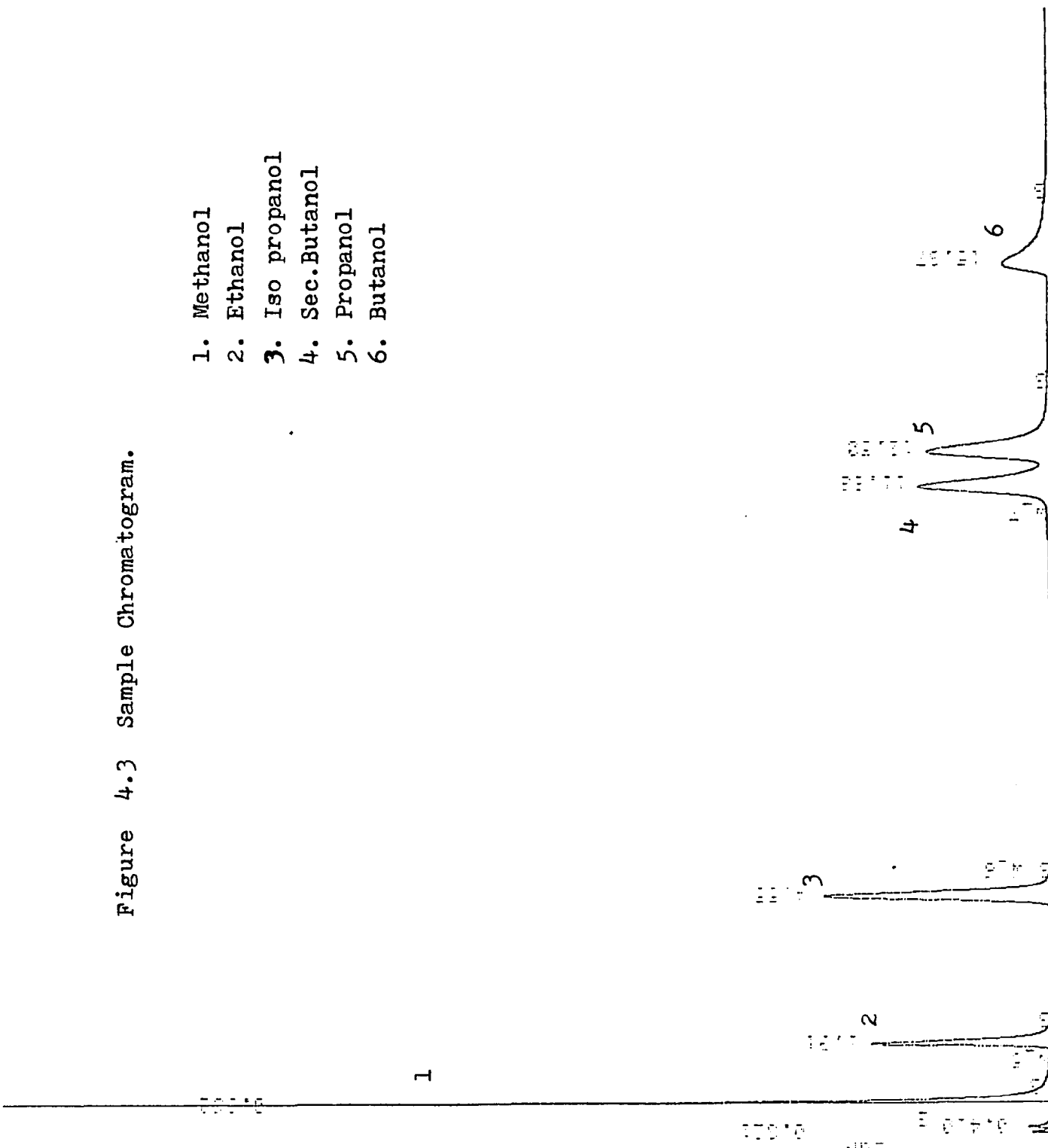
SECTION V

RESULTS AND DISCUSSIONS

The results obtained from this research are presented and discussed in the following sequence:

5.1   Single Dosage Adsorbability Tests.

5.2   Influence of Various Factors on Adsorption.

5.3   Kinetics of Adsorption.

5.4   Single-solute Adsorption Equilibria.

5.5   Multi-solute Adsorption Equilibria.

5.6   Single-solute Adsorption Dynamics.

5.7   Multi-solute Adsorption Dynamics.

5.8   Correlation of Adsorption Capacity with Various Molecular Properties of the Sorbate.

5.9   Thermodynamic Study and the Probable Adsorption Mechanisms and Forces.

5.10 Flyash as Residual Carbon.

5.11 Desorption Analysis.

5.1   SINGLE DOSAGE ADSORBABILITY TESTS

A logical beginning of this research was to investigate whether or not adsorption of the organic compound occurs onto flyash. In the initial laboratory work, 20 organic compounds from four functional groups, commonly found in the industrial waste streams, were selected.

Selection of optimum sorbent dose is an important parameter in adsorption process. The effect of flyash concentration on the adsorption of Phenol is presented in Figure

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5.1. It was observed that the adsorption increased with increasing flyash dose up to a certain concentration (20 g. of flyash per 750 ml. solution) and then there was no further change; i.e., the system reached the steady state condition. All the batch experiments were performed in this research by using 20 g. of flyash for 750 ml. of organic ("target" compounds) solution.

Table 2 lists the microgram of organic compounds removed per gram of flyash as well as the percent reduction. The influent concentrations of all the compounds (compounds belonging to the same functional group) were identical. A discussion of results obtained for each function group is as follows:

Alcohols: Four straight chain alcohols (Methanol, Ethanol, Propanol and Butanol) and two branch chain alcohols (Iso-propanol and Secondary Butanol) were used as pollutants. The lower alcohols are highly soluble in water. The oxygen atom present in the hydroxyl group in alcohols forms a hydrogen bond with water molecules. In the lower alcohols the hydroxyl group constitutes a large part of the molecule, whereas as the molecular weight of alcohol increases, the hydrocarbon character of the molecule increases and hence the solubility in water decreases. Highly soluble lower alcohols indicated relatively low amenability of these compounds onto flyash. However, as the molecular weight increases or, in other words, the solubility decreases (Fig. 5.2) a corresponding increase in amenability is noted.

Aldehydes: The aldehydes, like the alcohols, are relatively

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Figure 5.1. Effect of Flyash Dosage

Phenol onto Militant Flyash

Adsorption Capacity (ug/g)

Flyash Dosage gram/750 ml of solution
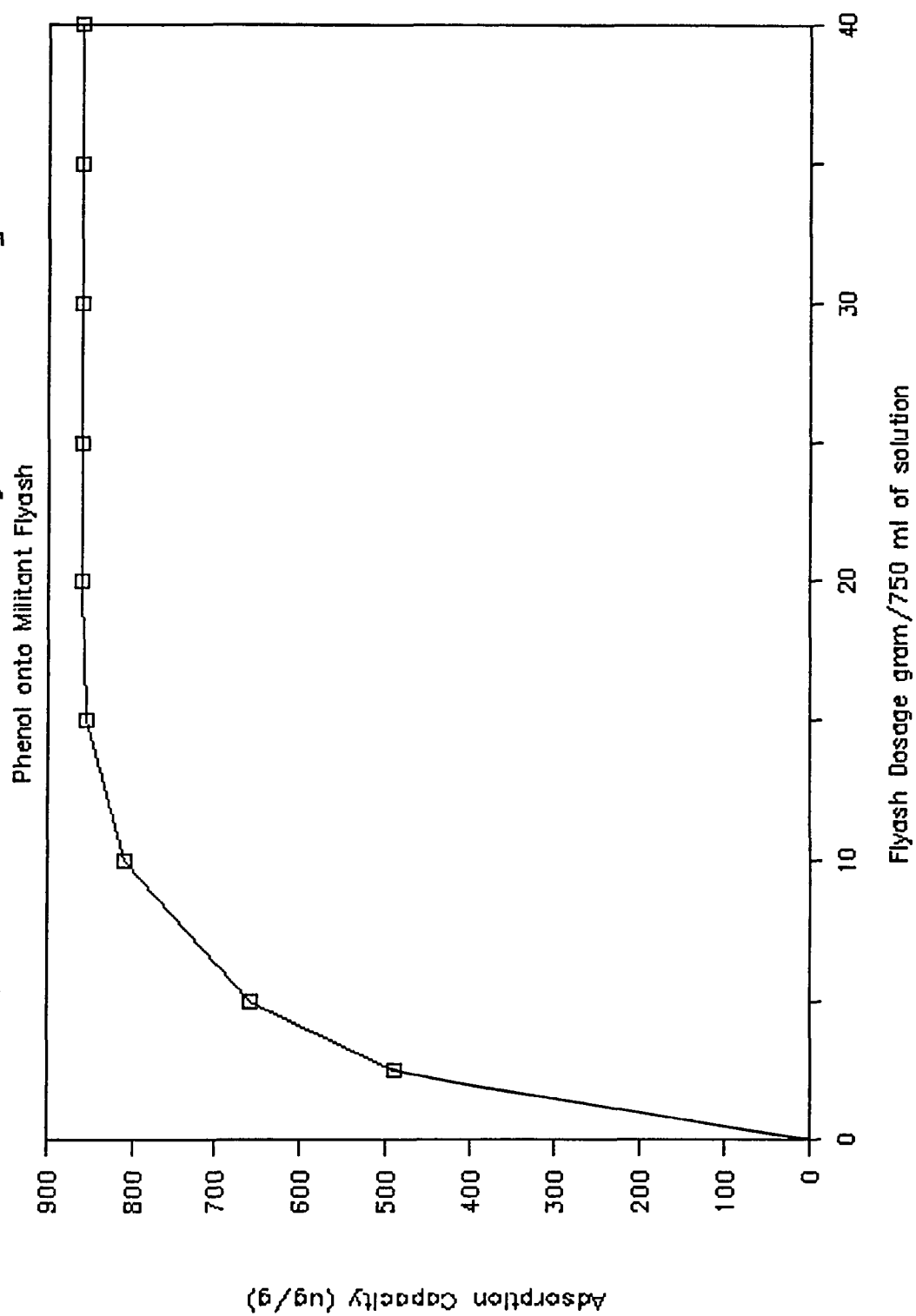
Figure 5.2   Single Dosage Adsorbability Tests.
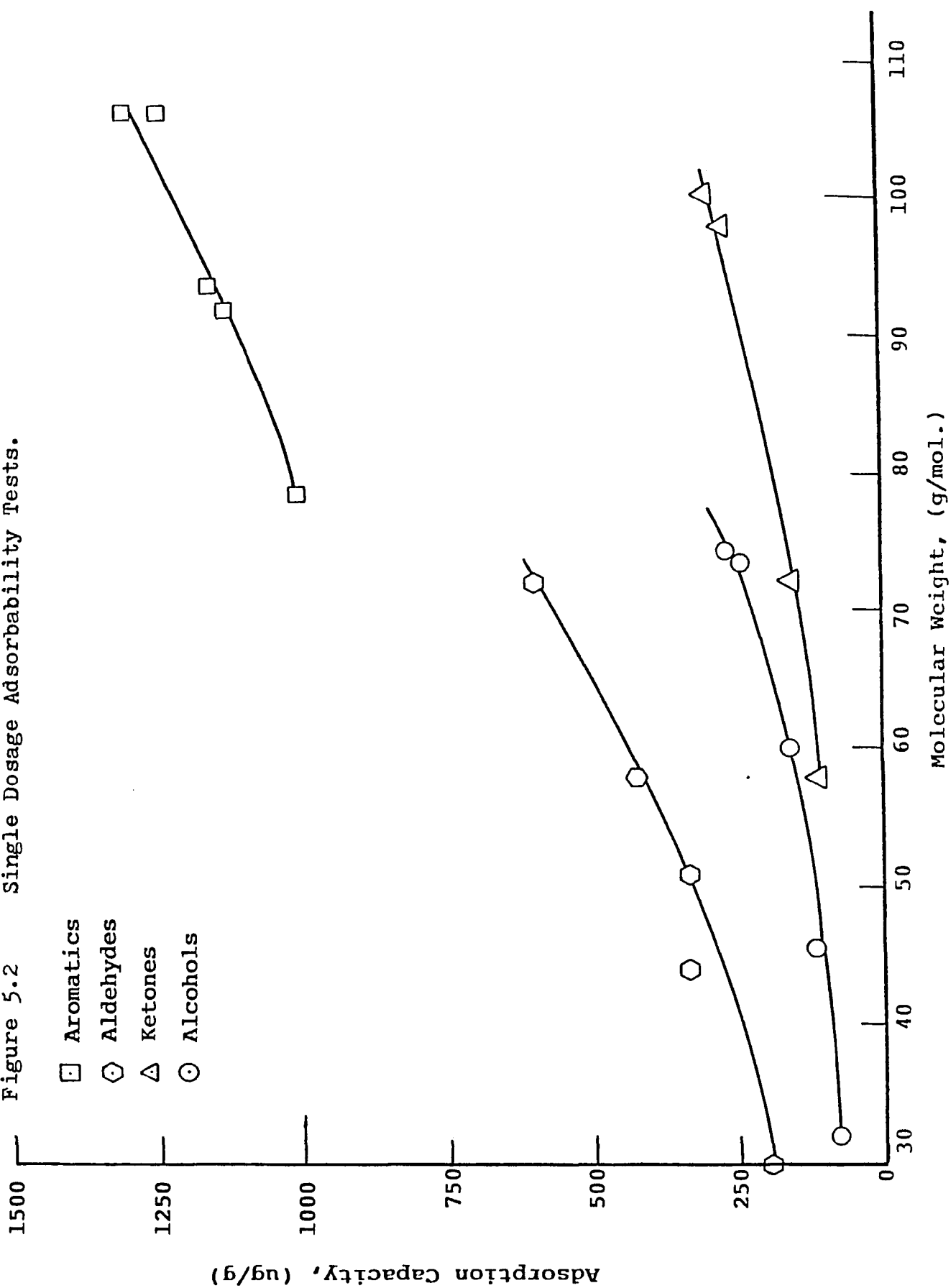
Table 2. Amenability of Typical Organic Compounds to High Fusion, Low Power Militant Flyash

Compounds	Mol.Wt.	Aqueous Solubility %	Concentration (mg/l)		Adsorbability	
			Initial (C_o)	Final (C_f)	ug/gm	Percent Reduction
Alcohols						
Methanol	32	∞	67	65	75	3
Ethanol	46.10	∞	67	64	113	5
Propanol	60.10	∞	67	63	150	6
Butanol	74.10	7.7	67	60	263	10
Isopropanol	60.10	∞	67	64	113	5
s-Butanol	74.12	12.5	67	61	225	9
Ketones						
Acetone	58.1	∞	58	55	113	5
MEK	72.1	26.8	58	54	150	7
MIBK	100.2	1.9	58	50	300	14
Cyclohexanone	98.2	2.5	58	51	263	12
Aldehyde						
Formaldehyde	30.0	∞	66	61	188	8
Acetaldehyde	44.10	∞	66	57	338	13
Propionald.	58.10	22.0	66	55	413	17
Butyraldehyde	72.10	7.1	66	50	600	24
Aromatics						
Benzene	78.12	0.06	95	67	1005	30
Toluene	92.15	0.05	95	65	1125	32
Ethylbenzene	106.16	0.015	95	62	1238	35
Phenol	94.11	6.0	95	71	900	25
Aniline	93.13	3.0	95	64	1163	33
o-Xylene	106.16	0.017	95	60	1312	37

$$\diagdown_{\diagup} C = O$$
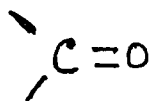
highly polar compounds and the polarity of the carbonyl group becomes less significant at higher molecular weight. The corresponding increase in amenability was observed in the case of higher molecular weight compounds which followed the same trend as the alcohols.

Ketones: The molecular weight-amenability correlation was observed in this case also.

Aromatics: Percent reductions of aromatics are much higher in comparison to other functional groups. The low polarity and the subsequent insolubility of the aromatics partially explains their easy removability i om aqueous solutions by flyash.

Single dosage adsorbability tests (on the same compounds as were used in the case of flyash) were also conducted using activated carbon as sorbent material. Table 3 lists the milligram of sorbate removed per gram of activated carbon, as well as percent reduction. Data reveals that the maximum percent reduction has been achieved on the following compounds: Butanol, Methyl isobutyl Ketone, Butyraldehyde and o-Xylene which represent Alcohols, Ketones, Aldehydes and Aromatics functional groups respectively. A strong molecular weight-amenability correlation was observed in this case also (using activated carbon) as was obtained in the case of flyash.

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Table 3. Amenability of Typical Organic Compounds to Activated Carbon.

| Compounds | Concentration (mg/l) | | Adsorbability | |
	Initial (C_O)	Final (C_f)	X/M, (mg/g)	Percent Reduction
Methanol	170	150	30	12
Ethanol	170	130	60	24
Propanol	170	119	77	30
Butanol	170	93	115	45
Isopropanol	170	107	95	37
s-Butanol	170	98	108	43
Acetone	200	160	60	20
MEK	200	125	113	38
MIBK	200	100	150	50
Cyclohexanone	200	110	135	45
Formaldehyde	170	105	98	38
Acetaldehyde	170	92	117	46
Propionald.	170	89	122	48
Butyraldehyde	170	80	135	53
Toluene	110	56	81	49
Ethylbenzene	110	42	102	62
Phenol	110	60	75	46
Aniline	110	45	98	59
o-Xylene	110	40	105	64

5.2 INFLUENCE OF VARIOUS FACTORS ON ADSORPTION

The effects of contact time, particle size of the sorbent material (flyash) and temperature on the adsorption of the 'target' organic compounds onto flyash have been addressed in other sections of this chapter. Therefore, the discussions below are limited to the influence of pretreatment (washing) of the flyash and pH of the system.

5.2.1 Effect of Washing of the Sorbent Material

Previous research [66](Liskowitz, et.al.,1983) indicated that flyash obtained from thermal power plants contains dusts and fine particulate matter which are water soluble materials. These materials block the pore openings, consequently the adsorption capacity of flyash gets reduced. Thus, in order to improve the adsorption property, flyash used in this study was washed by distilled water for about two and one half hours and dried overnight at 103 ± 2.0 °C. Results indicate that washed flyash creates better adsorptive property than unwashed flyash. An examination of the organic removal using high fusion, low power Militant flyash, in a batch study, showed that the removal of phenol waste by washed flyash is about one and one half to two times more than that of unwashed flyash (Fig. 5.3). The same trend was observed in the case of dynamic study, also. Washed, as well as unwashed, high fusion, low power Militant flyash was used to treat o-Xylene, Phenol and Aniline individually (in a dynamic system). Table 4 indicates that the adsorption capacity of unwashed flyash on o-Xylene, Phenol and Aniline are 370 ug/g, 160 ug/g, and 188 ug/g
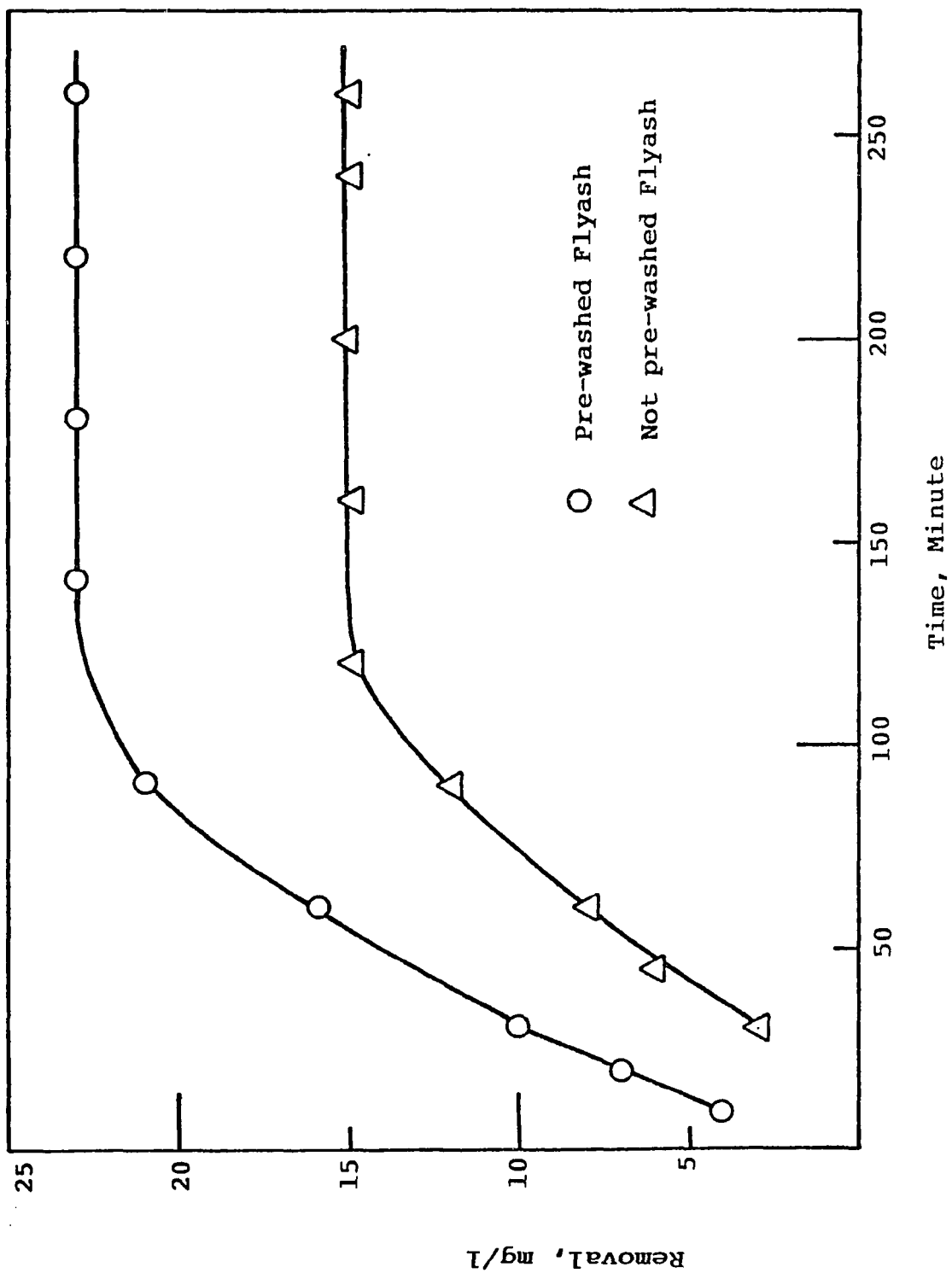
Figure5.3. Washing Effect on the Removal of Phenol Pollutant Species.

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Table 4. Effect of Washing on Adsorption Capacity (Dynamic Study)

Compound	Adsorption Capacity (ug/g) of Flyash Unwashed	Adsorption Capacity (ug/g) of Flyash Washed
o-Xylene	370	820
Phenol	160	425
Aniline	188	565

respectively; whereas, that of washed flyash on the same compounds are 820 ug/g, 425 ug/g and 565 ug/g, respectively.

5.2.2 Effect of pH on Adsorption

The effect of pH on adsorption from solution is a well established concept. The pH of a solution from which adsorption occurs influences the extent of adsorption. Hence, it was felt necessary to determine the effect of pH on flyash performance and also to evaluate the optimum pH condition for each sorbate-sorbent system separately.

High fusion, low power Militant flyash was used as sorbent material. Accurately weighed 20 g. of washed and dried flyash was placed in a 750 ml. glass media bottle, provided with a rubber lined septum and plastic screw cap. Then the appropriate solution was added into the bottle. The bottles were completely filled with the test solutions. Adjustment to acidic conditions was made using sulfuric acid, while adjustment to alkaline conditions was made using potassium hydroxide solution. System pH was maintained using a buffer solution. The natural pH of the flyash (Militant) used in this study produced acidic (pH between 4.5 to 5.0) leachate. This flyash was collected from a high fusion boiler (fusion temperature was more than 2500°F). Due to the complete combustion (complete with respect to the flyash obtained from a low fusion boiler) the percentage of acidic oxides on the surface of the Militant flyash was higher, which eventually produced acidic leachate. The adsorption capacity of flyash on the 'target' compounds has been determined under various pH conditions, and is

summarized in Table 5. Results indicate that the adsorption capacity of flyash increased with increasing pH up to a certain range, and then decreased with further increase of pH. The maximum adsorption took place in the pH range 4.5 to 5.0, which was the natural pH of the flyash. The adsorption capacity reduced significantly under the two extreme pH conditions. Most of the 'target' compounds used in this study (Alcohols, Aldehydes and Ketones) are weak acid. The ionization of those compounds under normal acid-base conditions is extremely difficult. However, when the pH was adjusted using acid and alkali, the concentration of hydrogen ions and hydroxyl ions in the system increased accordingly, and those free ions adsorbed more readily onto the flyash than the organic species. Consequently, the adsorption capacity decreased because a portion of the available area usually gets occupied by those ions (Hydrogen or hydroxyl ions). The same explanation is also applicable in the case of aromatic hydrocarbons (Benzene, o-Xylene, Ethylbenzene, etc.).

5.3   KINETICS OF ADSORPTION

The rate at which dissolved organic substances are removed from dilute aqueous solutions by solid adsorbent is a highly significant factor for applications of this process for water quality control. Several investigators, Weber and Morris [67](1963), Eagle and Scott [68](1950), Dryden and

Table 5.   Effect of pH on Adsorption

SORBENT: High Fusion, Low Power Militant Flyash

Compound	pH Range				
	2.0 - 2.5	4.5 - 5.0	6.5 - 7.0	8.5 - 9.0	10.5 - 11.0
Methanol	50	70	62	50	47
Ethanol	65	100	80	61	50
Propanol	90	150	130	100	70
Butanol	200	260	210	190	170
Acetone	70	100	85	72	67
MEK	97	115	102	90	78
MIBK	126	260	200	140	108
Cyclohexanone	100	180	122	90	53
Formaldehyde	90	150	132	100	86
Acetaldehyde	130	260	200	162	100
Butyraldehyde	340	585	525	450	330
Benzene	80	207	170	150	50
Ethylbenzene	300	1021	900	720	120
Phenol	200	510	375	300	230
Aniline	480	800	780	730	685
o-Xylene	384	1090	1055	850	195
m-Cresol	270	890	755	700	590

Kay [69](1954), worked on the kinetics of adsorption on carbon from solution and have concluded that the rate of uptake of the organic compounds onto activated carbon are best interpreted in terms of intraparticle diffusion as the rate limiting step; that is, the overall rate of adsorption appears to be controlled by the rate of diffusion of solutes (organic compounds) within the micropore structure of granular carbon. Hence, it was felt necessary to examine the kinetics effect of adsorption of organic compounds onto flyash.

5.3.1 <u>Effect</u> <u>of</u> <u>Contact</u> <u>Time</u> <u>on</u> <u>Adsorption</u>

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. Figure 5.4 shows a plot of typical data from the contact time study (all other relevant figures are shown in Appendix B). Adsorption is indicted by the decreasing concentration of solute remaining in the solution. Most of the removal (about 90%) takes place within the first one hour of the experiment. As the system approaches the equilibrium situation, the adsorption process becomes slower. The results revealed that the flyash takes about one to two and one half hours to reach the steady state condition. Generally speaking, the optimum contact time is higher during the adsorption of high water soluble compounds onto flyash than that of low water soluble compounds.

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Figure 5.4. Kinetic Study

Phenol onto Militant Flyash

Time (minutes)

Concentration Remaining (mg/L)
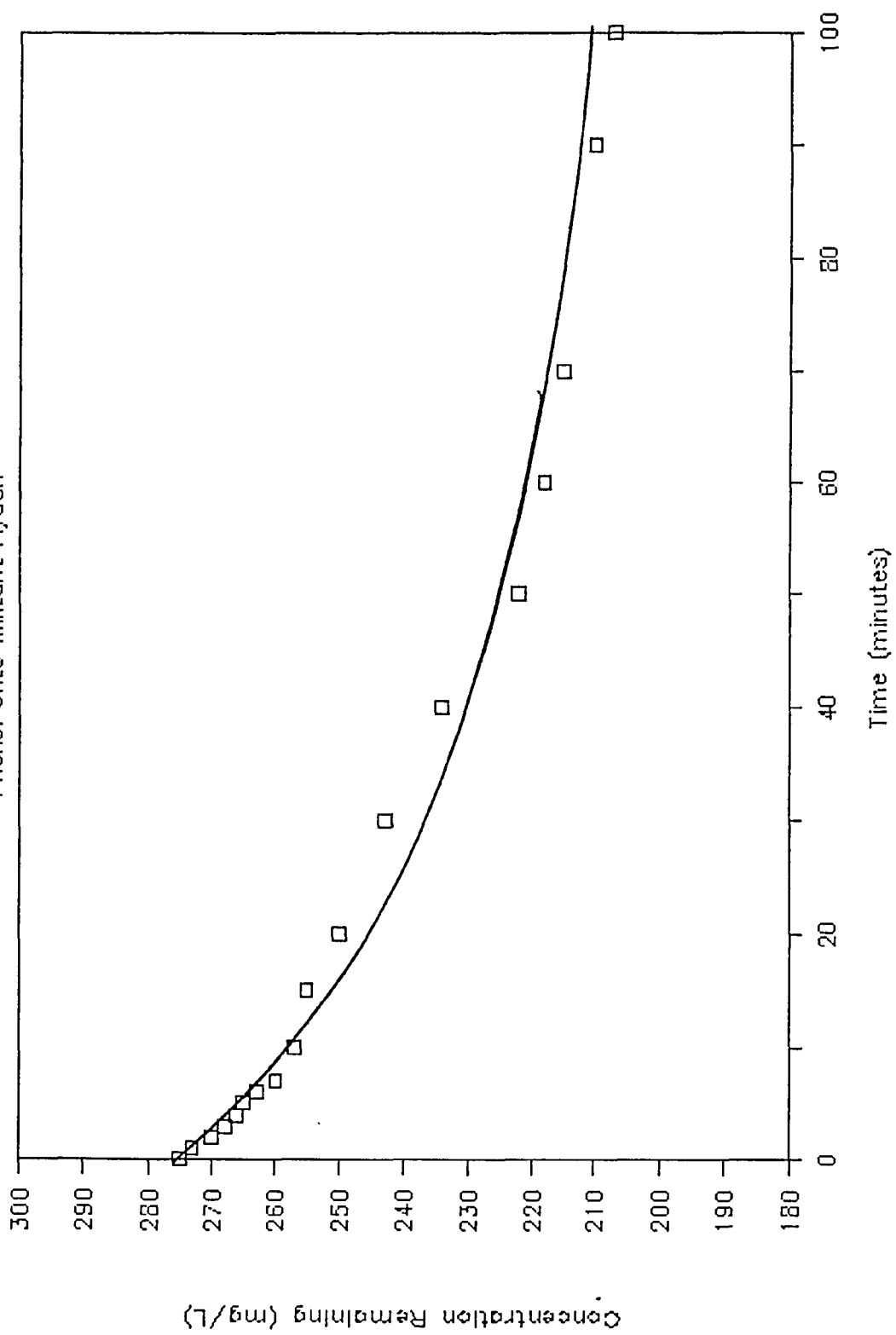
Fig 5.5 Kinetic Study
Sorbent:Act. Carbon, Sorbate:Phenol
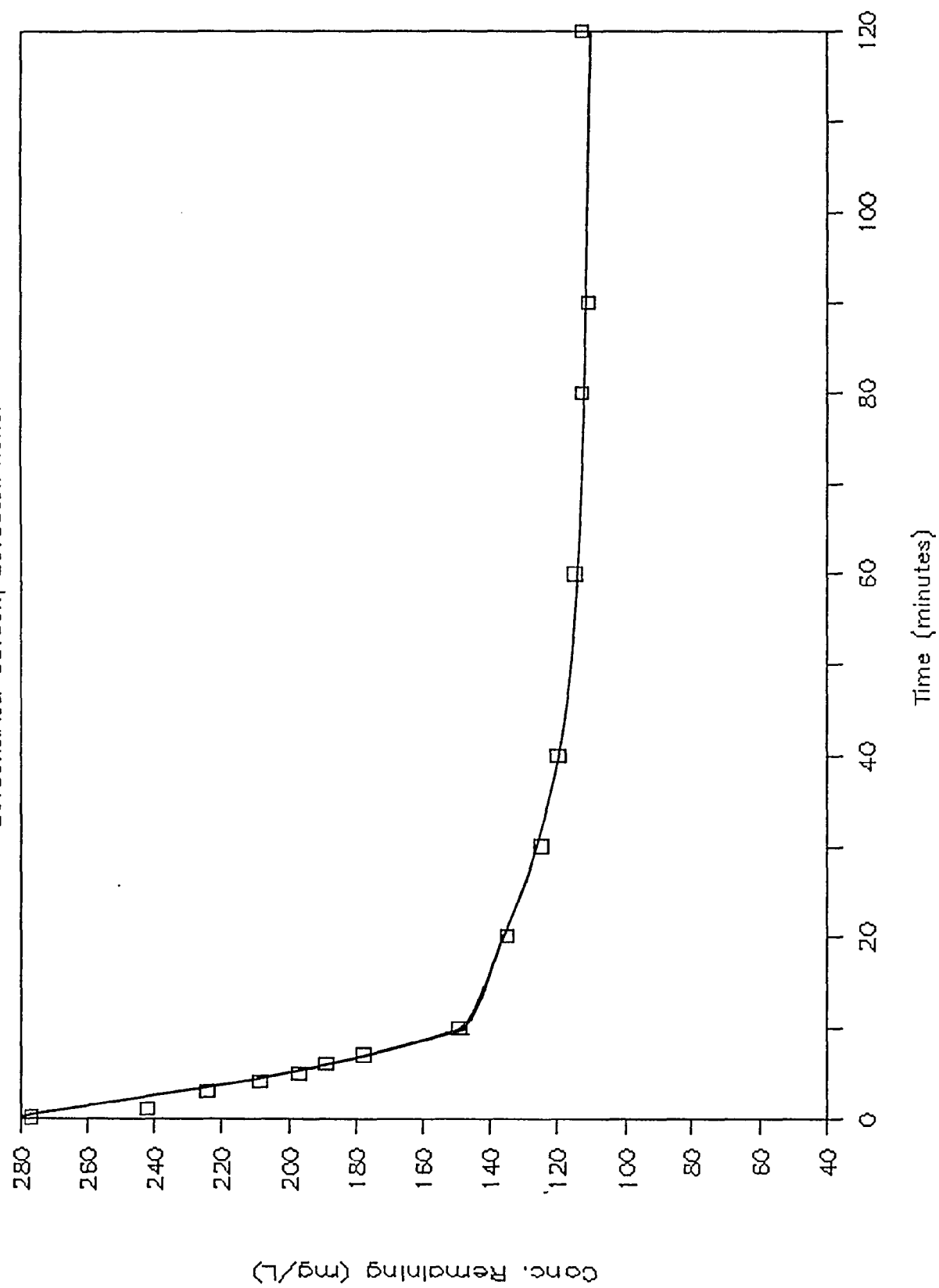
5.3.2 Calculation of Rate Constant

Rate constant, which indicates the solute uptake rate, which in turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption.

The sorption of the organic compounds from liquid phase to solid phase can be considered as a reversible reaction with an equilibrium being established between the two phases. A simple first order reaction kinetic model can be expressed as,

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B \qquad (33)$$

If the first order reversible kinetic model holds true, the rate equation for the reaction is expressed as

$$\frac{dC_B}{dt} = - \frac{dC_A}{dt} = K_1 C_A - K_2 C_B$$

$$= K_1 (C_{Ao} - C_{Ao} X_A) - K_2 (C_{Bo} + C_{Ao} X_A) \qquad (34)$$

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^{-1})

K_2 = first order desorption rate constant (Time^{-1})

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At equilibrium conditions,

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = 0 \tag{35}$$

and

$$X_{Ae} = \frac{K_c - \frac{C_{Bo}}{C_{Ao}}}{K_c + 1} \tag{36}$$

in which X_{Ae} is the fractional conversion at equilibrium
condition and K_c is the equilibrium constant defined as,

$$K_c = \frac{C_{Be}}{C_{Ae}} = \frac{C_{Bo} - C_{Ao}X_{Ae}}{C_{Ao} - C_{Ao}X_{Ae}} = \frac{K_1}{K_2} \tag{37}$$

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 34, 36 and 37,

$$\frac{dX_A}{dt} = (K_1 + K_2)(X_{Ae} - X_A) \tag{38}$$

Integration of equation 38 and substituting for K_2 from
equation 37, gives,

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = K_1\left(1 + \frac{1}{K_c}\right)t \tag{39}$$

or

$$\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = -K't \tag{40}$$

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

and $K' = K_1\left(1 + \frac{1}{K_c}\right) = K_1 + \frac{K_1}{K_c}$

$$K' = K_1 + K_2 \tag{41}$$

The slope of equation 40 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

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as per ASTM D421 and D422 (Mechanical as well as Hydrometer Method)[70] Bowles (1986). Dilute solution of o-Xylene was used as the target compound. The overall rate constant value (K') has been calculated from the plot of $ln\left(1- \dfrac{x_A}{x_{Ae}}\right)$ versus t (as per equation 40). It was observed that the overall rate constant value (K') increased with an increasing influent concentration until it reaches the steady state condition. The steady state condition was achieved in this case (adsorption of o-Xylene onto Militant flyash) at an influent concentration of 135 mg/l. Driving force does not have any effect on the rate constant after this value (influent concentration > 135 mg/l).

Data were plotted as per equation 40,

$$[ln (1 - \frac{x_A}{x_{Ae}})\ versus\ t]$$

at an initial o-Xylene concentration of 150 mg/l. A near straight line fit was observed in all cases (Appendix B) indicating that the sorption reaction can be approximated to first order reversible kinetics. Constants K_1, K_2 and K' were calculated using equations 37 through 41 and are presented in Table 6. This indicates that as the average particle diameter of the flyash decreases, the overall (solute) uptake rate increases; i.e., the flyash particle size established an inverse functional relationship with the overall rate constant value. This conforms extremely well to the hypothesis that the rate of adsorption is an inverse function of the sorbent's particle diameter [22] Weber, (1972); [71] Helfferich, (1962). Data on the adsorption kinetics of o-Xylene onto activated carbon are shown in

Table 6. Adsorption Kinetics of o-Xylene onto High Fusion, Militant Flyash

Average Particle Diameter, ϕ (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_2 = rate of desorption (per min.)

Table 7. Adsorption Kinetics of o-Xylene onto Activated Carbon

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
0.150 mm (- 70 to 100 mesh)	6.80	6.489	0.311

where:

K' = overall rate constant (per min.)

K_1 = rate of adsorption (per min.)

K_2 = rate of desorption (per min.)

Table 7 which reveals that the (solute) uptake rate of activated carbon is much higher (at least 30 times) than that of flyash. However, a near straight line fit of the plot of $\ln\left(1 - \frac{X_A}{X_{Ae}}\right)$ versus time, indicate that the adsorption of o-Xylene onto activated carbon also follows first order reversible kinetics.

5.4 SINGLE-SOLUTE ADSORPTION ISOTHERM

The adsorption characteristics of the flyash and activated carbon on the target organic pollutant species have been analyzed and evaluated primarily using the Freundlich isotherm equation because it is most useful for dilute solution over small concentration ranges [58](Gusti, 1974). As well as this, the isotherm (Freundlich) is frequently used in feasibility studies for industrial application.

The equation for the isotherm is:

$$X/M = K \, (C)^{1/n}$$

where,

X/M = loading of impurity on a unit weight of sorbent material, (mg/g)

X = weight of substance adsorbed, (mg)

M = weight of sorbent used, (g)

C = Equilibrium impurity concentration remaining in the solution, (mg/l)

K = Empirical constant equal to the intercept, known as capacity factor

1/n = slope of the line on a log-log plot, known as

intensity factor

K and n depends on temperature, characteristics of the sorbent materials, pH condition of the solution, and the properties of the substance to be adsorbed. By extrapolating this line to the initial impurity concentration ($C = C_o$) in the waste water being treated, the approximate ultimate capacity [X/M @ Co] can be calculated.

The single-solute isotherm data were fit to the Freundlich adsorption isotherm equation. The data points were transformed by taking the logarithm of C and X/M and the resulting values were fit by the least-squares method (Appendix C). Calculated values for K and 1/n are shown in Table 8.

The data were also statistically fitted to the Langmuir isotherm model. The linear form of the Langmuir isotherm equation is

$$\frac{1}{X/M} = \frac{1}{Q_o} + \frac{1}{bQ_o} \cdot 1/C$$

where:

X/M = loading of impurity on a unit weight of sorbent material

C = equilibrium impurity concentration remaining in the solution (mg/l)

Q_o = constant equal to the intercept. Weight of solute adsorbed per unit weight of sorbent in forming a complete monolayer on the surface (mg/g).

b = constant ($\frac{1}{bQ_o}$ = slope). Related to the energy of adsorption or net enthalpy.

Calculated values for Q_o and b are shown in Table 9.

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Table 8. Freundlich Parameters for Adsorption of Organic Pollutants onto High Fusion, Low Power Militant Flyash.

Compounds	K (ug/g)	1/n	R (Linear Regression Coefficient)	Concentration Range (mg/l)
Methanol	5.000	0.690	0.998	10 to 100
Ethanol	6.500	0.690	0.999	10 to 100
Propanol	8.300	0.700	0.997	10 to 100
Butanol	15.740	0.709	0.998	10 to 100
Iso-propanol	6.200	0.700	0.999	10 to 100
Sec-Butanol	12.150	0.710	0.992	10 to 100
Acetone	11.600	0.600	0.997	10 to 100
MEK	13.160	0.610	0.993	10 to 100
MIBK	20.420	0.650	0.997	10 to 100
Cyclohexanone	19.000	0.640	0.998	10 to 100
Formaldehyde	19.000	0.560	0.996	10 to 100
Acetaldehyde	35.100	0.560	0.999	10 to 100
Butyraldehyde	65.220	0.566	0.997	10 to 100
Benzene	6.050	0.908	0.992	10 to 100
Aniline	18.690	0.960	0.994	10 to 100
Phenol	31.190	0.720	0.990	10 to 100
m-Cresol	9.520	1.151	0.999	10 to 100
Ethylbenzene	30.200	0.900	0.999	10 to 100
o-Xylene	31.110	0.900	0.960	10 to 100

Table 9. Langmuir Parameters for Adsorption of Organic Compounds onto High Fusion, Low Power Militant Flyash.

Compounds	Q_O (ug/g)	b	R
Methanol	150	0.0194	0.997
Ethanol	217	0.0170	0.995
Propanol	340	0.0130	0.998
Butanol	578	0.0155	0.996
Iso-propanol	222	0.0152	0.997
Sec-Butanol	551	0.0112	0.998
Acetone	273	0.0170	0.996
MEK	334	0.0159	0.996
MIBK	500	0.0216	0.995
Cyclohexanone	476	0.0190	0.995
Formaldehyde	319	0.0240	0.994
Acetaldehyde	552	0.0277	0.993
Butyraldehyde	973	0.0300	0.973
Benzene	1400	0.0036	0.999
Aniline	9918	0.0017	0.999
Phenol	1200	0.0157	0.996
m-Cresol	2288	0.0056	0.999
EthylBenzene	4640	0.0055	0.999
o-Xylene	5940	0.0045	0.999

As discussed in Section 2.1, one of the major draw-
backs of the Freundlich isotherm equation is that it does
not reduce to "Henry's Law" relationship as the system
approaches infinite dilution, except when n = 1. This
restriction sometimes limits the use of the Freundlich
isotherm equation. The equation which obeys Henry's Law
(for adsorption) is called "simplest possible isotherm"
model, or "Linear isotherm" equation expressed as

$$X/M = KC$$

where:

K = constant, slope of the plot of X/M versus C,
      known as capacity factor.

(all other terms as previously defined)

All adsorption equations (or models) must reduce to
this linear isotherm equation as infinite dilution is
approached, in order to be valid from a theoretical stand-
point (for detailed discussion, see Section 2.1). The
experimental data were fit into the linear isotherm equation
through statistical correlation in order to check the above
validity. Calculated values for K (best fit parameter)
along with the corresponding correlation coefficient (R) are
presented in Table 10.

Tables 8, 9, 10 indicate that X/M established a strong
correlation (R > 0.99) with 'C' for each of the isotherm
equations. It is evident from the high R values that the
Freundlich, the Langmuir and the linear isotherm models
appear to fit the experimental data reasonably well. From
the data analysis it also appears that all the "target"

Table 10.   Linear Isotherm Parameters for Adsorption of Organic
Compounds onto High Fusion, Low Power Militant Flyash

Compounds	K ($\underline{ug/g}$ mg/l)	(R)
Methanol	1.14	0.996
Ethanol	1.36	0.995
Propanol	1.82	0.997
Butanol	3.73	0.996
Iso-propanol	1.44	0.997
Sec-Butanol	2.86	0.998
Acetone	1.39	0.996
MEK	1.43	0.996
MIBK	3.50	0.993
Cyclohexanone	3.03	0.995
Formaldehyde	1.96	0.994
Acetaldehyde	3.59	0.991
Butyraldehyde	7.60	0.992
Benzene	3.86	0.999
Aniline	15.53	0.999
Phenol	7.81	0.996
m-Cresol	18.73	0.999
Ethylbenzene	19.04	0.999
o-Xylene	20.34	0.999

compounds can be treated to some degree using flyash as
sorbent material. The adsorption amenability of high
fusion, low power Militant flyash on the "target" compounds
is as follows:

1. Alcohols.

Butanol>s-Butanol>Propanol>Ethanol>Iso-propanol>Methanol.

2. Ketones.

Methyl isobutyl Ketone>Cyclohexanone>Methyl ethyl
Ketone>Acetone.

3. Aldehydes.

Butyraldehyde>Acetaldehyde>Formaldehyde.

4. Aromatics.

o-Xylene>Ethylbenzene>Aniline>m-Cresol>Phenol>Benzene

Isotherm experiments were also conducted on the
"target" compounds using activated carbon as the sorbent
material. The Freundlich isotherm constants, the Langmuir
constants and the Linear isotherm constants, along with
their respective linear regression coefficients (R)
are presented in Tables 11, 12, 13. The amenability of
adsorption (for activated carbon) can be summarized as
follows.

1. Alcohols.

Butanol>s-Butanol>Isopropanol>Propanol>Ethanol>Methanol.

2. Ketones.

Methyl isobutyl Ketone>Cyclohexanone>Methyl ethyl
Ketone>Acetone.

3. Aldehydes.

Butyraldehyde>Acetaldehyde>Formaldehyde.

Table 11. Freundlich Parameters for Adsorption of Organic Pollutants onto Activated Carbon.

Compounds	K(mg/g)	1/n	R (Linear Regression Coefficient)	Concentration Range (mg/l)
Methanol	1.500	0.600	0.997	10 to 100
Ethanol	3.080	0.610	0.999	10 to 100
Propanol	3.850	0.600	0.973	10 to 100
Butanol	5.067	0.660	0.992	10 to 100
Iso-propanol	3.960	0.680	0.998	10 to 100
Sec-Butanol	4.990	0.640	0.996	10 to 100
Acetone	3.500	0.560	0.990	10 to 100
MEK	5.940	0.560	0.991	10 to 100
MIBK	6.795	0.602	0.990	10 to 100
Cyclohexanone	6.100	0.600	0.980	10 to 100
Formaldehyde	6.300	0.590	0.976	10 to 100
Acetaldehyde	7.800	0.590	0.999	10 to 100
Butyraldehyde	9.200	0.582	0.993	10 to 100
Benzene	0.0016	2.594	0.931	10 to 100
Aniline	40.46	0.276	0.992	10 to 100
Phenol	8.082	0.615	0.997	10 to 100
m-Cresol	7.30	0.687	0.998	10 to 100
Ethylbenzene	11.50	0.600	0.937	10 to 100
o-Xylene	12.550	0.600	0.992	10 to 100

Table 12. Langmuir Parameters for Adsorption of Organic Pollutants onto Activated Carbon.

Compounds	Q_O (mg/g)	b	R (Linear Regression Coefficient)
Methanol	28.27	0.0256	0.993
Ethanol	71.90	0.0105	0.996
Propanol	66.45	0.0073	0.993
Butanol	134.33	0.0202	0.997
Iso-propanol	131.53	0.0036	0.996
Sec-Butanol	127.97	0.0031	0.996
Acetone	62.05	0.0118	0.996
MEK	92.61	0.0042	0.992
MIBK	123.17	0.0277	0.995
Cyclohexanone	115.03	0.0028	0.996
Formaldehyde	110.07	0.0029	0.994
Acetaldehyde	162.06	0.0017	0.995
Butyraldehyde	174.31	0.0219	0.996
Benzene	62.00	0.0350	0.970
Aniline	125.52	0.1640	0.989
Phenol	179.52	0.0200	0.997
m-Cresol	181.05	0.0260	0.998
Ethylbenzene	167.00	0.0008	0.995
o-Xylene	190.00	0.0730	0.994

Table 13. Linear Isotherm Parameters for Adsorption of Organic Compounds onto Activated Carbon.

Compounds	$\dfrac{K\ (mg/g)}{(mg/l)}$	R (Linear Regression Coefficient)
Methanol	0.225	0.971
Ethanol	0.496	0.975
Propanol	0.601	0.978
Butanol	1.112	0.985
Iso-propanol	0.879	0.986
Sec-Butanol	0.923	0.982
Acetone	0.445	0.970
MEK	0.747	0.964
MIBK	1.147	0.975
Cyclohexanone	0.900	0.978
Formaldehyde	0.931	0.977
Acetaldehyde	1.170	0.977
Butyraldehyde	1.390	0.970
Benzene	0.717	0.935
Aniline	1.986	0.923
Phenol	1.474	0.975
m-Cresol	1.963	0.987
Ethylbenzene	2.000	0.978
o-Xylene	2.79	0.976

4. <u>Aromatics.</u>

Aniline>o-Xylene>Ethylbenzene>m-Cresol>Phenol>Benzene

Solute/sorbate properties and sorbent characteristics are the two most significant parameters that affect the adsorption process. Hence, it was felt necessary to establish the following:

a) Relationship between the adsorption capacity and the sorbent properties.

b) Relationship between the adsorption capacity and the solute properties.

The above correlations have been established and discussed in detail in the following sections (Section 5.6.1 and 5.8) of this dissertation.

5.5 <u>MULTI-SOLUTE ADSORPTION EQUILIBRIA</u>

The objective of a multi-component adsorption study is to examine the competitive equilibria for situations where more than one target compound is present. Competition for adsorption sites occurs when a wide spectrum of contaminants are present in the solution. In this section, the results of a series of adsorption studies in multi-component mixtures are presented and discussed. The theoretical background of the models used in this section to verify the experimental data has been discussed in detail in Section 2.4, the related single-component isotherms in Section 2.1, and the experimental method in Section 4.3.4.

The multi-component adsorptive behavior of the follow-

ing combinations were examined:

     i)   o-Xylene and Butanol

    ii)   o-Xylene and Butyraldehyde

  iii)   o-Xylene, Butanol, Methyl isobuty Ketone and
         Butyraldehyde

    iv) o-Xylene, Aniline, m-Cresol and Phenol

For each case the experimental data are compared with the predicted/theoretical values. This comparison was achieved by calculating the square of the correlation coefficient (R-Square). These values were obtained through the following formulae [72](Parratt, 1961).

(1) The sum of the squares of all experimental measurements, noted as SSY, is calculated by

$$SSY = \frac{\Sigma \, (X/M)^2}{N}$$

where,

    X/M = adsorption capacity

    N   = total number of data

(2) SSE (sum of the square of the error) is calculated from the sum of the squares of the differences between the experimental measurement, in this case X/M, and the corresponding predicted values, $\widehat{X/M}$, from the Simplified Ideal Adsorb Solution Theory (SIAST) model.

$$SSE = \frac{\Sigma \, (X/M) - (\widehat{X/M})^2}{N}$$

(3) R-Square is then calculated from SSY and SSE:

$$R\text{-Square} = 1 - \frac{SSE}{SSY}$$

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A. Calculation of adsorption capacity (X/M) from experimental measurement.

Data obtained from the experiment has been utilized to calculate the adsorption capacity of the sorbent using mass balance equation,

$$X/M = \frac{(C_1 - C_2)V}{M}$$

where,

X/M = adsorption capacity (mg/g) or (ug/g)

X/M = weight of substance adsorbed (mg) or (ug)
           weight of sorbent used (g)

C_1 = influent concentration, (mg/l)

C_2 = equilibrium concentration, (mg/l)

V = volume of the reactor, (1)

M = weight of sorbent used, (g)

B. Calculation of adsorption capacity (X/M) from the theoretical model.

Simplified Ideal Adsorb Solution Theory/Simplified Competitive Model:

$$q_i = K'^{\left(\frac{n'-1}{n'}\right)} (K_i c_i)^{1/n'} \left[\sum_{i=1}^{N} \left(\frac{K_i}{K'} c_i^{n_i}\right)^{1/n'} \right]^{n'-1}$$

where:

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

c_i = liquid phase equilibrium concentration of solute i in multi-solute system.

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

n = Avg. value of n_i; i.e., $\dfrac{n_1 + n_2 + \cdots + n_n}{N}$

K = Avg. value of K_i; i.e., $\dfrac{K_1 + K_2 + \cdots + K_n}{N}$

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N = number of components, 1,2,3,.....N

5.5.1 Competitive Adsorption of o-Xylene and Butanol

The first case examined was the adsorption of a mixture containing o-Xylene and Butanol. This pair of compounds was selected because when adsorbed singly, each of them indicated maximum adsorption amenability (when compared within the same functional group). Isotherm tests were performed mixing equal amounts (concentrations) of each of the compounds (o-Xylene/Butanol) at various concentration ranges (5 mg/l to 50 mg/l). Table 14 shows that the adsorption capacity of high fusion, low power Militant flyash (experimental value) on o-Xylene and Butanol during the multi-component system are 585 ug/g and 90 ug/g respectively, whereas the adsorption capacity of the same flyash on the same compounds during single-solute system are 682 ug/g and 175 ug/g, respectively (values obtained from Figures D.1 and D.2 using equilibrium concentration = 30 mg/l). Data indicate that the individual compounds in the mixture are each adsorbed to a lesser extent when compared with their relative adsorbabilities in the single component tests. It also revealed that the organics in the mixture at 60 mg/l total concentration adsorbed to a lesser extent (675 ug/g. of flyash) than that which would be predicted from the sum of the single component tests at 30 mg/l each (857 ug/g. of flyash). When the mixture data (cumulative) are compared with extrapolated data for pure butanol (without o-Xylene) at the 60 mg/l concentration, adsorption from the mixture is

greater. A lesser extent of adsorption is observed in the mixture when compared with extrapolated data for pure o-Xylene solution (without Butanol). This can be explained in that the total surface area available for the adsorption of the two solutes was not more than that available for the adsorption of o-Xylene from pure solution. Since this area was shared with the other (Butanol) less effectively adsorbed compounds, less efficient use of the available area resulted. Butanol is a less efficient sorbate because it is highly water soluble material. Table 16 lists, for each equilibrium concentration, the corresponding adsorption capacity of flyash determined experimentally, and the predictive values. The square of the correlation coefficient R^2, obtained was equal to 0.976. This indicates that the experimental data matches well with the predicted/ theoretical values.

5.5.2 Competitive Adsorption of o-Xylene and Butyraldehyde

Equal amounts (concentrations) of o-Xylene and Butyraldehyde were used in this binary system at various ranges (5 mg/l to 50 mg/l). Data followed the same pattern as was observed in the other (o-Xylene/ Butanol) two-component system. Table 15 indicates clearly that a competition for the adsorption sites takes place when more than one sorbate (compound) is present in the system. Data also indicates (Table 17) that the experimental results are within the acceptable range with the predictive values (R^2 = 0.923).

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Table 14. Competitive Adsorption of o-Xylene and Butanol.

SORBENT: Flyash

Compound	Complete Monolayer Q_0 (ug/g)	Single Solute System (ug/g)	Multi-solute System (ug/g)
o-Xylene	5,940	682	585
Butanol	578	175	90
		857	675

Adsorption capacity of flyash on each target compound has been calculated (using C = 30 mg/l) from Figures D.1 and D.2.

Table 15. Competitive Adsorption of o-Xylene and Butyraldehyde.

SORBENT: Flyash

Compound	Complete Monolayer Q_0 (ug/g)	Single Solute System (ug/g)	Multi-solute System (ug/g)
o-Xylene	5,940	682	480
Butyraldehyde	973	447	280
		1129	760

Adsorption capacity of flyash on each target compound has been calculated (using C = 30 mg/l) from Figures D.3 and D.4.

Table 16. Competitive Adsorption of o-Xylene and Butanol.

SORBENT: High Fusion, Low Power Militant Flyash.

No.	Equilibrium Concentration (mg/l)	Adsorption Capacity, (X/M), (ug/g)			
		Experimental		SIAST*	
		Butanol	o-Xylene	Butanol	o-Xylene
1	5	31.25	110.20	37.05	127.78
2	10	52.25	230.00	59.02	241.41
3	15	66.25	330.00	77.47	350.11
4	20	77.50	420.00	93.95	455.71
5	25	81.87	510.00	109.10	559.04
6	30	90.00	585.00	123.26	660.59
7	40	104.40	715.00	149.43	859.56

* Simplified Ideal Adsorbed Solution Theory

$R^2 = 0.976$

Table 17. Competitive Adsorption of o-Xylene and Butyraldehyde.

SORBENT: High Fusion, Low Power Militant Flyash

| No. | Equil. Concentration (mg/l) | Experimental Capacity, (X/M), (ug/g) | | | |
| | | Experimental | | SIAST* | |
		Butyral.	o-Xylene	Butyral.	o-Xylene
1	5	130.00	99.10	139.50	107.83
2	10	190.00	190.00	198.38	211.51
3	15	235.00	275.00	242.98	312.69
4	20	269.00	360.00	280.19	412.08
5	25	292.00	400.00	312.69	510.08
6	30	300.00	480.00	341.86	606.86
7	40	325.00	590.00	393.16	797.62

*Simplified Ideal Adsorbed Solution Theory

$R^2 = 0.923$

5.5.3 Competitive Adsorption of o-Xylene, Butanol, Methylisobutyl Ketone and Butyraldehyde

The objective of this experiment was to explore the adsorption mechanism(s) that takes place when more than two compounds from different functional groups are mixed together. Data indicates that an increasing number of compounds (sorbates) in a system, increases the competition among the solutes for adsorption sites, as a result of which the adsorption capacity of the sorbent on that particular compound as well as the ultimate (overall) sorbent capacity decreases. For example, the adsorption capacity of flyash on o-Xylene in the single component system was 682 ug/g, whereas the same for two component systems (o-Xylene/ Butanol) and 4-component systems (o-Xylene /Butanol/MIBK and Butyraldehyde) are 585 ug/g and 390 ug/g respectively (values obtained from Figures D.6, D.7, D.8 and D.9, using equilibrium concentration = 30 mg/l). The same trend was also observed in the case of other compounds. Data (Table 18) also reveals that the ultimate capacity (766 ug/g) obtained from the 4-component system was about 50% less than what would be predicted from summing the single component data (1491 ug/g). The solubility effect makes the sorbate less efficient, and consequently less efficient use of the available surface area is also apparent in a 4-component system. Tables 14, 15 and 18 show that the percentage of overall adsorption capacity of flyash in the case of two 2-component systems (o-Xylene/ Butanol and o-Xylene/Butyraldehyde) was higher than that of 4-component systems. This

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indicates that there must be considerable interaction among the solutes and this interaction increases as the number of components in the system increases. Because of this high competition and interaction, the sorbent cannot make full utilization of its available adsorption sites and consequently adsorption capacity decreases. Table 20 lists the results of this experiment.

5.5.4 Competitive Adsorption of o-Xylene, Aniline, meta-Cresol and Phenol

Selecting the compounds from the same functional groups, the multi-component adsorption equilibria of the second 4-component mixture was examined. Equal amounts of o-Xylene, Aniline, m-Cresol and Phenol were mixed together at various concentration ranges and their competitive effect (during adsorption) onto high fusion low power militant flyash was investigated. Data (Table 19) followed the same pattern as was obtained in the case of other multi-component systems, i.e., a clear trend of competition among the solutes was observed in this case also. However, higher utilization of the adsorption sites (80 %) has been realized in this case than the other 4-component (mixture of Butanol/ Butyraldehyde/Methyl isobuty Ketone/o-Xylene) system where only about 50% of the total adsorption sites were utilized. Each of the compounds selected (Aromatics) in this case indicated a higher affinity than the other three functional groups in the single solute system due to their relatively low solubility in water. Hence, more area has been utilized efficiently in this 4-component system. However, the cumu-

Table 18. Competitive Adsorption of o-Xylene, Butyraldehyde, Methyl isobuty Ketone and Butanol.

SORBENT: Flyash

Compound	Complete Monolayer Q_0 (ug/g)	Single Solute System (ug/g)	Multi-solute System (ug/g)
o-Xylene	5,940	682	390
Butyraldehyde	973	447	250
Methyl isobutyl Ketone	500	187	70
Butanol	578	175	56
		1491	766

Adsorption capacity of flyash on each target compound has been calculated (using C = 30 mg/l) from Figures D.5, D.6, D.7 and D.8.

Table 19. Competitive Adsorption of o-Xylene, m-Cresol, Aniline and Phenol.

SORBENT: Flyash

Compound	Complete Monolayer Q_0 (ug/g)	Single Solute System (ug/g)	Multi-solute System (ug/g)
o-Xylene	5,940	682	540
m-Cresol	2,288	477	453
Aniline	9,918	490	375
Phenol	1,200	361	264
		2010	1632

Adsorption capacity of flyash on each target compound has been calculated (using C = 30 mg/l) from Figures D.9, D.10, D.11 and D.12.

Table 20. Competitive Adsorption of Butanol, Butyraldehyde, MIBK and o-Xylene.

SORBENT: High Fusion, Low Power Militant Flyash.

No.	Equilib. Concentration (mg/l)	Adsorption Capacity, X/M, (ug/g)							
		Experimental Value				SIAST			
		Butanol	Butyraldehyde	MIBK	o-Xylene	Butanol	Butyraldehyde	MIBK	o-Xylene
1	5	20.00	112.00	25.00	80.20	23.99	129.10	30.30	98.72
2	10	32.50	165.00	40.00	160.50	39.11	182.93	46.62	195.56
3	15	40.00	202.00	50.00	230.20	51.88	223.61	59.80	290.76
4	20	45.00	220.00	57.50	285.00	63.32	257.47	71.25	384.71
5	25	51.20	240.00	62.50	345.00	73.83	287.00	81.55	410.64
6	30	56.25	250.00	70.00	390.50	83.66	313.47	91.01	490.70
7	40	62.50	262.00	75.00	460.00	101.81	359.92	108.13	530.00

*Simplified Ideal Adsorbed Solution Theory

$R^2 = 0.94$

lative capacity of the four compounds is less than the
adsorption capacity for o-Xylene and m-Cresol from their
pure solution. This can be explained in the same way as it
was explained in the case of the two component system (o-
Xylene/Butanol and o-Xylene/Butyraldehyde); o-Xylene and m-
Cresol were the most effectively adsorbed compound of the
four, and the total surface area available for its adsorp-
tion was shared with the other two less effectively adsorbed
compounds.

Multi-component adsorption equilibria studies were also
performed using activated carbon as sorbent material. Exact-
ly identical experimental procedures were followed in this
case as that which was performed in the case of flyash.
Data are summarized in Tables 21, 22 and 23 which reveals
the existence of competition among the solutes in this case
(multi component adsorption onto activated carbon) also.
The square of the correlation coefficients (R^2) obtained in
all the cases (Tables 24, 25, 26) were even stronger
(greater than 0.99) than the values obtained in the case of
flyash. The homogeneous characteristics of the activated
carbon partially explains the experimental accuracy.

5.6   SINGLE SOLUTE ADSORPTION DYNAMICS

If the batch isotherm studies indicate that the liquid
can be treated to the desired purity level at a particular
dosage, then the next step is to evaluate the liquid in a
dynamic test. The purpose of performing continuous column
studies, in this research, was to establish data on dynamic

Table 21. Competitive Adsorption of o-Xylene and Butanol

SORBENT: Activated Carbon

Compound	Complete Monolayer Q_O (mg/g)	Single Solute System (mg/g)	Multi-solute System (mg/g)
o-Xylene	190	97	84
Butanol	134	48	27
		145	111

Adsorption capacity of activated carbon on each target compound has been calculated (using C = 30 mg/l) from Figures D.13 and D.14.

Table 22. Competitive Adsorption of o-Xylene and Butyraldehyde.

SORBENT: Activated Carbon

Compound	Complete Monolayer Q_O (mg/g)	Single Solute System (mg/g)	Multi-solute System (mg/g)
o-Xylene	190	97	79
Butyraldehyde	174	67	41
		164	120

Adsorption capacity of activated carbon on each target compound has been calculated (using C = 30 mg/l) from Figures D.15 and D.16.

Table 23. Competitive Adsorption of o-Xylene, Butyraldehyde, Methyl isobutyl Ketone and Butanol.

SORBENT: Activated Carbon

Compound	Complete Monolayer Q_0 (mg/g)	Single Solute System (mg/g)	Multi-solute System (mg/g)
o-Xylene	190	97	67
Butyraldehyde	174	67	35
Methyl isobutyl Ketone	123	53	25
Butanol	134	48	20
		265	147

Adsorption capacity of activated carbon on each target compound has been calculated (using C = 30 mg/l) from Figures D.17, D.18, D.19, and D.20.

Table 24. Competitive Adsorption of o-Xylene and Butanol.

SORBENT: Activated Carbon

No.	Equil-ibrium Concen-tration (mg/l)	Adsorption Capacity, (X/M), (mg/g)			
		Experimental		SIAST	
		Butanol	o-Xylene	Butanol	o-Xylene
1	5	7.50	25.00	7.50	25.20
2	10	13.25	44.90	13.40	45.40
3	15	17.97	57.50	18.21	58.00
4	20	21.42	68.43	21.57	68.43
5	25	24.37	76.25	25.62	79.38
6	30	26.56	83.75	28.50	86.93
7	40	30.00	93.75	34.72	103.10

$R^2 = 0.996$

Table 25. Competitive Adsorption of o-Xylene and Butyraldehyde.

SORBENT: Activated Carbon

No.	Equil. Concen-tration (mg/l)	Experimental Capacity, (X/M), (mg/g)			
		Experimental		SIAST	
		Butyral.	o-Xylene	Butyral.	o-Xylene
1	5	13.00	23.75	13.12	23.80
2	10	23.00	41.25	23.01	41.75
3	15	29.37	53.75	29.50	54.00
4	20	33.90	62.50	34.26	63.48
5	25	38.12	71.25	39.50	72.00
6	30	41.25	78.75	43.24	81.09
7	40	46.25	87.50	50.99	96.50

$R^2 = 0.996$

Table 26. Competitive Adsorption of Butanol, Butyraldehyde, MIBK and o-Xylene.

SORBENT: Activated Carbon

No.	Equilib. Concentration (mg/l)	Adsorption Capacity, X/M, (mg/g)							
		Experimental Value				SIAST			
		Butanol	Butyral dehyde	MIBK	o-Xylene	Butanol	Butyral dehyde	MIBK	o-Xylene
1	5	5.62	11.56	7.40	21.25	5.64	11.60	7.50	21.50
2	10	10.40	20.20	13.47	36.10	10.42	20.61	13.53	36.50
3	15	13.12	26.25	17.00	47.50	13.75	26.40	17.50	48.00
4	20	15.62	30.00	19.50	55.48	16.88	30.56	20.53	55.48
5	25	18.12	32.50	22.50	61.25	20.00	34.38	23.12	63.75
6	30	20.00	34.69	25.00	66.87	22.38	38.47	26.19	70.69
7	40	23.12	38.75	28.70	75.00	27.33	45.29	31.12	83.94

$R^2 = 0.994$

systems as well as to verify the data trend that was obtained from batch isotherm studies. Single solute adsorption dynamic study has been performed in two different phases. The objective of the first phase of the experiment was to verify the batch study data and that of the second phase of the experiment was to examine the effect of chemical composition of flyash on its (flyash's) sorptive property.

The following organic compounds were used as sorbate (target compound) in the first phase of the single solute adsorption (dynamic) study –

Butanol, Methyl isobuty Ketone, Butyraldehyde,

o-Xylene, Phenol and Aniline

High fusion, low power Militant flyash and activated carbon were used separately as sorbent material. The details of the experimental procedure are summarized in Section 4.3.5.

All flyashes were washed with distilled water and then dried overnight before use. As mentioned before (Section 5.2.1) that the washing was done in order to improve the adsorption capacity of flyash by removing its water soluble materials. Dynamic study data (Table 27) indicate that the treatment of the above mentioned target compound is feasible using flyash as sorbent material. The amenability of adsorption of the compounds onto Militant flyash can be summarized as follows:

o-Xylene>Aniline>Butyraldehyde>Phenol>Methyl isobutyl

Ketone>Butanol.

This followed the same pattern as was obtained in the batch

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experiment.

Activated carbon was also used as sorbent material during this phase (phase I of single solute adsorption dynamics) of the experiment. The influent concentration of each of the target organic compounds was the same as was used in the case of flyash. Comparative studies between activated carbon and flyash indicate (Table 28) that the treatment capacity of activated carbon is about 200 fold higher than that of flyash. The comparison made here was only on a pound for pound basis. However, the data followed the same pattern as was observed in the case of flyash.

5.6.1   Sorbent Characteristics of Flyash and Its Correlation with the Composition.

As discussed in Section 4.1, flyash is composed of different chemical compounds such as Aluminum oxide, Calcium oxide, Iron oxide, Silica, and sulfur, along with the residual carbon. One of the major objectives of this research is to examine and establish a relationship between the sorbent characteristics of flyash with its chemical constituents. The following flyashes were used as sorbent material: Militant, Conemough, Wellmore Cactus, Deep Hollow, Blender, Keystone and Upshore. Detailed analysis (surface composition) of flyash is summarized in Table 29. An equal amount (450 g) of each flyash (washed and dried) was placed in a column. A dilute solution of the "target" compound was passed through the column till the flyash reached the exhaustion point. The volume of the solution

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Table 27. Adsorption Capacity of High Fusion, Low Power
Militant Flyash.

| Compound | Equilibrium Conc. (mg/l) | Adsorption Capacity (ug/g) | |
		Batch Study	Dynamic Study
o-Xylene	30	683	820
Butyraldehyde	30	447	525
Methyl Isobutyl Ketone	30	187	220
Butanol	30	175	200
Phenol	30	361	425
Aniline	30	490	565

Table 28. Adsorption Capacity of Militant Flyash and Activated
Carbon from Dynamic Study.

| Compound | Influent Conc. (mg/l) | Adsorption Capacity * | |
		Flyash (ug/g)	Act. Carbon (ug/g)
o-Xylene	30	820	114,000
Aniline	30	565	120,000
Butyraldehyde	30	525	78,000
Phenol	30	425	72,000
Methyl Isobutyl Ketone	30	220	57,000
Butanol	30	200	52,000

* Adsorption capacity values are from dynamic study results.

Table 29. % Composition of Elemental Oxides at the Surface of Flyash. [63](Liskowitz, et.al, 1982)

Element	Militant (front)	Conemough	Wellmore Cactus (outlet)	Deep Hollow (back)	Blender (outlet)	Keystone	Upshore
SiO$_2$ (%)	37.8	57.0	36.40	29.60	38.3	38.7	47.90
Al$_2$O$_3$ (%)	36.6	29.3	36.10	55.20	29.9	36.4	42.3
CaO (%)	2.95	2.46	6.14	2.65	7.57	2.61	1.87
S (%)	14.60	6.32	15.90	9.31	15.90	10.70	3.94
Residual Carbon (%)	1.52	2.50	3.73	1.17	2.14	1.71	0.81

passed through the column was monitored carefully. Samples, at particular time intervals, were analyzed using a Perkin-Elmer Flame Ionization Detector Gas Chromatograph (for detail, see Section 4.3.5). Four compounds were selected as "target" compounds in this phase of the experiment (2nd phase of the single-solute dynamic study). Each of these represented its functional group, such as Butanol, Methyl isobuty Ketone, Butyraldehyde and o-Xylene, representing Alcohols, Ketones, Aldehydes and Aromatics functional groups. The influent concentration of each of the compounds was maintained at 30 mg/l.

An attempt has been made to establish a correlation between the sorptive capacity of flyash and its (flyash) composition using the following regression equation:

$$X/M = A C + B$$

where:

X/M = adsorption capacity of flyash (ug/g)

C = % composition of various elemental oxides and residual carbon of flyash

A and B are the constants of the above equation.

The linear regression coefficient (R) determined from the above equation, indicates how well the two variables linearly correlate (for detail see Section 5.8). The adsorption capacity of various flyash on the "target" compounds are summarized in Table 30. Data reveal that the adsorption capacity of flyash is directly proportional to the residual carbon content of the flyash. Table 31 presents the resulting linear correlation coefficients (R)

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Table 30. Adsorption Capacity of Various Flyash on the Target Compounds.

ORGANIC COMPOUND: Butanol (Alcohol Group)

Flyash	Militant	Conemough	Wellmore Cactus	Deep Hollow	Blender	Keystone	Upshore
X/M (ug/g)	200	340	496	140	262	218	87

ORGANIC COMPOUND: Methyl Isobutyl Ketone (Ketone Group)

Flyash	Militant	Conemough	Wellmore Cactus	Deep Hollow	Blender	Keystone	Upshore
X/M (ug/g)	220	370	546	150	300	240	105

ORGANIC COMPOUND: Butyraldehyde (Aldehyde Group)

Flyash	Militant	Conemough	Wellmore Cactus	Deep Hollow	Blender	Keystone	Upshore
X/M (ug/g)	552	780	900	400	672	592	300

ORGANIC COMPOUND: o-Xylene (Aromatics Group)

Flyash	Militant	Conemough	Wellmore Cactus	Deep Hollow	Blender	Keystone	Upshore
X/M (ug/g)	883	1107	1346	600	1070	943	562

Adsorption capacity (X/M) of all the flyashes obtained from dynamic study using influent concentration = 30 mg/l.

Table 31. Correlation Coefficients (R) for Regressions of Adsorption Capacity of Flyash (X/M) versus Flyash Composition.

Compound	X/M versus				
	Residual Carbon %	Al_2O_3 (%)	CaO(%)	S(%)	S_IO_2(%)
Butanol	0.998	−0.532	0.573	0.518	0.088
Methyl Isobutyl Ketone	0.999	−0.549	0.597	0.527	0.102
Butyraldehyde	0.962	−0.672	0.593	0.550	0.151
o-Xylene	0.955	−0.722	0.647	0.610	0.126

from these regressions which indicate a strong correlation between adsorption capacity of flyash and its residual carbon content (R > 0.95). Besides residual carbon content, all other elemental oxides/elements such as Al_2O_3, Cao, S_iO_2 and S indicated poor correlation with the sorptive capacity (X/M) of flyash (R < 0.72). It is also clear from the experimental data and regression analysis that the residual carbon content of flyash is mainly responsible for its (flyash) sorptive property. The higher the residual carbon content, the better the removal. An identical trend was also observed by [73]Mancy, et.al., during their study (Adsorption of ABS, i.e., Alkyl Benzene Sulfonate onto Flyash).

The organophilic behavior of carbon is a well established phenomenon and because of this, the adsorption capacity of carbon on the organic compounds is highly significant. With the above observations, data and explanation flyash can be considered as a non-polar sorbent like activated carbon. This could be explained as follows :-

Carbon is a non-polar sorbent material. The sorption property of flyash (on the organics) is governed by its residual carbon content and also it follows the identical sorption mechanism(s) as that of activated carbon (for details, see Section 5.10).

5.7 MULTI-SOLUTE ADSORPTION DYNAMICS

Multi-solute adsorption dynamics closely followed the

approach and methods discussed in the single solute adsorption dynamics. Two 2-component systems (mixture of o-Xylene/Butyraldehyde and mixture of o-Xylene/Butanol) and one 4-component system (mixture of o-Xylene/ Butyraldehyde/Methyl isobutyl Ketone/Butanol) were used in this study as sorbate. High fusion low power Militant flyash and activated carbon were used as sorbent material separately.

5.7.1   o-Xylene/Butyraldehyde System

Equal amounts (concentration) of o-Xylene and Butyraldehyde were mixed together in this binary system as was used in the case of a batch study. Data reveals (Table 33) that the individual compound in the mixture are each adsorbed to a lesser extent when compared with their single solute system. It was observed from the experimental data (dynamic study) that the adsorption capacity of high fusion, low power Militant flyash on o-Xylene and Butyraldehyde during a binary component study are 520 ug/g and 330 ug/g respectively, whereas the adsorption capacity of the same flyash on o-Xylene and Butyraldehyde during single component study are 820 ug/g and 525 ug/g respectively. The ultimate capacity (850 ug/g) obtained from binary solute system was about 63.5 % of what would be predicted from summing the single component data (1,345 ug/g). This indicates that presence of more than one component in a system tends to decrease the adsorption capacity of sorbent due to inter-action and competition among the solutes. Identical adsorption mechanism was observed during multi-component adsorption equilibria (i.e., batch experiment) as was

Table 32. Fusion Temperature of Different Coal Flyash and their Respective Adsorption Capacities on the "Target" Organic Compound.

Coal Flyash	Fusion Temperature (oF)	Adsorption Capacity, X/M (ug/g)*			
		Butanol	Methyl Isobutyl Ketone	Butyraldehyde	o-Xylene
Militant	2555	200	220	552	883
Conemough	2125	340	370	780	1107
Wellmore Cactus	2190	496	546	900	1346
Deep Hollow	2575	140	150	400	600
Blender	2143	262	300	672	1070
Keystone	2183	218	240	592	943
Upshore	2700	87	105	300	562

* Adsorption capacity (X/M) of all the flyashes obtained from dynamic study using Influent concentration = 30 mg/l.

Table 33. Competitive Adsorption of o-Xylene and Butyraldehyde

SORBENT: Flyash

Compound	Single Solute System (ug/g)	Multi-Solute System (ug/g)
o-Xylene	820	520
Butyraldehyde	525	330
	1345	850

Adsorption capacity of flyash on each target compound has been calculated from Figure F.1.

observed here (i.e., dynamic experiment).

5.7.2   o-Xylene/Butanol System

The ultimate capacity (750 ug/g) obtained from this binary system was about 73.5 % than what would be predicted from summing the single component data (1020 ug/g). The competition for adsorption sites between o-Xylene and Butanol molecule is lower than that of o-Xylene and Butyraldehyde molecule (because the adsorption affinity of Butanol is much lower than that of o-Xylene). As a result, 10 % more area has been utilized in this binary system than the other binary (o-Xylene/ Butyraldehyde) system. However, the data (Table 34) shows that still some competition exists in this binary system also.

5.7.3   4-Component Multi-Solute System

A 4-component synthetic organic wastewater was prepared by mixing equal amounts (concentrations) of o-Xylene/Butyraldehyde/Methyl isobutyl Ketone/Butanol. It followed the same trend as was observed in the case of 2-component systems, i.e., individual compounds in the mixture are each adsorbed to a lesser extent when compared with their relative adsorbabilities in the single component tests. Table 35 shows that the adsorption capacity of high fusion low power Militant flyash on o-Xylene, Butyraldehyde, Methyl isobutyl Ketone and Butanol during multi-solute dynamic studies are 400 ug/g, 270 ug/g, 77 ug/g and 60 ug/g respectively, whereas the adsorption capacity of the same flyash on them (same solute) during single component dynamic

Table 34. Competitive Adsorption of o-Xylene and Butanol
(Dynamic Study)

SORBENT: Flyash

Compound	Single Solute (ug/g)	Binary Solute (ug/g)
o-Xylene	820	650
Butanol	200	100
	1,020	750

Adsorption capacity of flyash on each of the target compounds has been calculated from Figure F.2.

Table 35. Competitive Adsorption of o-Xylene, Butyraldehyde, Methyl isobutyl Ketone and Butanol

SORBENT: Flyash

Compound	Single Solute (ug/g)	Multi Solute (ug/g)
o-Xylene	820	400
Butyraldehyde	525	270
Methyl isobutyl Ketone	220	77
Butanol	200	60
	1,765	807

Adsorption capacity of flyash on each of the target compounds has been calculated from Figure F.3.

study are 820 ug/g, 525 ug/g, 220 ug/g and 200 ug/g
respectively. Data also reveals that only about 46 % of the
ultimate capacity has been realized in 4-component multi-
solute system than its single component predicted data.
This indicates that there must be considerable interaction
between components adversely affecting their respective
adsorbabilities. The same trend was observed during 4-
component batch isotherm experiments.

Adsorption dynamic experiments, using one 2-component
system (mixture of o-Xylene and Butyraldehyde) and one 4-
component system (mixture of o-Xylene/Butyraldehyde/Methyl
isobutyl Ketone/Butanol) were performed using activated
carbon as sorbent. The same influent concentration was used
in this case as was used in the case of flyash. Tables 36
and 37 follow the identical data trend as was observed
during the flyash study, i.e., individual solutes in the
mixture are each adsorbed to a lesser extent when compared
with their relative adsorbabilities in the single component
tests.

5.8 CORRELATION OF ADSORPTION CAPACITY WITH VARIOUS MOLECULAR PROPERTIES OF THE SORBATE

Tables 38 and 39 summarize the adsorption capacity of
high fusion low power Militant Flyash and activated carbon
on the 'target' compounds. The adsorption capacity has been
calculated using the Freundlich Isotherm equation

Table 36. Competitive Adsorption of o-Xylene and Butyraldehyde.

SORBENT: Activated Carbon

Compound	Single Solute System (mg/g)	Multi-Solute System (mg/g)
o-Xylene	114	83
Butyraldehyde	78	46
	192	129

Adsorption capacity of activated carbon on each of the target compounds has been calculated from Figure F.4.

Table 37. Competitive Adsorption of o-Xylene, Butyraldehyde, Methyl isobutyl Ketone and Butanol.

SORBENT: Activated Carbon

Compound	Single Solute System (mg/g)	Multi-Solute System (mg/g)
o-Xylene	114	72
Butyraldehyde	78	41
Methyl isobutyl Ketone	57	30
Butanol	52	24
	301	167

Adsorption capacity of activated carbon on each of the target compounds has been calculated from Figure F.5.

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Table 38. Adsorption Capacity of High Fusion, Low Power Militant Flyash.

ORGANIC COMPOUND: Alcohol Group

Compound	Methanol	Ethanol	Propanol	Butanol	Isopropa-nol	Sec. Butanol
X/M (ug/g)	52	68	90	176	67	136

ORGANIC COMPOUND: Ketone Group

Compound	Acetone	MEK	MIBK	Cyclohexanone
X/M (ug/g)	89	105	186	168

ORGANIC COMPOUND: Aldehyde Group

Compound	Formaldehyde	Acetaldehyde	Butyraldehyde
X/M (ug/g)	127	236	447

ORGANIC COMPOUND: Aromatics Group

Compound	o-Xylene	Phenol	m-Cresol	Ethyl Benzene
X/M (ug/g)	682	361	477	645

X/M has been calculated using the Freundlich Isotherm parameters from Table 8.

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Table 39. Adsorption Capacity of Activated Carbon.

ORGANIC COMPOUND: Alcohol Group

Compound	Methanol	Ethanol	Propanol	Butanol	Isopropa-nol	Sec. Butanol
X/M (mg/g)	12	24	30	48	40	44

ORGANIC COMPOUND: Ketone Group

Compound	Acetone	MEK	MIBK	Cyclohexanone
X/M (mg/g)	23	40	52	47

ORGANIC COMPOUND: Aldehyde Group

Compound	Formaldehyde	Acetaldehyde	Butyraldehyde
X/M (mg/g)	47	60	66

ORGANIC COMPOUND: Aromatics Group

Compound	o-Xylene	Phenol	m-Cresol	Ethyl Benzene
X/M (mg/g)	97	65	76	89

X/M has been calculated using the Freundlich Isotherm from Table 11., at C = 30 mg/l.

(Freundlich Parameters are shown in Table 8) at an equilibrium concentration of 30 mg/l.

Tables 40 through 43 present a variety of properties of the target compounds used in this research, which include:

(a) Molecular weight - weight of one mol of the compound, expressed in grams.

(b) Dipole moment, (u) - when a bond is formed between two atoms that differ in electro-negativity, there is an accumulation of negative charge on the more electronegative

$$u \quad = \quad Qr$$
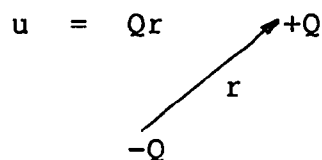
atom, leaving a positive charge on the more electropositive one. The bond then consititutes an electric dipole, which is by definition an equal positive and negative charge, $\pm Q$, separated by distance, r.   Dipole moment, $u = Qr$, usually expressed in debye(D) or esu.cm (the unit 10^{-18} esu.cm is called the debye).

(c) Electronic Polarizability, (α) - an atom's polarizability is a measure of how "loosely" the nucleus controls its electron distribution under the influence of an applied electric field. It is the proportionality constant, α, in the following equation:

$$u_{induce} \quad = \alpha \, E$$

where, u_{induce} is the dipole induced by the applied electric field, E.

α has been calculated using the Lorentz-Lorentz equation:

Table 40. Summary of Organic Compounds (Alcohol Group) Properties to be used in Adsorption Correlations. [74](Weast, 1977/78)

Property	Methanol	Ethanol	Propanol	Butanol	Isopropanol	Sec-Butanol
Molecular weight (M, g/Mol)	32.04	46.07	60.09	74.10	60.09	74.12
Dipole Moment (μ, [Debye])	1.70	1.67	1.67	1.67	1.67	1.67
Electronic Polarizibility (α, 10^{-24} cm^3)	41.0	64.34	89.98	110.30	87.80	109.64
Molar Volume ($\bar{V}$, cm^3/Mol)	40.49	58.37	77.08	91.50	76.53	91.73
Parachor (P, $cm^3 \frac{dynes^{1/4}}{Mol, cm^{1/4}}$)	88.29	127.48	170.21	203.78	165.18	200.89
Density (g/cm^3) at 20°C	0.7914	0.7893	0.7796	0.8908	0.7851	0.8080
Refractive Index n_D at 20°C	1.3288	1.3611	1.3850	1.3992	1.3776	1.3954
Surface Tension α dynes/cm at 20°C	22.61	22.75	23.78	24.60	21.70	23.00

Table 41. Summary of Organic Compounds (Ketone Group) Properties to be used in Adsorption Correlation [74] (Weast, 1977/78).

Property	Acetone	MEK	MIBK	Cyclohexanone
Molecular weight $(M,\ g/Mol)$	58.10	72.10	100.2	98.20
Dipole Moment $(u,\ [Debye])$	2.89	2.72	3.08	3.25
Electronic Polarizibility $(\alpha,\ 10^{-24},cm^3)$	80.52	103.62	150.00	132.30
Molar Volume $(\tilde{v},\ cm^3/Mol)$	73.47	89.52	125.10	98.41
Parachor $(P,\ \frac{cm^3,dynes^{1/4}}{Mol,\ cm\ 1/4})$	162.10	199.34	282.50	221.36
Density (g/cm^3) at $20^{\circ}C$	0.7908	0.8054	0.801	0.9978
Refractive Index n_D at $20^{\circ}C$	1.3588	1.3814 at $15^{\circ}C$	1.396	1.4522
Surface Tension σ dynes/cm at $20^{\circ}C$	23.70	24.60	26.00	25.6

Table 42. Summary of Organic Compounds (Aldehyde Group) Properties to be used in Adsorption Correlation [74](Weast, 1977/78)

Property	Formal-dehyde	Acetal-dehyde	Butyraldehyde
Molecular weight (M, g/Mol)	30.0	44.10	72.10
Dipole Moment (u, [Debye])	2.27	2.72	2.72
Electronic Polarizibility (α, 10^{-24}, cm^3)	42.46	57.45	102.84
Molar Volume ($\bar{v}$, cm^3/Mol)	36.81	56.29	88.25
Parachor (P, $\frac{cm^3, dynes^{1/4}}{Mol, cm\ 1/4}$)	83.29	120.80	199.28
Density (g/cm^3) at $20^{o}C$	0.815	0.7834	0.817
Refractive Index n_D at $20^{o}C$	1.3799	1.3316	1.3843
Surface Tension α dynes/cm at $20^{o}C$	26.20	21.20	26.00

Table 43. Summary of Organic Compounds (Aromatic Group) Properties to be used in Adsorption Correlation. [74](Weast, 1977/78)

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 (α, 10^{-24})cm^3	175.11	139.46	163.43	178.10
Molar Volume ($\bar{v}$, cm^3/Mol)	118.37	87.77	104.61	122.41
Parachor (P, cm^3,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
Refractive Index n_D at 20°C	1.5058	1.5509	1.5398	1.4959
Surface Tension σ/dynes/cm at 20°C	30.10	40.90	39.0	29.20

$$\alpha = \frac{3M}{N_O \rho} \frac{(n^\nu_D - 1)}{(n^\nu_D + 2)} \quad . \quad '\alpha' \text{ expressed in cm}^3$$

where, M = molecular weight of the compound (g).

ρ = density of the compound at $T = 20^\circ C$ (g/cm^3)

N_O = Avagadro's number (6.023×10^{23} $\underline{\text{molecules}}$)
$\hspace{10cm}$ Mol

N_D = Index of refraction for compound at $T = 20^\circ C$

(d) Molar volume, $\bar{v}$ - It is the volume of one mole of the compound. $\bar{v}$ calculated from molecular weight and density data as:

$\bar{v} = M/\rho$, where M = molecular weight of the compound (g)

ρ = density of the compound at $20^\circ C$ (g/cm^3)
$\bar{v}$ expressed as cm^3/Mol

(e) Parachor - A compound's parachor, p, is a function of molecular structure and, for liquids, is defined as

$$p = \frac{M \alpha^{1/4}}{\rho_L - \rho_\nu}$$

where ρ_L = liquid density, g/cm^3

ρ_ν = vapor density, g/cm^3

α = surface tension, dynes/cm

since, $\rho_L \gg \rho_\nu$

therefore, $p = \dfrac{M \alpha^{1/4}}{\rho_L}$

$p = \bar{v} \alpha^{1/4}$ (since $\bar{v} = M/\rho$).

The dipole moment and polarizability are the ones of primary interest, since they are the only compound properties which enter into the equations for intermolecular forces and energies (equations 13 through 17 of Section II). However, an attempt has been given also to establish a

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correlation between the adsorption capacity (X/M) and other

properties such as molecular weight, molar volume, and

parachor. In order to test for this possible mutual

correlation (adsorption capacity, X/M versus various

properties), a linear regression of each variable (i.e.,

property) in turn with X/M has been employed using the

regression equation:

$$X/M = AP + B$$

where "P" is the property in question, and "A" and "B"

are the coefficients. The most important coefficient to be

determined in these regressions is the linear correlation

coefficient, R, which is a measure of how well the two

variable are linearly correlated. (The value of R ranges

from -1 to +1, with values of $R \approx 0$ indicating negligible

correlation, and R = 1 indicating "Perfect" linear correl-

ation between the two variables). Table 44 presents the

resulting linear correlation coefficients (R) from these

regressions (the regression coefficients "A" and "B" are not

given since these are not pertinent to this discussion, and

furthermore, are only valid for the particular sorbents used

in this research) for high fusion low power Militant flyash.

Results indicate the following:

(A) <u>Aromatics</u>. The following physical properties of the

hydrocarbon compound such as polarizability, molar volume

and parachor showed a strong correlation (R > 0.94) with the

adsorption capacity, X/M, of flyash. This indicates that

each of the above physical properties have sighnificant

roles during the sorption process. Molecular weight of the

Table 44. Correlation Coefficients (R) for Regressions of X/M (Flyash) versus u, α, M, $\bar{v}$, P.

Functional Group	X/M versus				
	u	α	M	$\bar{v}$	P
Alcohols	-0.47	0.84	0.85	0.82	0.84
Ketones	0.80	0.98	0.98	0.91	0.92
Aldehydes	0.76	0.99	0.99	0.99	0.99
Aromatics	-0.89	0.95	0.71	0.97	0.94

u = Dipole moment, Debye

α = Electronic Polarizibility

M = Molecular weight

$\bar{v}$ = Molar volume

P = Parachor

hydrocarbon compounds established a relatively poor (poor with respect to polarizability, molar volume and parachor) correlation (R = 0.71) with X/M which reveals that during the adsorption of aromatic hydrocarbons onto flyash, molecular weights of the compounds do have some effect on the adsorption mechanisms but not as significant as polarizability, molar volume and parachor. The dipole moment of the hydrocarbon compounds established an inverse correlation (R = - 0.89) with the adsorption capacity of flyash.

(B) Aldehydes. Polarizability, molecular weight, molar volume and parachor each of the physical properties of the Aldehyde compounds established a strong correlation (R = 0.99) with the adsorption capacity of flyash. The correlation coefficient of the dipole moment (u) with X/M (R = 0.76) indicates that the influence of the dipole moment during the adsorption of Aldehyde compounds onto flyash is not that significant in comparison to the compound's other properties.

(C) Ketones. The same type of result was observed in this case also, as was the case of Aldehyde compounds. The influence of the compound's polarizability, molecular weight, molar volume and parachor on the adsorption capacity of flyash is very clear in this case also. Each of the above physical properties of Ketones established a correlation coefficient greater than 0.90, whereas a relatively poor (poor with respect to the other physical properties) correlation was observed (R = 0.80) between the compound's

dipole moment and the adsorption capacity of flyash (X/M).
(D) Alcohols. The dipole moment could not establish a
strong correlation (R = -0.47) with the adsorption capacity
of flyash in this case also, which indicates that the
sorptive property of flyash is independent of the compound's
dipole moment. Results also reveal that the polarizability,
molar volume, molecular weight and parachor, each of the
compound's physical properties, influence the sorption
process (adsorption of Alcohols onto flyash) to some extent
but not that significant as was observed in the case of
Ketones, Aldehydes and Aromatics compounds.

Solubility/octanol-water partition coefficient (K_{OW}) is
another important physical property of the organic compound.
Hence, it was felt necessary to evaluate the influence of
the above property on the adsorption capacity of flyash.
Data are summarized in Table 45. The solubility-amenability
correlation was observed in all cases. As solubility of
the organic compound decreases a corresponding increase in
amenability is noted. Table 47 shows that the octanol-water
partition coefficient (K_{OW}) of Alcohols and Aromatic hydro-
carbons established a strong correlation (R > 0.97) with the
adsorption capacity of flyash. The regression coefficient
(between K_{OW} and X/M) obtained during the adsorption of
Ketones onto flyash was in the order of 0.80. The K_{OW} value
for Aldehyde compounds are not available, hence it was not
possible to calculate the regression coefficient in this
case. However, it is clear from the available data (Tables
44 and 47) that the octanol-water partition coefficient of

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Table 45. Effect of Solubility and Partition Coefficient (Octanol-water system) on the Sorptive Property [75](Leo, et.al., 1971)

Compound	Solubility (%)	K_{ow}	X/M(ug/g) @ 30 mg/l for FlyAsh	X/M(mg/g) @ 30 mg/l for Acti Carbon
Methanol	∞	0.22	52	12
Ethanol	∞	0.48	68	24
Propanol	∞	2.18	90	30
Butanol	7.7	7.60	176	48
Isopropanol	∞	0.70	67	40
Sec-Butanol	12.5	4.07	136	44
Acetone	∞	0.58	89	23
MEK	26.8	3.22	105	40
MIBK	1.90	29.20	186	52
Cyclohexanone	2.5	6.45	168	47
Formaldehyde	∞	n.a	127	47
Acetaldehyde	∞	n.a	236	60
Butyraldehyde	7.1	15.14	447	66
o-Xylene	0.017	589.50	682	97
Phenol	6.0	28.86	361	65
m-Cresol	0.50	91.20	447	76
Ethylbenzene	0.015	660.00	645	89

n.a = not available

Table 46. Correlation Coefficients (R) for Regressions of X/M (Activated Carbon) versus u, , M, v, P.

Functional Group	X/M versus				
	u	α	M	$\bar{v}$	P
Alcohols	-0.76	0.97	0.97	0.97	0.96
Ketones	-0.53	0.97	0.95	0.91	0.92
Aldehydes	0.95	0.88	0.92	0.94	0.92
Aromatics	-0.87	0.92	0.70	0.94	0.90

Table 47. Correlation Coefficients (R) for Regressions of X/M (Activated Carbon) versus K_{ow}

Functional Group	Regression Coefficient (R)	
	Flyash	Activated Carbon
Alcohols	0.99	0.76
Ketones	0.80	0.73
Aldehydes*	not available	not available
Aromatics	0.97	0.92

* Octanol-water partition coefficient (K_{ow}) values are not available

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the compound has more significant effect than the molecular weight during the adsorption of Alcohols and Aromatic hydrocarbons onto flyash. Exactly the opposite result was observed in the case of Ketones where the influence of molecular weight is more than that of octanol-water partition coefficient.

The correlation coefficients (R) for regression of adsorption capacity (X/M) versus various properties (u, α, M, $\bar{v}$, p) of "target" compounds for activated carbon are presented in Table 46. The data followed the same trend as was observed in the case of flyash except for the Alcohol compounds. In this case, (Adsorption of the Alcohols onto activated carbon) a strong correlation was observed between X/M and polarizability, molecular weight, molar volume and parachor. (R $>$ 0.95 in each case). Polarizability, molar volume and parachor showed a strong correlation with X/M in the case of Aromatics. The adsorption capacity (X/M) of activated carbon on the Aldehyde compounds seems to be influenced very much by the compound's dipole moment (u) since it (dipole moment) shows a strong correlation (R = 0.95) over polarizability (R = 0.88). X/M also showed a fairly good/ acceptable correlation with polarizability, molecular weight, molar volume and parachor during the adsorption of the Ketones onto activated carbon.

The octanol-water partition coefficient (K_{ow}) of the Aromatic hydrocarbons established a strong correlation (R = 0.92) with the adsorption capacity of activated carbon

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whereas relatively poor correlations were observed
(R < 0.75) in the case of Alcohols and Ketones (Table 47).
Results also indicate that the octanol-water partition
coefficient predominates over the molecular weight during
the adsorption of Aromatic hydrocarbons onto activated
carbon, whereas the influence of molecular weight is more
significant than that of octanol-water partition coefficient
in the case of adsorption of Alcohols and Ketones onto
activated carbon.

5.9 DETERMINATION OF SORPTION THERMODYNAMIC PROPERTIES (FREE ENERGY, ENTHALPY AND ENTROPY) AND DISCUSSION OF PROBABLY SORPTION MECHANISM

Adsorption is normally an exothermic process. Thus the
extent of adsorption generally decreases with increasing
temperature. Heat of gas-phase adsorption is generally
higher than liquid (water) phase adsorption, because water
is desorbed from the surface when adsorption from aqueous
solutions occur. Thus, the heat effects for the latter
process are somewhat smaller than those for gas-phase
adsorption. However, one of the objectives of this research
is to determine the influence of some fundamental thermo-
dynamic properties (such as free energy, enthalpy and
entropy) on adsorption and also to correlate this data with
that obtained from activated carbon adsorption processes.

(1) Calculation of Free Energy (ΔG^o)-

Free energy has been calculated using Gibb's Equation -

$$\Delta G^O = -RT \ln k$$

where:

ΔG^O = free energy in cal/Mol

R = universal gas constant, 1.987 $\dfrac{Cal}{Mol\ ^OK}$

T = temperature, ^OK [273 + ^OC = ^OK]

K = Freundlich isotherm constant/capacity-parameter

(2) Calculation of Enthalpy/Heat of Adsorption

Using VantHoff's Equation -

$$\ln k = - \frac{\Delta H^O}{RT} + constant$$

The slope $(-\Delta H^O/R)$, obtained from the plot of $\ln k$ and 1/T, helped to find ΔH^O value.

Where:

ΔH^O = enthalpy/heat of adsorption

R = Universal gas constant, R = 1.987 $\dfrac{Cal}{Mol\ ^OK}$

T = temperature, ^OK

(3) Calculation of Entropy

Entropy has been calculated using -

$$\Delta S^O = \frac{\Delta H^O - \Delta G^O}{T}$$

where:

ΔS^O = entropy, cal/Mol.^OK

ΔH^O = enthalpy, cal/Mol

ΔG^O = free energy, cal/Mol

T = temperature, ^OK

Adsorption isotherm study was conducted on the following organic compounds at 50° C:

o-Xylene, Methyl Isobutyl Ketone, Butyraldehyde,

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Butanol, Phenol and Aniline. The experimental procedure was exactly identical as that which was followed during the isotherm study at 20°C. Table 48 shows that Freundlich isotherm capacity parameter, i.e. K values obtained at 50°C are lower than that obtained at 20°C. The adsorption intensity parameter, i.e., $1/n$ values remain almost unchanged. Consequently, the overall adsorption capacity of flyash decreased at 50°C, when compared with that of at 20°C. Hence, it appears that the adsorption of organics onto flyash is an exothermic process as was expected.

The relatively low values for the sorption free energies and enthalpies determined in this research (Table 50) are the characteristics of the weaker physical sorption forces (e.g. van der Waals-London, ion-dipole, and ion-induced dipole interaction), and therefore chemisorption of these compounds with flyash as well as activated carbon can be ruled out. The probable adsorption mechanism(s) observed in this research are:

    a)   van der Waals-London forces

    b)   ion-dipole and ion-induced dipole forces

A) Van der Waals-London Forces

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

    1)   dipole - dipole

    2)   dipole - induced dipole

    3)   induced dipole - induced dipole

The last interaction is usually known as the London or

Table 48. Effect of Temperature on Freundlich Isotherm Parameter. Militant (c = 1.52%) flyash used as sorbent .

Compound	Temperature = 20°C		Temperature = 50°C	
	K(ug/g)	1/n	K(ug/g)	1/n
o-Xylene	31.11	0.908	26.50	0.900
Methyl Isobutyl Ketone	20.42	0.650	18.20	0.587
Butyraldehyde	65.22	0.566	57.50	0.450
Butanol	15.74	0.709	14.25	0.653
Phenol	31.19	0.720	28.00	0.600
Aniline	18.69	0.960	16.70	0.920

Table 49. Effect of Temperature on Freundlich Isotherm Parameter (Activated Carbon Used as Sorbent).

Compound	Temperature = 20°C		Temperature = 50°C	
	K (mg/g)	1/n	K (mg/g)	1/n
o-Xylene	12.55	0.600	6.50	0.580
Methyl Isobutyl Ketone	6.80	0.602	4.00	0.600
Butyraldehyde	9.200	0.582	7.20	0.560
Butanol	5.067	0.660	3.50	0.620
Phenol	8.082	0.615	5.00	0.58

Table 50. Heat of Adsorption.

SORBENT: High Fusion, Low Power Militant Flyash

Compound	ΔG^O (KCal/Mol) $= -RTlnK*$	ΔH^O (KCal/Mol) $= (Slope)R$	$\Delta S = \dfrac{\Delta H^O - \Delta G^O}{T}$ $(10^{-3}, KCal/Mol.^{O}K)$
o-Xylene	-2.002	-0.800	4.103
MIBK	-1.757	-0.720	3.539
Butyraldehyde	-2.432	-0.782	5.632
Butanol	-1.605	-0.620	3.362
Phenol	-2.003	-0.672	4.543
Aniline	-1.704	-0.745	3.300

* Using K value at $20^{O}C = 293^{O}K$

Table 51. Heat of Adsorption.

SORBENT: Activated Carbon

Compound	$\Delta G^O = -RTlnK$ (KCal/Mol)	$\Delta H^O = (Slope)R$ KCal/Mol	$\Delta S^O = \dfrac{\Delta H^O - \Delta G^O}{T}$ $(10^{-3}, KCal/Mol.^{O}K)$
o-Xylene	-5.49	-4.36	3.85
MIBK	-5.14	-3.51	5.56
Butyraldehyde	-5.31	-3.72	5.42
Butanol	-4.97	-2.45	8.60
Phenol	-5.24	-3.18	7.03

ΔG^O calculated using K at $20^{O}C = 293^{O}K$.

"dispersion" force.

The London interaction is present between all atoms and molecules in close proximity. The force originates from the oscillating motion of electrons in their orbitals around atoms/molecules, which results in an instantaneous dipole. The instantaneous dipole of one molecule/ atom will induce a synchronous dipole in a nearby molecule/atom, and an attractive energy will result. This energy, E(r), between two different atoms is given by the following expression:

$$E(r) = - \frac{3}{2} \frac{\alpha_1 \alpha_2}{\gamma^6 \left[\frac{1}{h\upsilon_1} + \frac{1}{h\upsilon_2} \right]}$$

where,

α_1, α_2 = polarizability of atoms 1 and 2, respectively.

r = distance between two atoms

υ_1, υ_2 = oscillating frequency of the electron-nucleus system for atoms 1 and 2, respectively

h = Plank's constant.

The dipole-dipole attractive interaction results when two polar molecules approach each other. The average dipole-dipole attractive interaction energy between two molecules is given by the following equation:

$$E(r) = - \frac{\mu_1^2 \mu_2^2}{24 \pi^2 \epsilon_0^2 \epsilon^2 K_B T \gamma^6}$$

where,

μ_1, μ_2 = dipole moment of molecules 1 and 2 respectively

ϵ_0 = permittivity in vacuum

ϵ = permittivity in medium

K_B = Boltzmann constant

T = Temperature

r = distance between the two atoms.

The dipole-induced dipole interaction results when a molecule with a permanent dipole moment is in the vicinity of another molecule (which may itself be polar or nonpolar). The first molecule will induce a dipole in the second, and an attractive force will result, whose average interaction energy is:

$$E(r) = -\frac{\mu_1^2 \alpha_2}{16\pi^2 \epsilon_0 \epsilon \gamma^6}$$

where the symbols have the meaning as given previously.

B) Ion-dipole and Ion-induced Dipole Forces.

The electric field surrounding an ion will cause an attractive force toward a polar molecule with an interaction potential given by:

$$E(r) = -\frac{z e \mu \cos\theta}{4\pi \epsilon_0 \epsilon \gamma^2}$$

where,

z = ion valance

e = electron charge

θ = angle between the dipole moment and an imaginary line connecting the ion with the polar molecule.

(The remaining terms have been previously defined).

An ion can also induce a dipole moment in a molecule which has no permanent dipole. The energy of this interaction is:

$$E(r) = -\frac{\alpha (ze)^2}{8\pi\epsilon_0\epsilon r^4}$$

where, (all the symbols have been previously defined).

As discussed in Section 5.8, the sorptive capacity (X/M) of flyash demonstrates better correlation with the polarizability (α) than their dipole moment (μ). This holds true for all the "target" compounds (Alcohols, Ketones, Aldehydes and Aromatics). Since α and μ are the only sorbate properties which enter into the fundamental equations of intermolecular forces, this finding tends to implicate that the following "induction" forces predominate over the other forces:

1)   Induce dipole - induce dipole or London (Dispersion) forces

2)   Ion-induced dipole force

3)   Dipole-indiced dipole force.

It has been observed also, in this research, that the residual carbon content of flyash plays a significant role during the sorption process (for details, see Section 5.6.1). Carbon is considered as a non-polar sorbent. With this explanation, flyash can also be considered as a non-polar sorbent. The major contribution (during flyash adsorption process) comes from the residual carbon content of flyash. As it has been mentioned at the beginning of this section, while discussing van der Waal's force of adsorption that the dipole-dipole attractive interaction results when two polar molecules approach each other which is directly proportional

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to the sorbate's dipole moment (μ). In other words, dipole-dipole intermolecular force predominates the system at that time which yields better correlation of X/M with μ. But in this research, μ always showed poor (poor with respect to α) correlation with X/M. The reason is due to the fact that flyash is a nonpolar sorbent and dipole-dipole interaction cannot predominate between polar-nonpolar systems. In order to predominate, it has to have a polar-polar system. Hence, the possibility of dipole-dipole interaction in this research can be ruled out.

The same reasoning can be applied in the case of "ion-dipole" interaction systems. Ion-dipole forces probably play an important role in the complexation of neutral and polar molecules with metal cations associated with the solid surface. It has been observed in this research that the adsorptive capacity of flyash depends primarily on its residual carbon content (for detail see Section 5.6.1), therefore the possibility of the association of metal cations with the sorbate molecules may be neglected and hence the ion-dipole interaction force.

In conclusion, the sorption of organic compounds onto flyash is believed to occur principally via the weak induction forces of London (dispersion), ion-induced dipole and/or dipole induced dipole. However, since the London and ion-induced dipole are typically much stronger than the dipole-induced dipole interaction [35]Laidler (1982), it is surmised that these two mechanisms (London and ion-induced dipole) are the ones primarily involved in this sorption

process.

5.10 FLYASH AS RESIDUAL CARBON

As discussed in Section 5.6.1, residual carbon content
of the flyash is primarily responsible for its organophilic
behavior. In order to check the validity of the above
conclusion, all the data (related to the flyash) has been
recalculated and expressed as the 'residual carbon' content
of flyash only. These data when compared to those of
activated carbon, indicate that they (data) are very much
comparable.

The sorbent used in the kinetic study was high fusion,
low power Militant flyash and activated carbon. The
residual carbon content of the flyash (Militant) was 1.52%.
When the data are expressed as "flyash" the overall rate
constant (in the case of average particle diameter, 0.150
mm) value is 0.058 per min. as indicated in Table 6 (20 g.
of flyash was used as sorbent material). However, if this
rate constant value is expressed as "residual carbon
content" of flyash only the value increases to 3.87 per min.
which is in the same order of magnitude with that obtained
from activated carbon. Table 52 reveals that the free
energy value, which indicates the affinity of sorbent
towards the sorbate, obtained from the activated carbon
adsorption process is close to the free energy value of the
flyash when expressed as residual carbon content only. The
data, obtained from each phase of the experiment using

flyash as sorbent material, of this dissertation when expressed as the "Residual Carbon Content" are very much comparable to that of activated carbon. These findings help us to arrive at the conclusion that although flyash is a heterogenous material, it behaves almost like homogenous sorbent material (activated carbon). This is because the adsorption onto flyash takes place due to the presence of residual carbon content.

5.11 DESORPTION STUDY OF SELECTED ORGANIC COMPOUNDS

One of the objectives of this research was to examine the desorption (leaching) characteristics of flyash. This was performed in a continuous column system. After the saturation of sorbent (i.e., after adsorption) the same was washed continuously with distilled water at ambient temperature (approximately 20°C) until the effluent concentrations reached trace/zero. The volume of the water passing through the column was continuously monitored. Effluent samples were analyzed using the Perkin-Elmer Model 900 Flame Ionization Detector Gas Chromatograph and LCI-100 Integrator.

Desorption studies of o-Xylene, Aniline, Methyl isobutyl Ketone, Butyraldehyde and Butanol from high fusion Militant flyash indicate that the percent desorption of each of the organic compounds are very low (Table 53). Maximum desorption was observed in the case of Butanol (i.e., 5 %). o-Xylene and Aniline showed minimum desorption (less than

Table 52. Flyash as Residual Carbon versus Activated Carbon.

Compound	Free Energy (ΔG^O) Flyash (as carbon) u (KCal/Mol.)	Activated Carbon u (KCal/Mol.)
o-Xylene	-4.95	-5.49
MIBK	-4.21	-5.14
Butyraldehyde	-4.85	-5.31
Butanol	-4.08	-4.97
Phenol	-4.49	-5.24

Values calculated at 293° K = 20° C.

Table 53. Desorption Study

Compound	Adsorption Capacity of Militant Flyash (ug/g)*	Desorption (leaching) (ug/g)	% Desorp.
o-Xylene	820	1	< 0.5
Aniline	565	2.5	< 0.5
Methyl Isobutyl Ketone	220	7	3.20
Butyraldehyde	525	4	< 1.
Butanol	200	10	5

* Results are based on dynamic study. Influent concentration used, 30 mg/l.

0.5 %). Data also reveal that the desorption is inversely proportional to the heat of adsorption. This finding was not unexpected because o-Xylene and Aniline, both the organic compounds, indicated higher heat of adsorption (800 Cal/mol and 745 Cal/mol, respectively) than that of Butanol (620 Cal/mol). Heat of adsorption is the direct measure of bonding strength [32](Ruthven, 1984). Higher heat of adsorption signifies higher bonding strength between sorbate and sorbent and consequently lower desorption/leaching.

Identical experimental procedures were followed, as was performed in the case of flyash, during the desorption of o-Xylene, Butyraldehyde, Methyl isobutyl Ketone and Butanol from activated carbon. The results indicated that the desorption of each of the above organic compounds from activated carbon is trace/negligible.

SECTION VI

CONCLUSIONS, EXPECTED CONTRIBUTIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The major findings and conclusions of this research are as follows.

6.1.1. The free energies and enthalpies of adsorption of organic compounds onto flyash, obtained in this research, were very low. The sorption free energies determined ranged from about -1 to -3 KCal/mol; the enthalpies of adsorption ranged from -0.5 to -1.0 KCal/mol. These lower values indicate that the adsorption of organic compounds onto flyash are the characteristics of weak physical adsorption forces. Based on these results, adsorption via the chemisorption mechanism was ruled out.

6.1.2. The electronic polarizability (α) of the compound established stronger correlations with the adsorption capacity of flyash than compound's dipole moment (μ). This suggests that the following induction-type of intermolecular forces are primarily responsible for the adsorption of organics onto flyash -

    a)   dispersion forces (induced-dipole, induced dipole)

    b)   ion-induced dipole forces

    c)   dipole-induced dipole forces.

6.1.3. The residual carbon content of flyash plays a very significant role during the adsorption process. It (carbon content) established a very strong correlation with the adsorption capacity than all other elemental oxides of flyash. Results demonstrate that the higher the residual

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carbon content, the better the removal.

6.1.4.   A near straight line fit, of the plot of ln (1 – $\frac{X_A}{X_{Ae}}$) versus time, was observed during the adsorption of o-Xylene onto flyash as well as onto activated carbon. This can be approximated to first order reversible kinetics.

6.1.5.   It has been established in this research that the following parameters influence the sorptive property:

a.   Washing of the material (flyash) by distilled water prior to its use improved the adsorption capacity.

b.   The adsorption capacity of flyash increased with increasing pH upto a certain range and then decreased with further increase in pH. The maximum adsorption was observed in the pH range 4.5 to 5.0.

c.   The study demonstrated that flyash favors adsorption of low water soluble compounds.

d.   The compounds' octanol-water partition coefficients (K_{ow}) established a strong correlation (R > 0.95) with the adsorption capacity indicates that the adsorption amenability increases, as the octanol-water partition coefficient of the compounds increases.

e.   The influence of compound's Parachor P. (which is a direct function of compound's molar volume and molecular weight) on the sorptive capacity of flyash is very clear. The compound's Parachor established a strong correlation (R > 0.90) with the adsorption capacity.

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f.   The rate of adsorption is an inverse function of the sorbent's (flyash) particle diameter.

6.1.6.   Individual compounds in the mixture are each adsorbed to a lesser extent when compared with their relative adsorbabilities in the single-solute tests. Results also indicate that the ultimate capacity of the sorbent is considerably less than that which would be predicted from summing the single component data. This indicates that there must be considerable interaction between the components adversely affecting their respective adsorbabilities. The competition among the solutes (for adsorption sites) increases as the number of solute in the system increases. Because of this high competition and interaction sorbent cannot make full utilization of its available adsorption sites and consequently its adsorption capacity goes down.

6.1.7.   The desorption/leaching of the organic species from flyash were relatively low. The percent desorption of the target organic compounds determined in this research ranged from about 0.5% to 5%, which indicates that the retentive capacity of flyash is quite significant.

6.1.8.   Comparative studies between activated carbon and flyash indicate that although the treatment efficiencies of the above two sorbent materials are not the same (activated carbon is about 200 fold higher than flyash), they closely follow the identical pattern. The data trend obtained from activated carbon studies were very much similar to that obtained from fly ash studies. This finding helps us to

arrive at the conclusion that the adsorption mechanisms and forces that take place during the adsorption of organic compounds onto flyash are identical to that of the activated carbon.

6.2 EXPECTED CONTRIBUTION

Sanitary landfilling is an engineered method of disposal that involves the spreading and compacting of waste into cells and covering it each day with earth in a manner that poses no threat to the public health or to the environment. But, the main problems in landfills are the production of leachate that may contaminate ground and surface water. These problems have been overcome to some extent by isolating the landfill site from its immediate soil surroundings by lining the base and sides of the landfill with compacted soil of low permeability. Polyvinyl chloride and butyl rubber liners have also been used for this purpose. This, however, creates drainage problems. This could be accomplished using gravity outlets such as drainage tiles or perforated corrugated metal pipe installed in the lowest portion or along the base of the landfill to remove and collect the leachate. Further treatment of the collected leachate would be required in most of the cases to reduce the pollutants to acceptable discharge levels. This can be achieved by percolating the collected leachate through a bed of inexpensive sorbent material. Results of this study demonstrate that isolation/immobilization of

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organic pollutants/contaminants is technologically feasible
using flyash. Hence, there is a possibility that the
desired level of pollutants can be achieved by treating the
leachate through flyash and thereby ground and surface water
contamination will be avoided.

Another possibility exists that flyash can be used as
an alternative treatment source for on-site groundwater
reclamation. The diversity and number of existing and
potential sources of groundwater contamination are quite
large. The sources can be categorized according to use or
by the method by which the pollutant is transferred to the
subsurface system. By far the most common aquifer restora-
tion measure is removal of the contaminated groundwater
followed by surface treatment and reinjection or discharge.
Although a wide variety of technologies exists, the treat-
ment options used for groundwater contamination are usually
limited to air stripping, carbon adsorption or biological
treatment for organic removal. Biological treatment process
is limited to biodegradable materials (organics) only. Air
stripping and carbon adsorption is an extremely effective
process but the high cost of these processes sometimes
limits their use. Data developed in this research indicate
potential use of flyash as an alternative treatment source.
However, further investigation and a detailed feasibility
study is required in order to use flyash in actual field
conditions. It is expected that the method developed here
will be used as a preliminary guideline for future exploration.

6.3 RECOMMENDATIONS

While this study has developed the sorbate character-
istics of flyash and adsorption mechanisms and forces that
take place during the sorption process, there are still many
other areas which need further investigation. Outlined
below are several areas that require additional research
efforts:

a) A project should be undertaken to improve the adsorp-
    tion capacity of flyash. Chemical pretreatment of
    flyash prior to its use may increase the sorptive
    capacity of the flyash. Another possibility is to add
    inorganic salts into the system and to use this as a
    useful tool to enhance the sorptive property of flyash.

b) By passing the dilute solution of the pollutant upward
    through a bed of sorbent at a velocity sufficient to
    suspend the solid particles (of the sorbent bed), the
    problem of increasing pressure drop can be eliminated.
    Also, when using sorbent of a smaller particle size in
    an expended bed, the adsorption capacity of the sorbent
    can be improved.

c) Details of leaching characteristics of flyash should be
    examined using "EP" Toxicity Procedures.

d) Based on the leaching study result, a scheme should be
    undertaken (if necessary) to investigate the stability
    and fixation (encapsulation) of the adsorbed compound
    using the following binding/fixing agents:

Cement based techniques

Lime and lime-based techniques

Thermoplastic based techniques

Organic polymer techniques

Glassification

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APPENDIX - 'A'

EFFECT OF pH ON ADSORPTION

Figure A.1. Effect of pH on Adsorption

Methanol onto Militant Flyash

Adsorption Capacity (ug/g)

pH
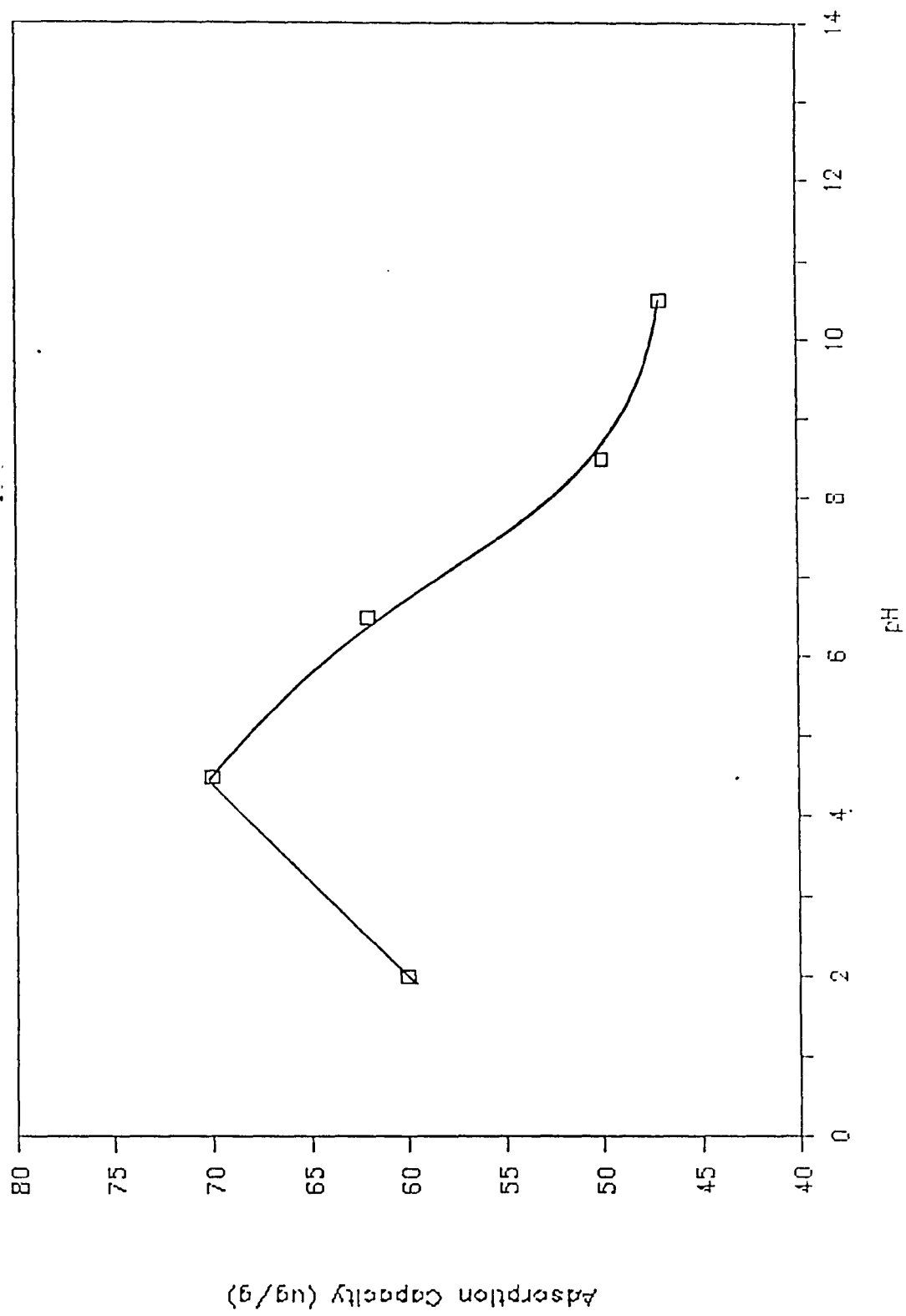
Figure A.2. Effect of pH on Adsorption

Ethanol onto Militant Flyash

A.2
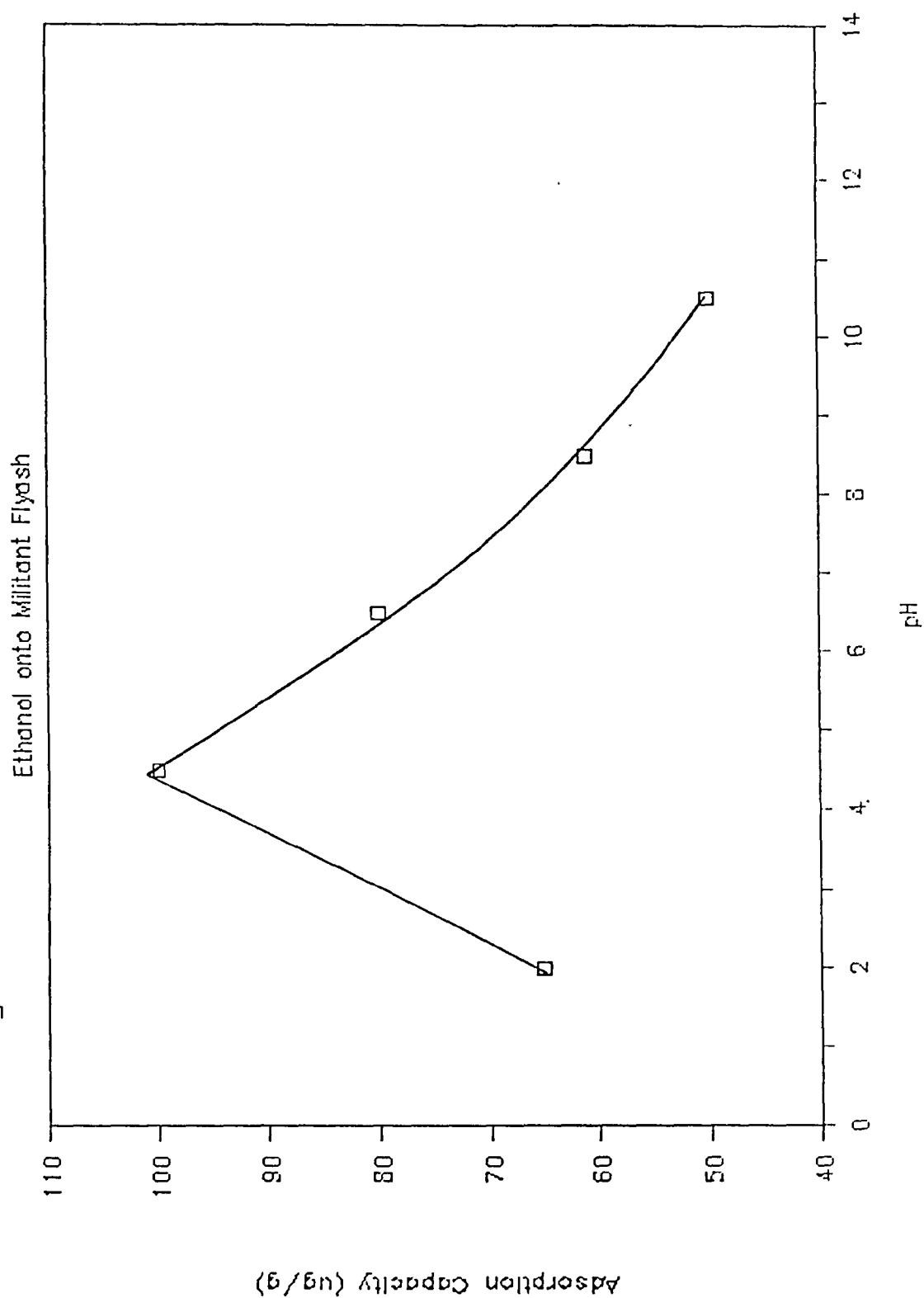
Figure A.3. Effect of pH on Adsorption

Propanol onto Militant Flyash
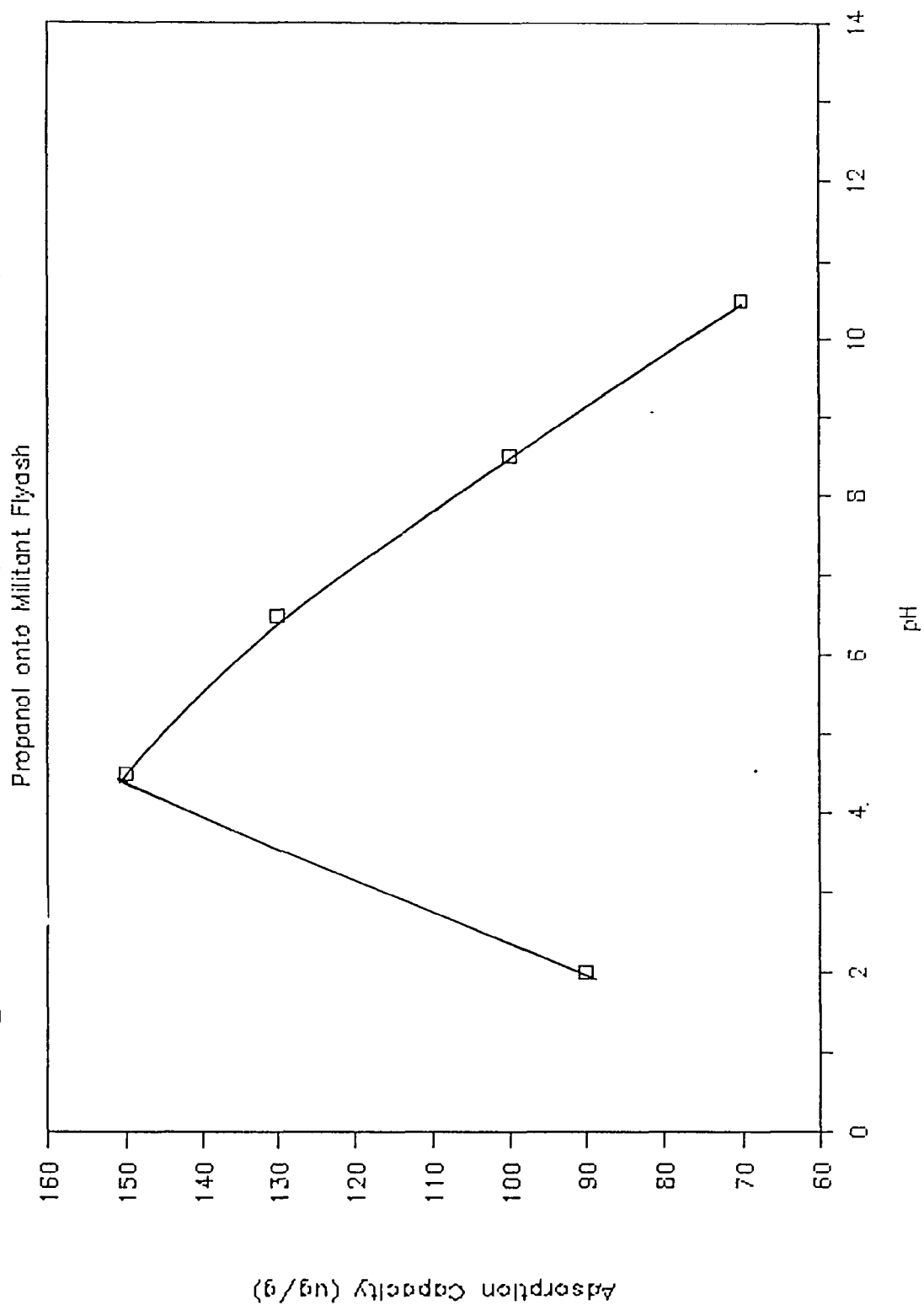
Figure A.4. Effect of pH on Adsorption

Butanol onto Militant Flyash

Adsorption Capacity (ug/g)

pH

A.4
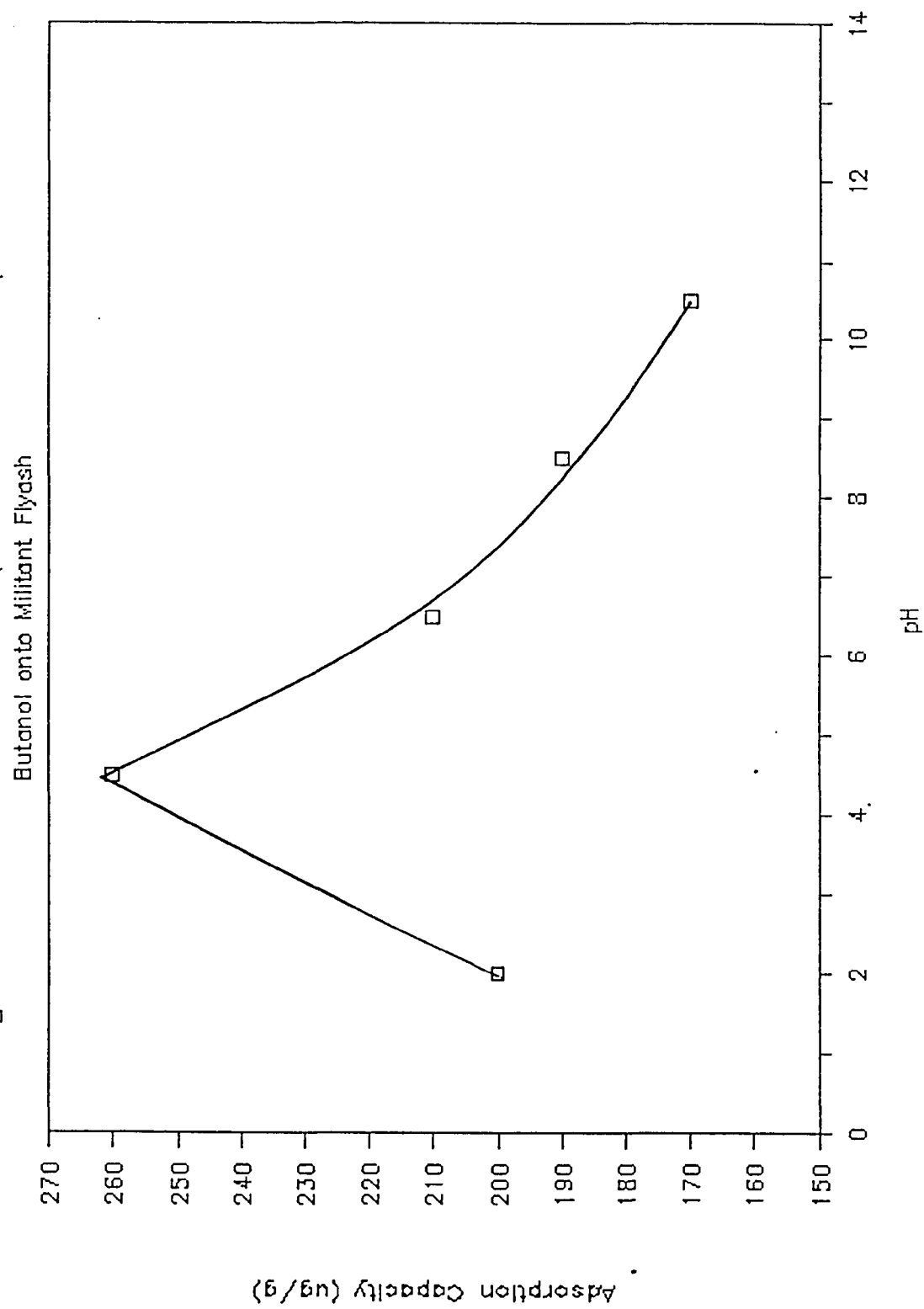
Figure A.5. Effect of pH on Adsorption

Acetone onto Militant Flyash

Adsorption Capacity (ug/g)

pH

A.5
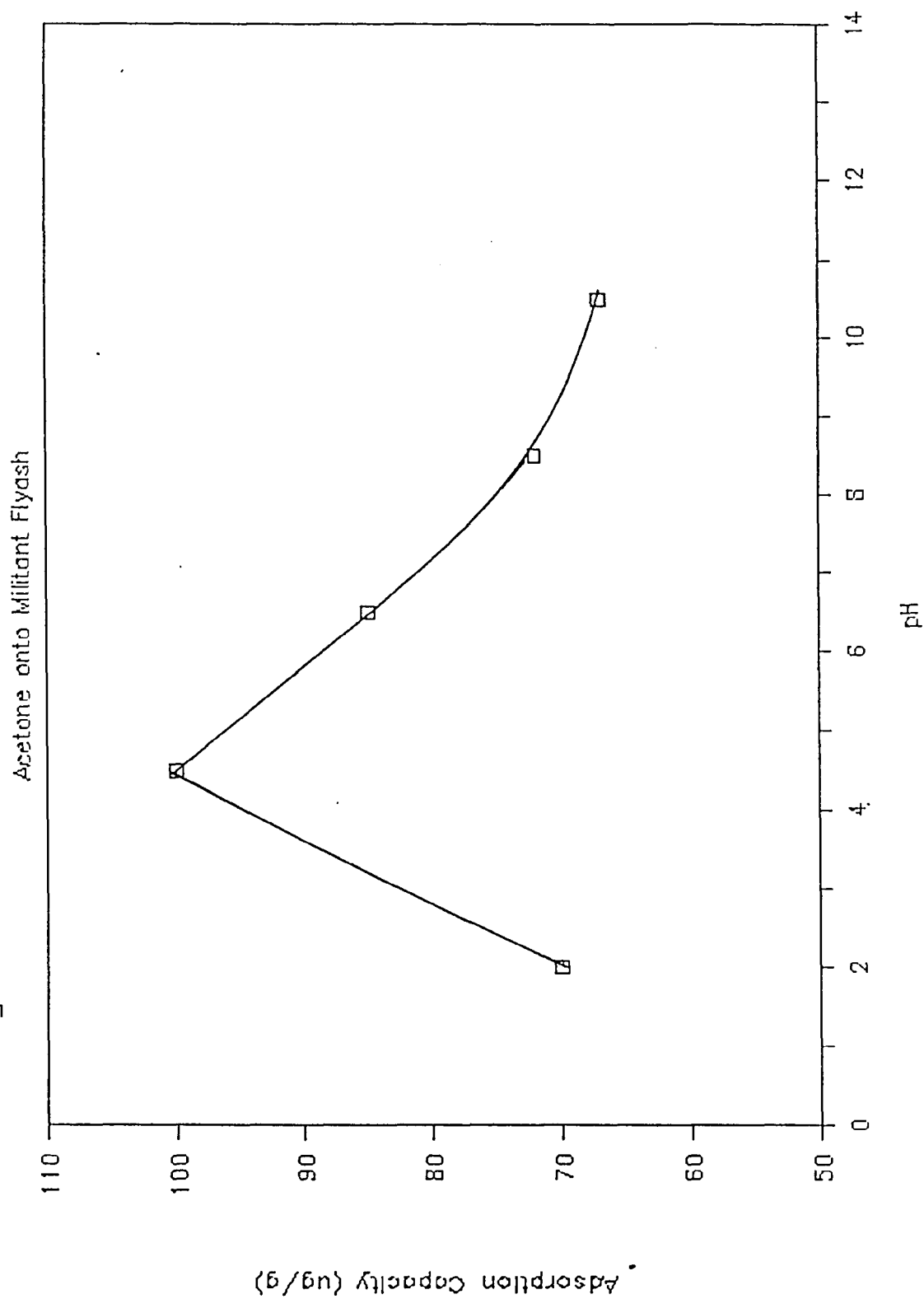
Figure A.6. Effect of pH on Adsorption

MEK onto Militant Flyash

A.6
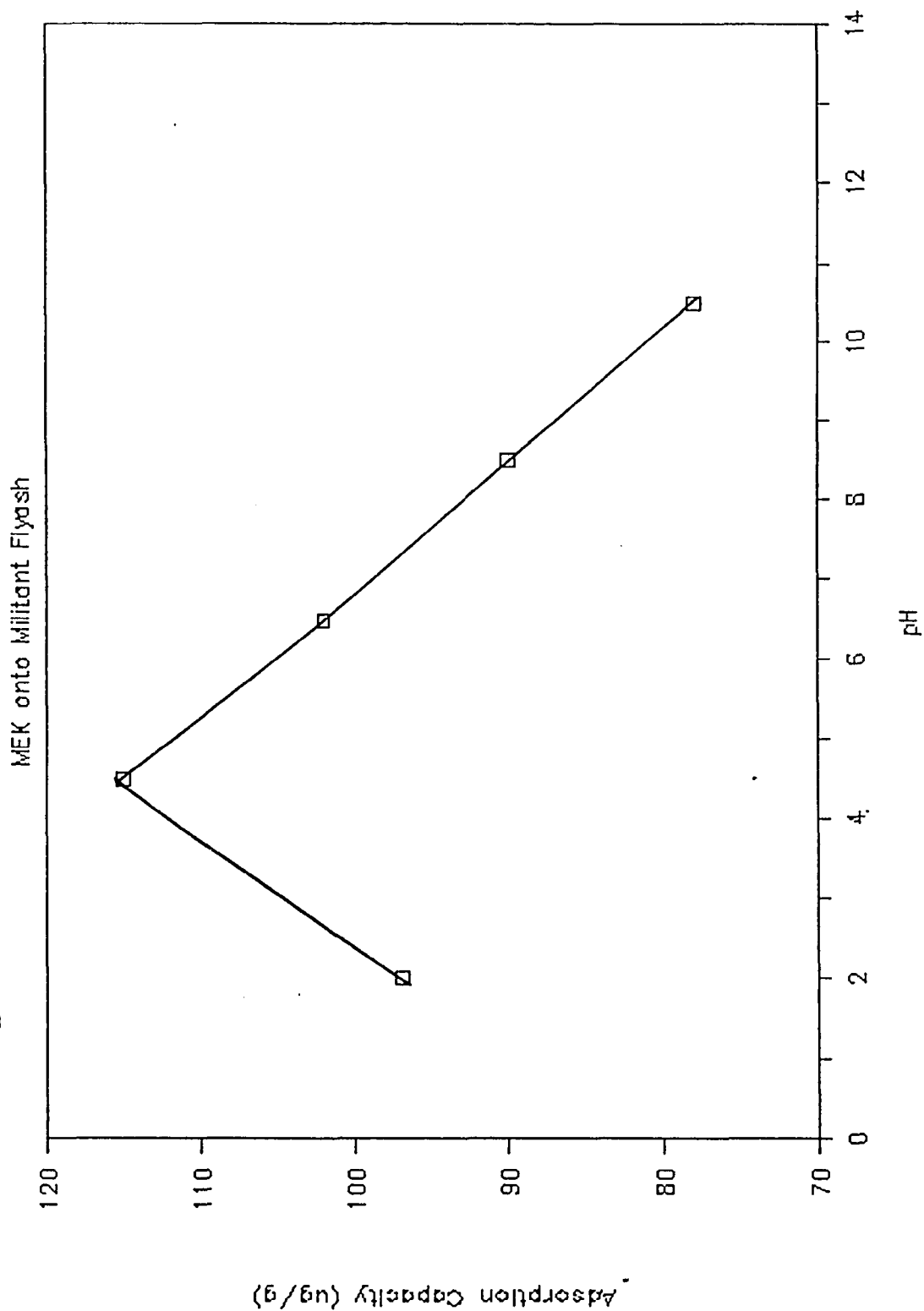
Figure A.7. Effect of pH on Adsorption

MIBK onto Militant Flyash

Adsorption Capacity (ug/g)

pH

A.7
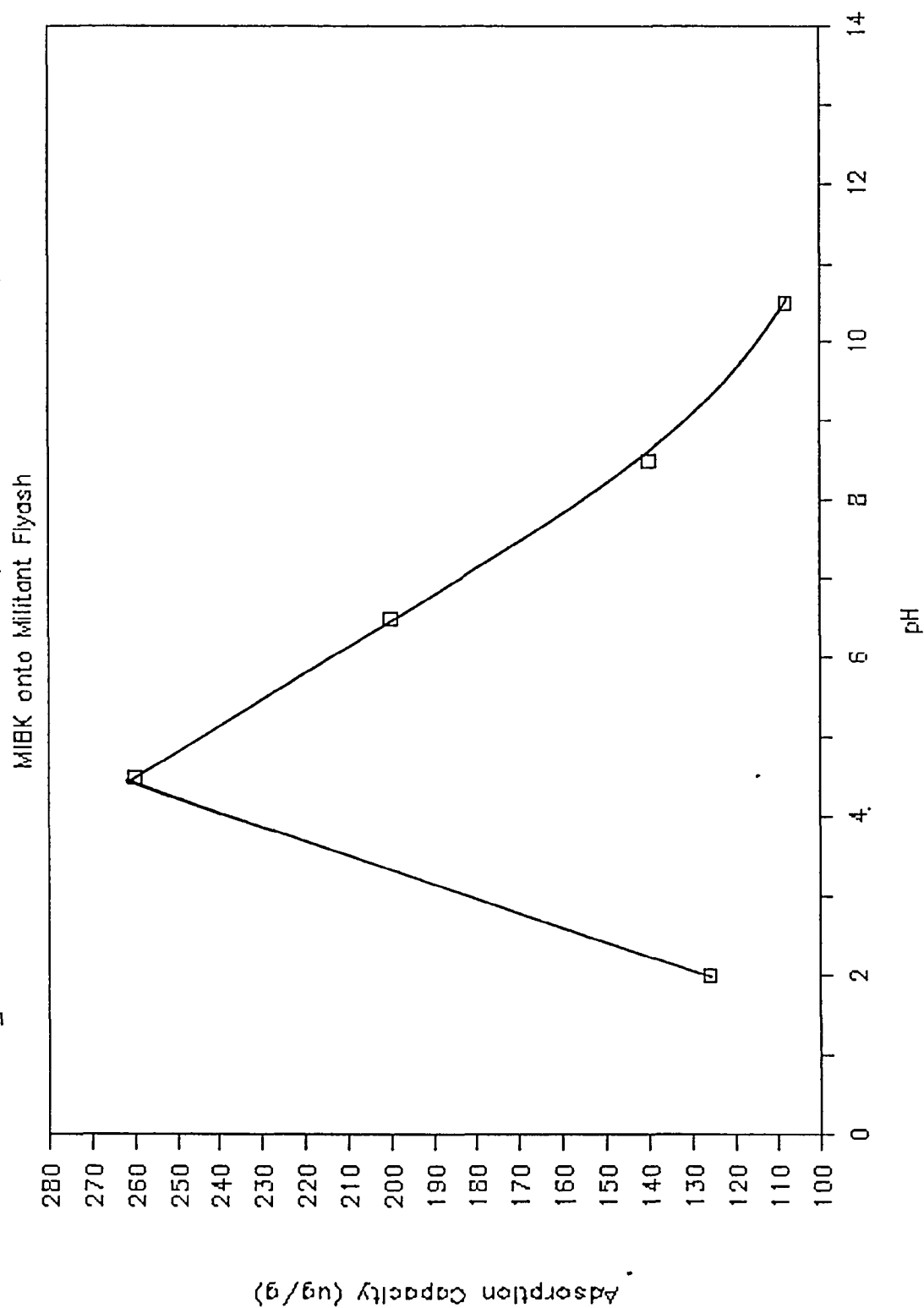
Figure A.8. Effect of pH on Adsorption
Cyclohexanone onto Militant Flyash

pH

Adsorption Capacity (ug/g)

A.8
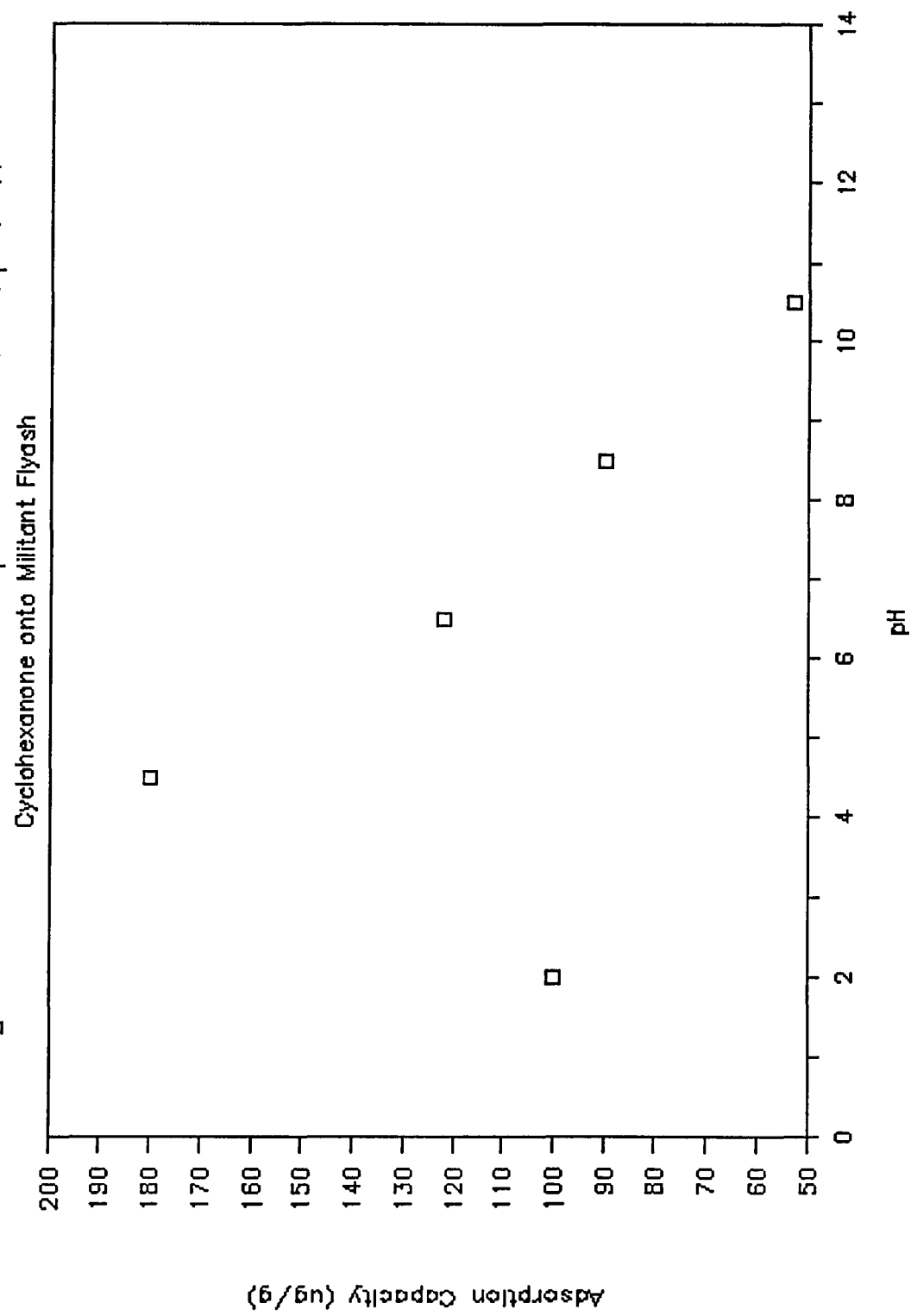
Figure A.9.Effect of pH on Adsorption

Formaldehyde onto Militant Flyash

Adsorption Capacity (ug/g)

pH

A.9
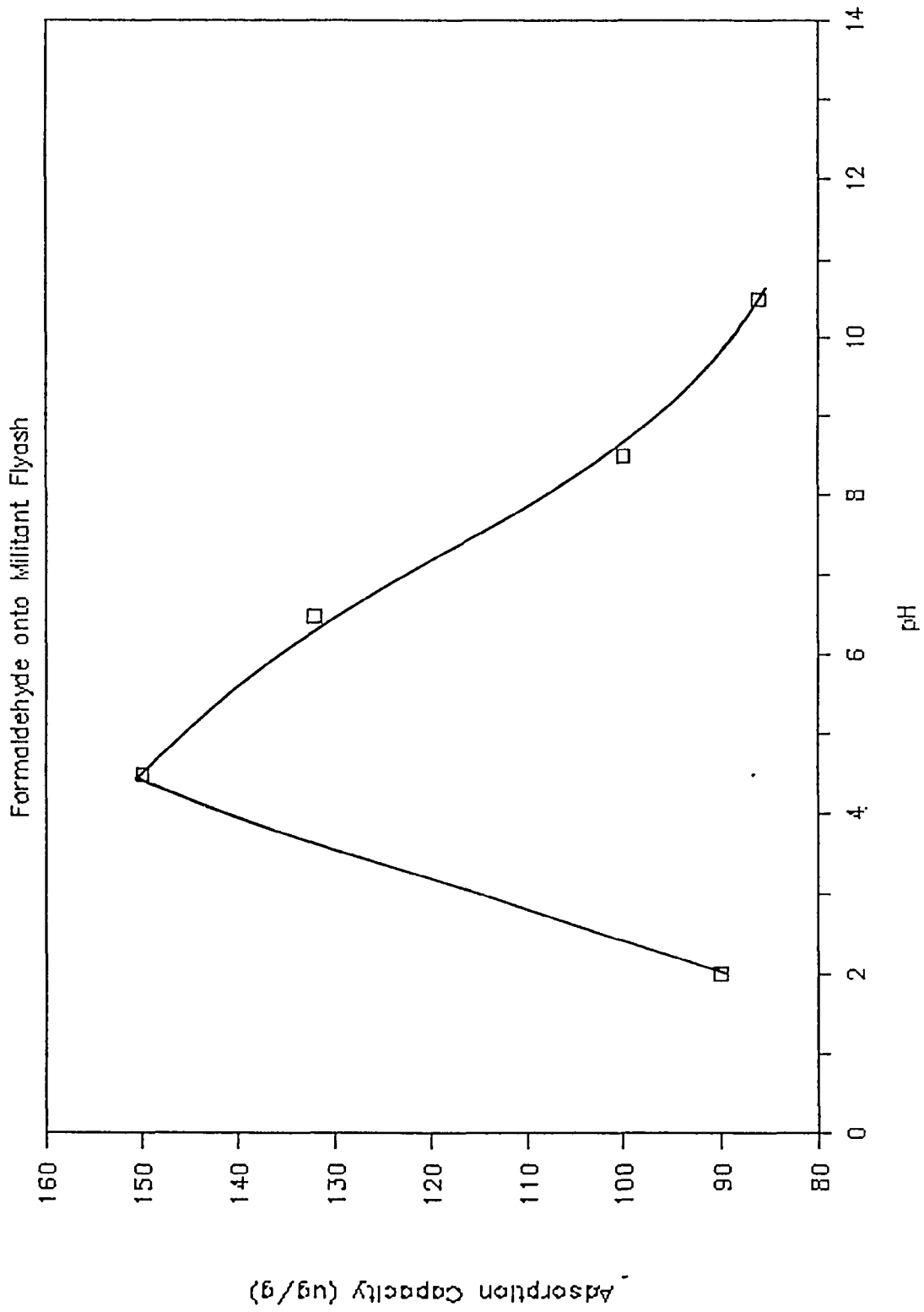
Figure A.10 Effect of pH on Adsorption
Acetaldehyde onto Militant Flyash
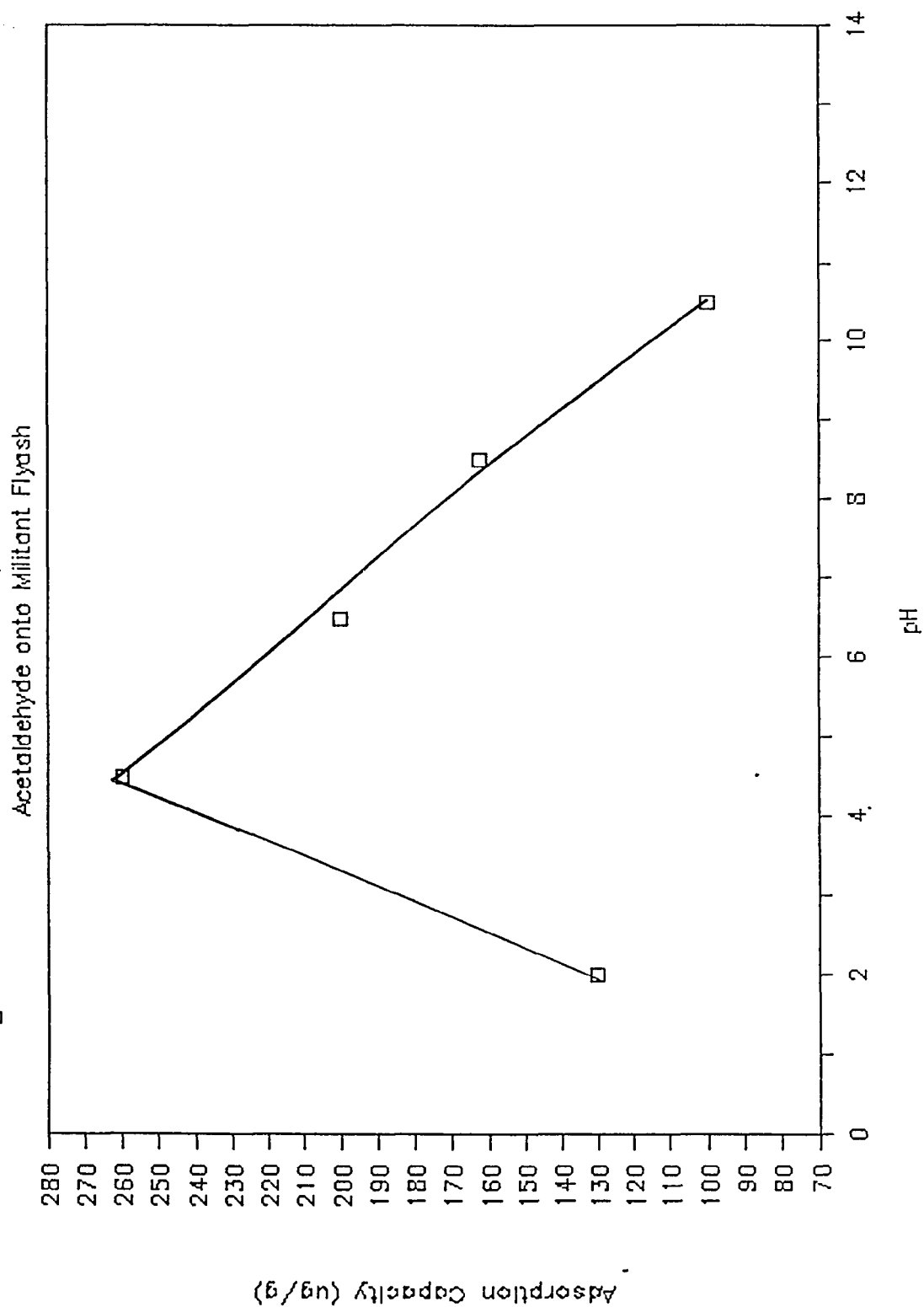
Figure A.11 Effect of pH on Adsorption
Butyraldehyde onto Militant Flyash

Adsorption Capacity (ug/g)

pH
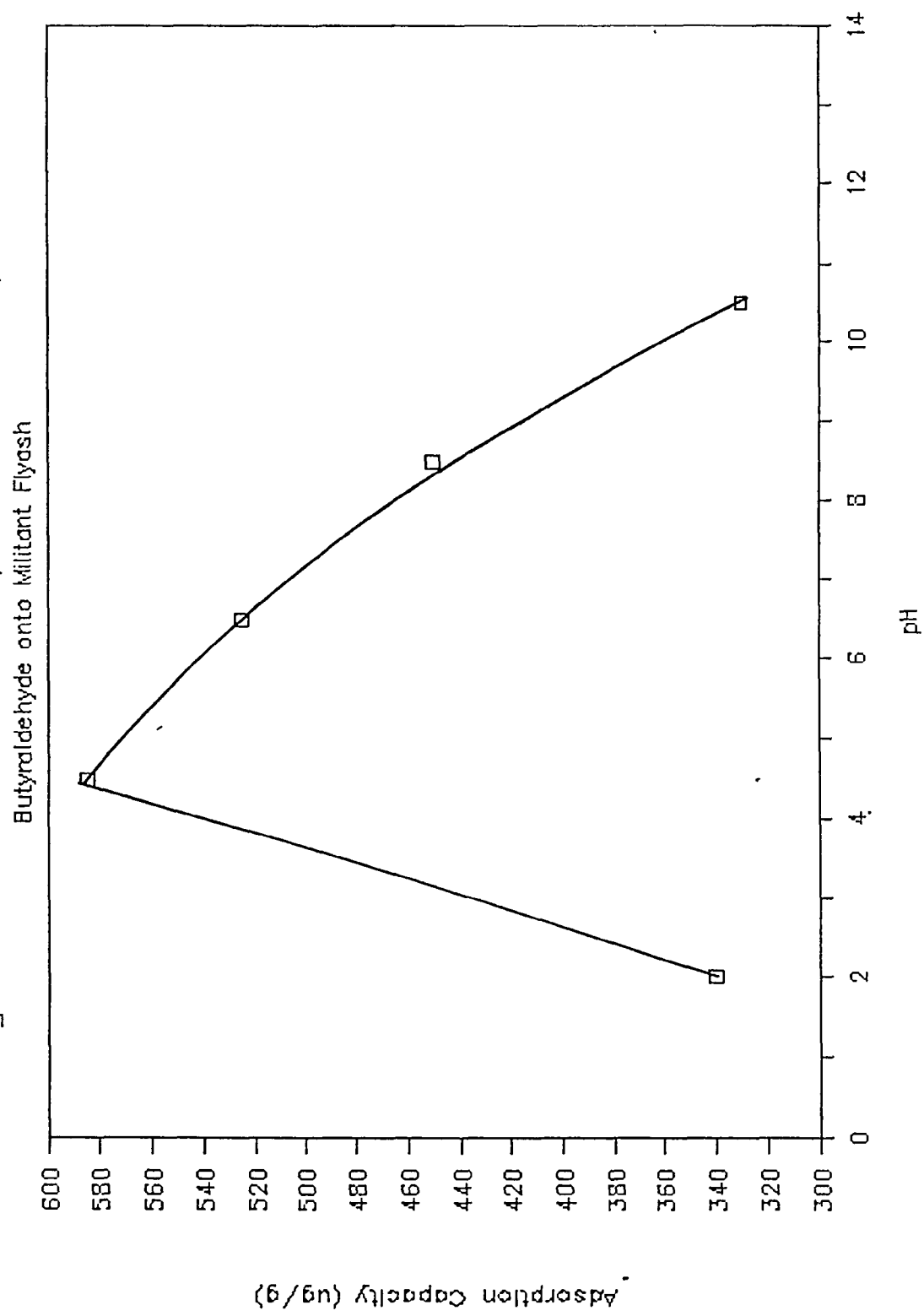
Figure A.12 Effect of pH on Adsorption
Aniline onto Militant Flyash

Adsorption Capacity (ug/g)

pH

A.12
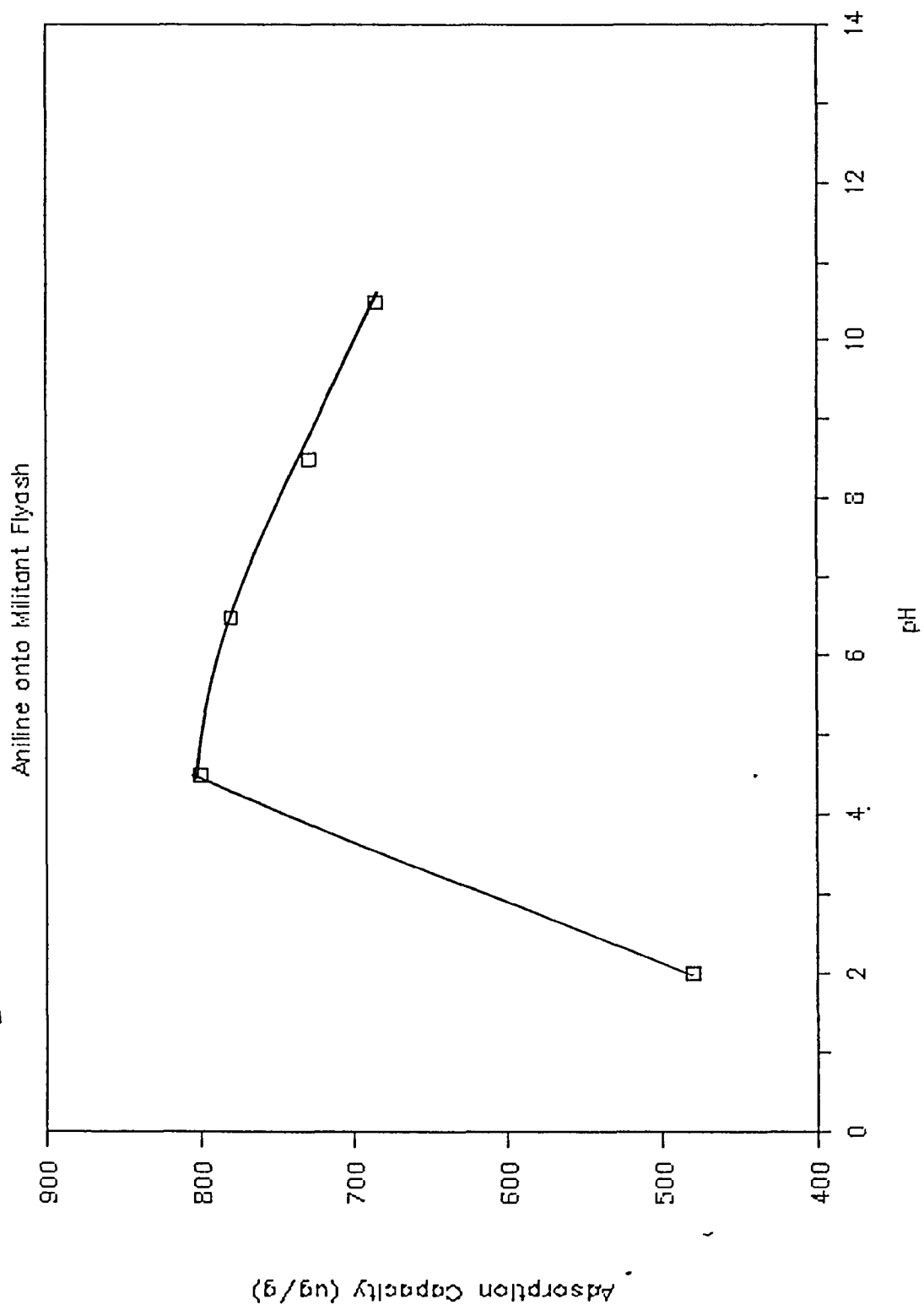
Figure A.13 Effect of pH on Adsorption

Phenol onto Militant Flyash

A.13
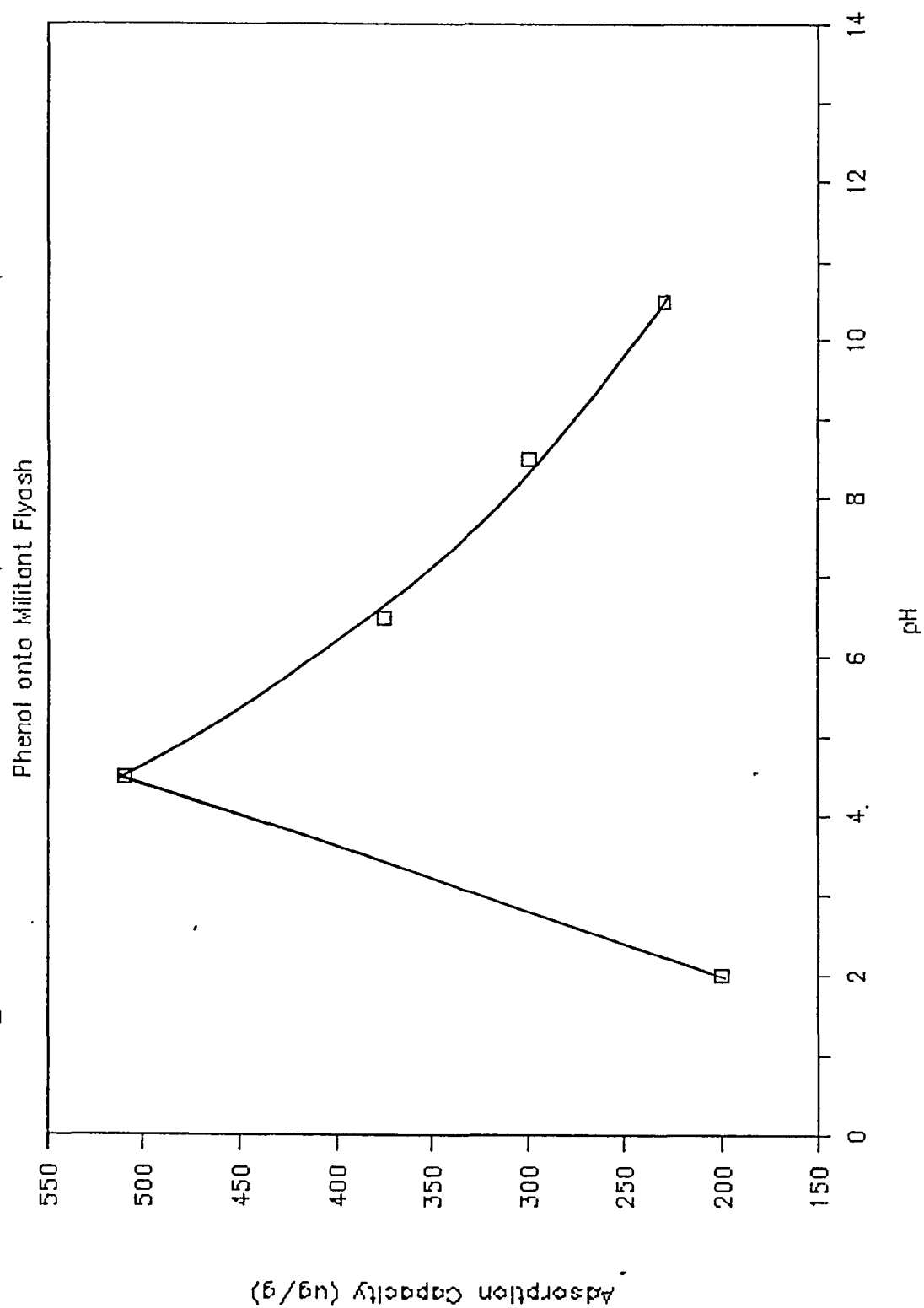
Figure A.14 Effect of pH on Adsorption

meta-Cresol onto Militant Flyash

pH

Adsorption Capacity (ug/g)

A.14
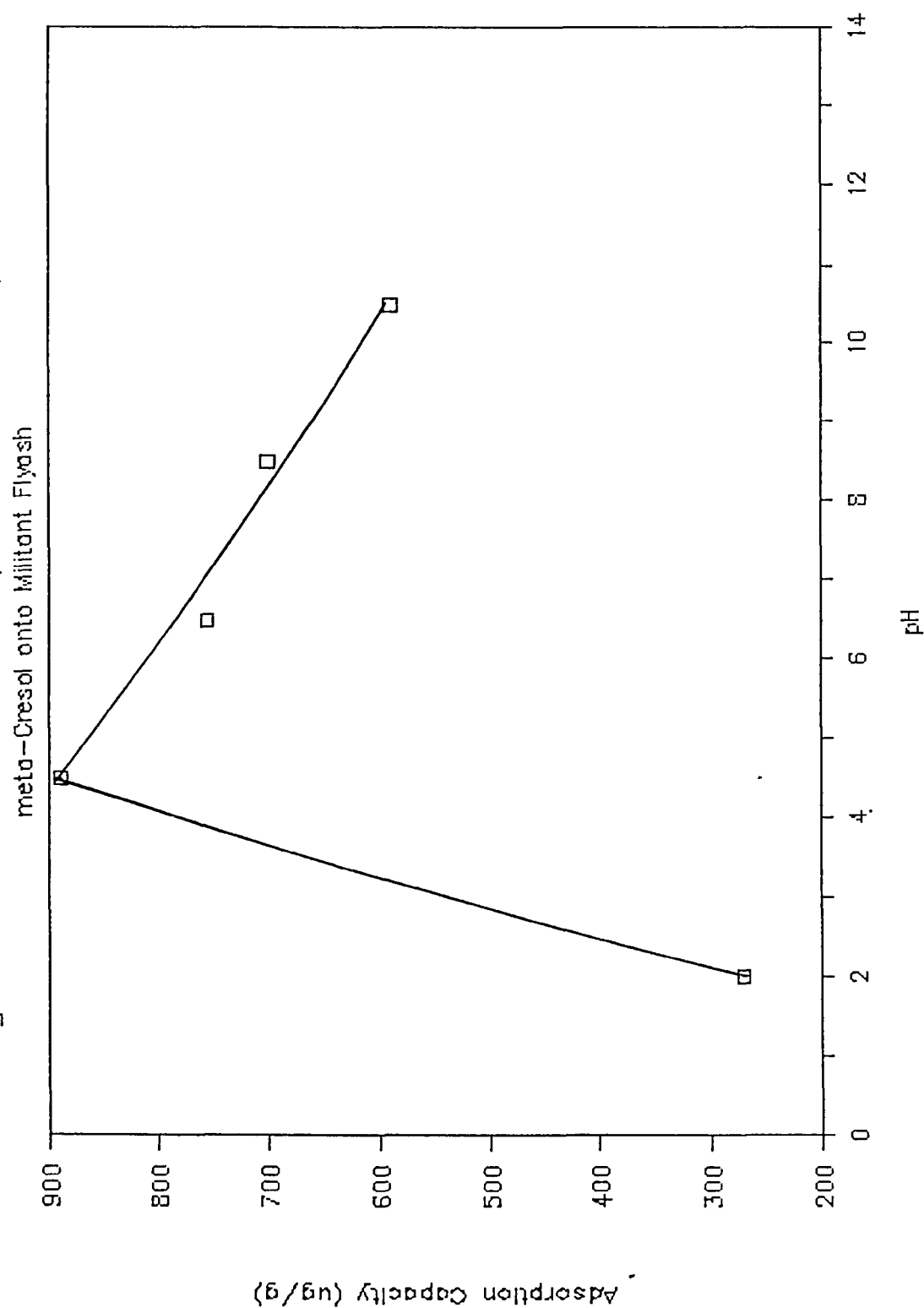
APPENDIX - 'B'

KINETICS OF ADSORPTION

Figure B.1.Kinetic Study

o-Xylene onto Militant (dia. 0.15mm)

Time (minutes)

Concentration Remaining (mg/L)

B.1
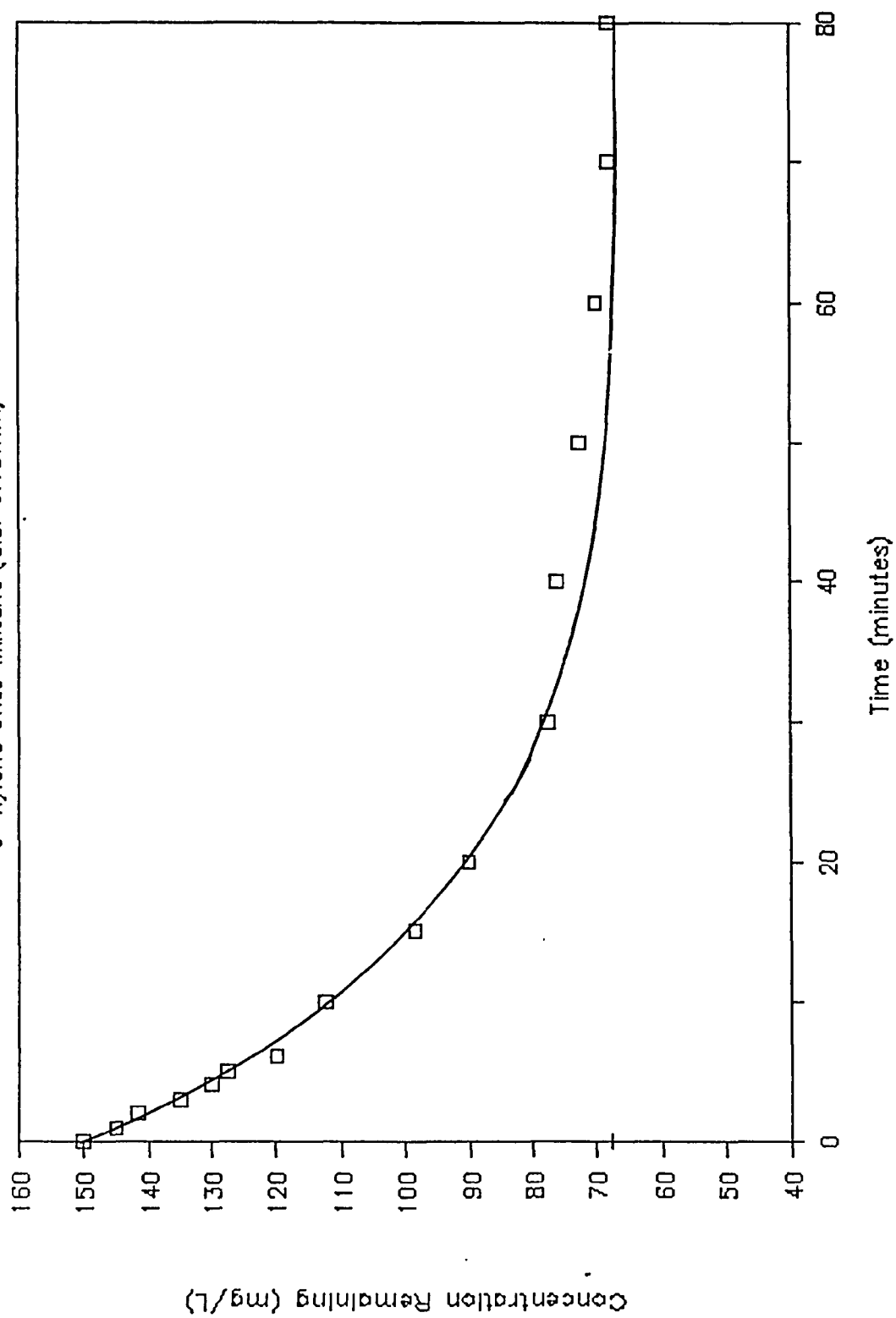
Figure B.2. Kinetic Study
o-Xylene onto Militant (dia. 0.075mm)

Concentration Remaining (mg/L)

Time (minutes)

B.2
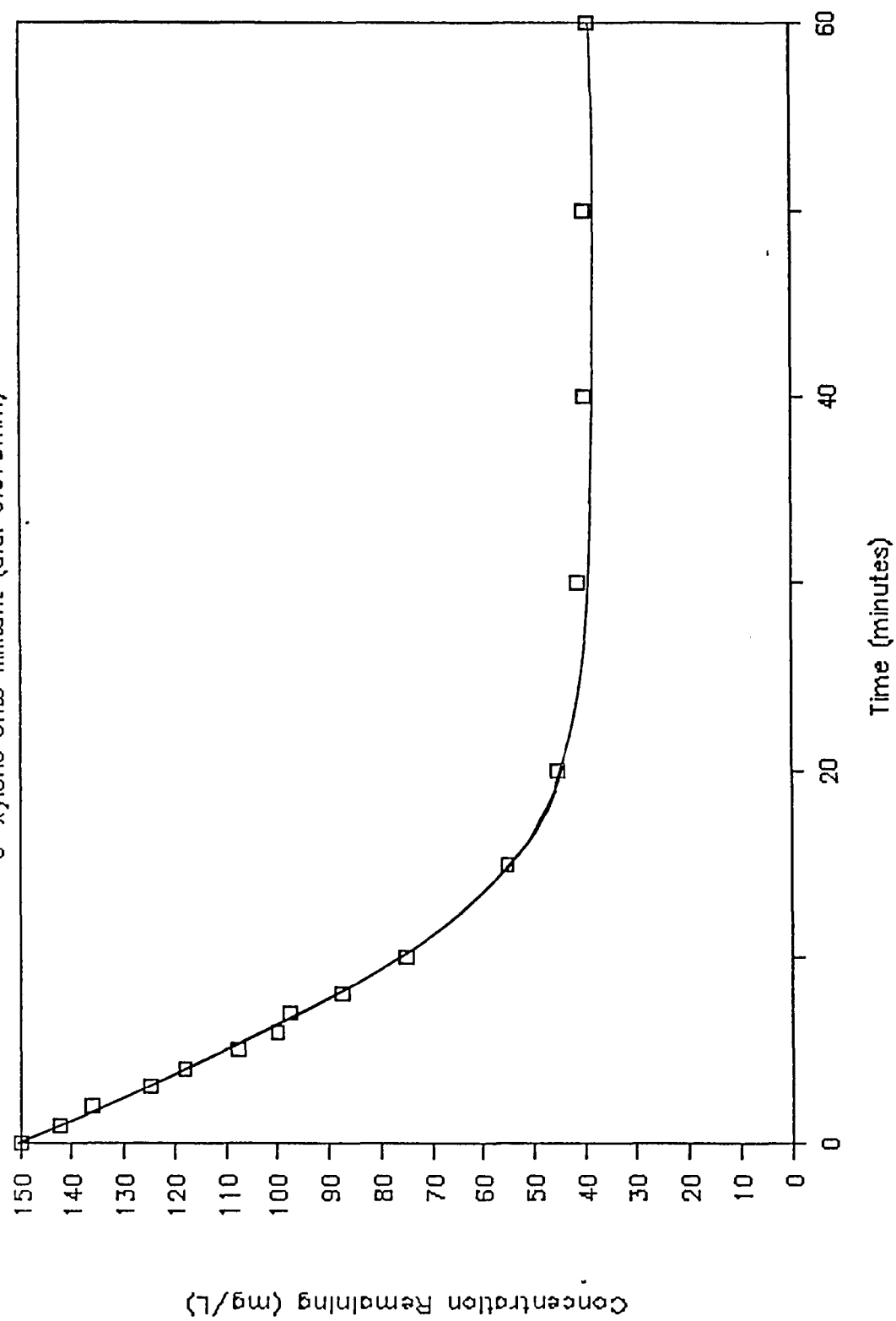
Figure B.3. Kinetic Study
o—Xylene onto Militant (dia. < 0.075mm)

Time (minutes)

Concentration Remaining (mg/L)

B.3
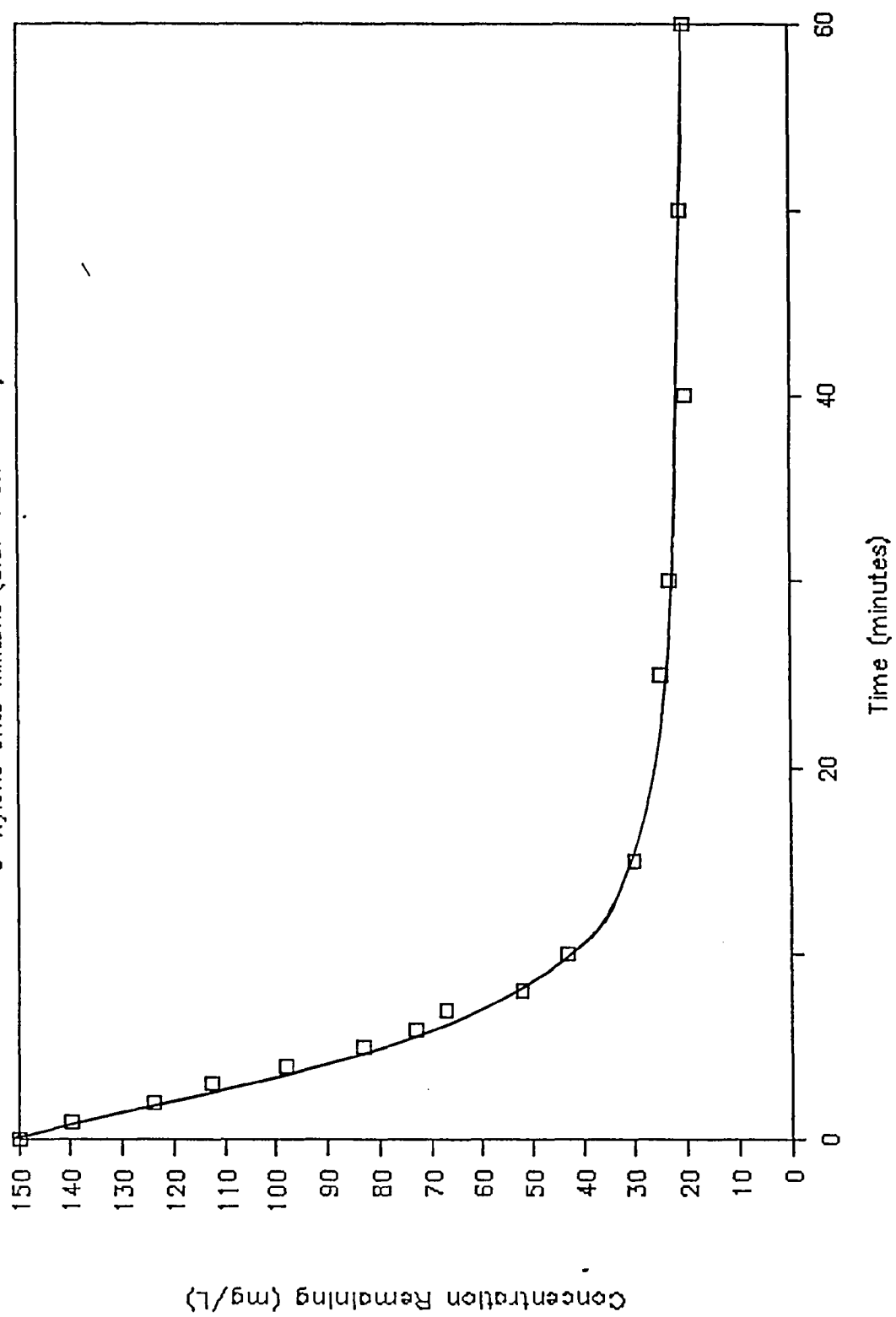
Figure B.4. Kinetic Study
o-Xylene onto Activated Carbon

B.4
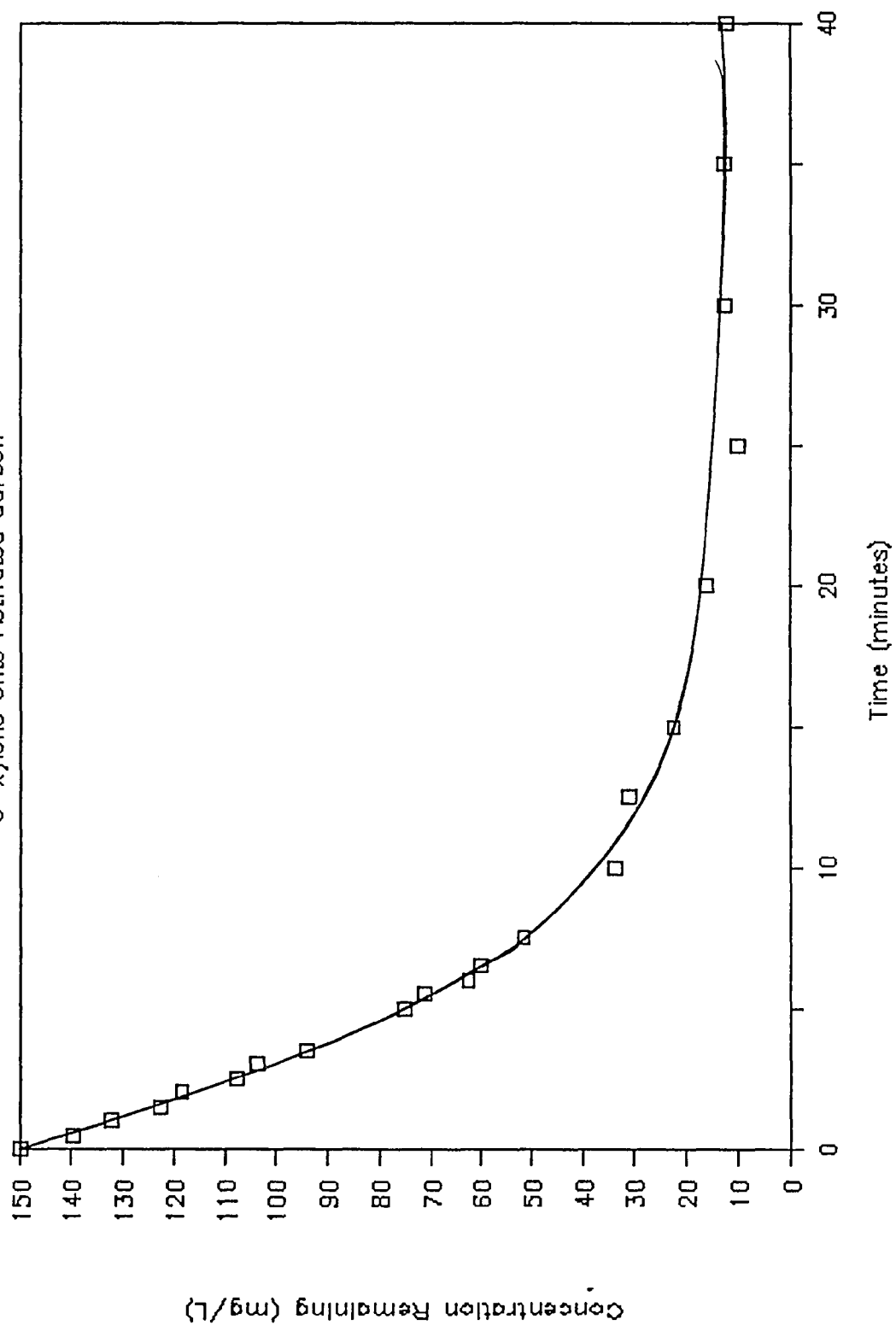
Figure B.5 First order Reversible Kinetic Fit.
O-Xylene onto Militant Flyash.(Dia.< 0.075mm).

Slope,K'=-0.200 per min.

$1-\dfrac{X_A}{X_{Ae}}$

Time, (Min)
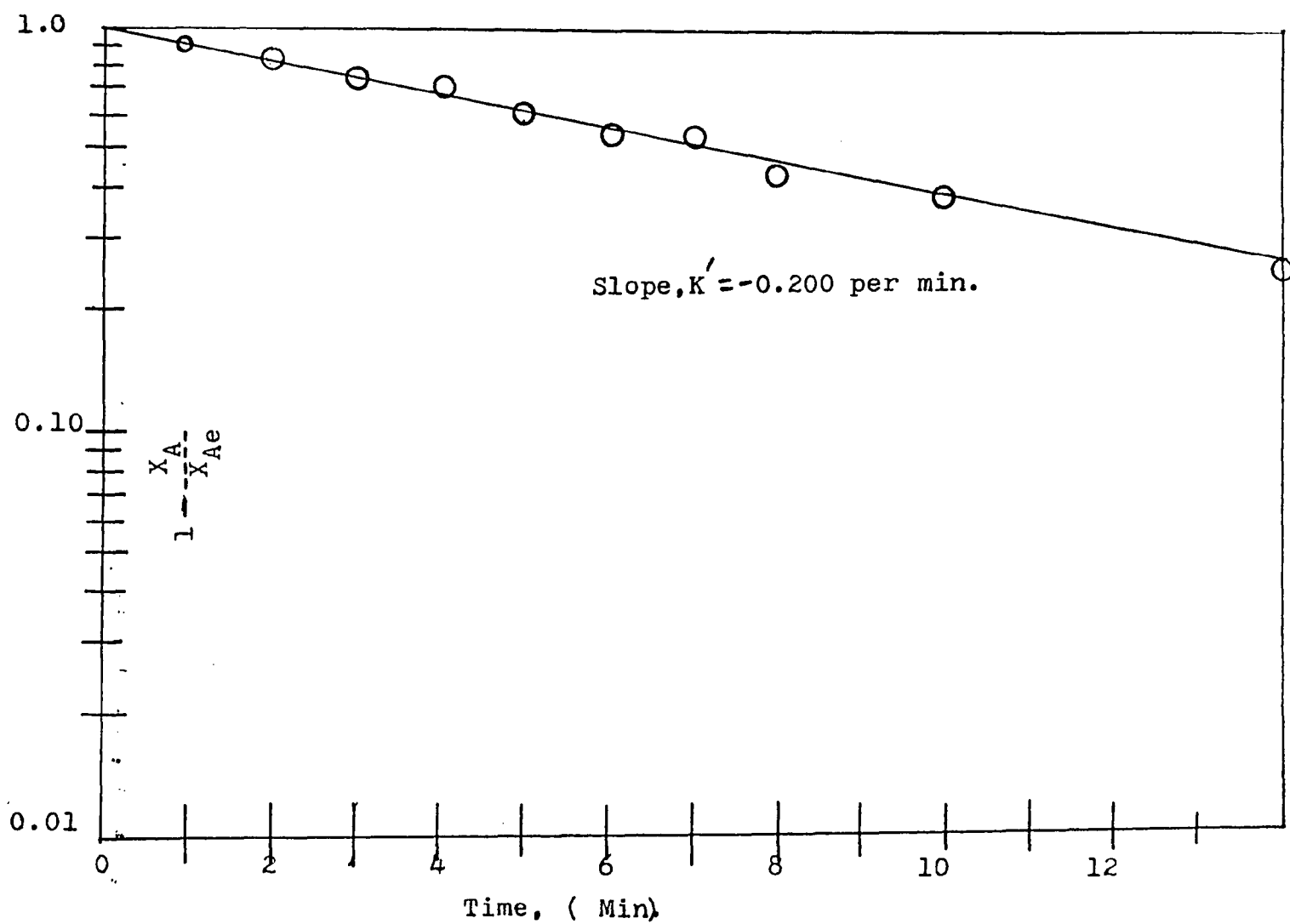
Figure B.6   First order Reversible Kinetic Fit.
             o-Xylene onto Militant Flyash,(Dia. ≃ 0.075mm).

Slope, $K' = -0.162$ per min.

Time, (Min.)
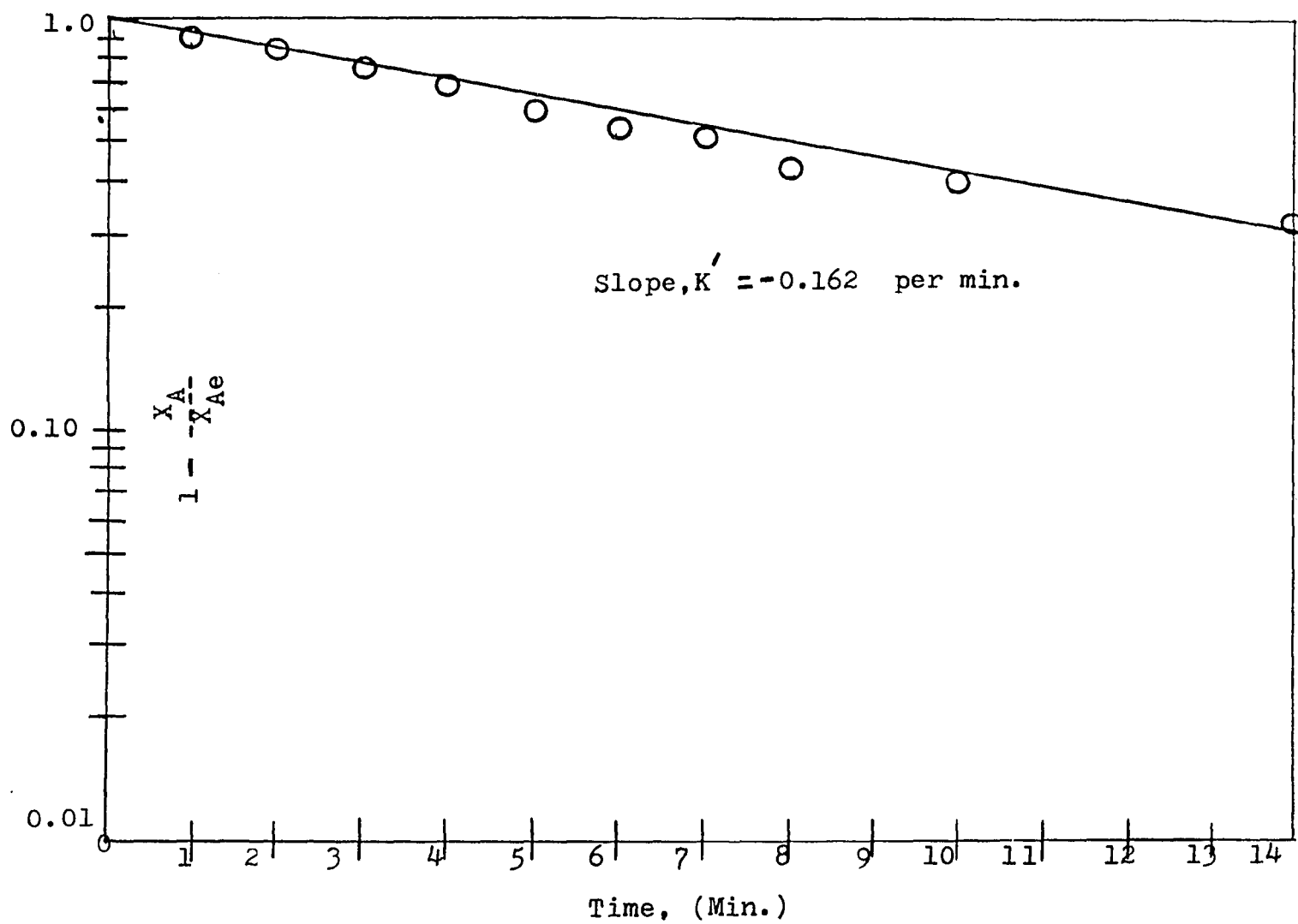
Figure B.7 First order Reversible Kinetic Fit.
O-Xylene onto Militant Flyash,(Dia.≃ 0.150 mm).

Slope, $K' = -$ 0.058 per min.

$1 - \dfrac{X_A}{X_{Ae}}$

Time, (Min.)
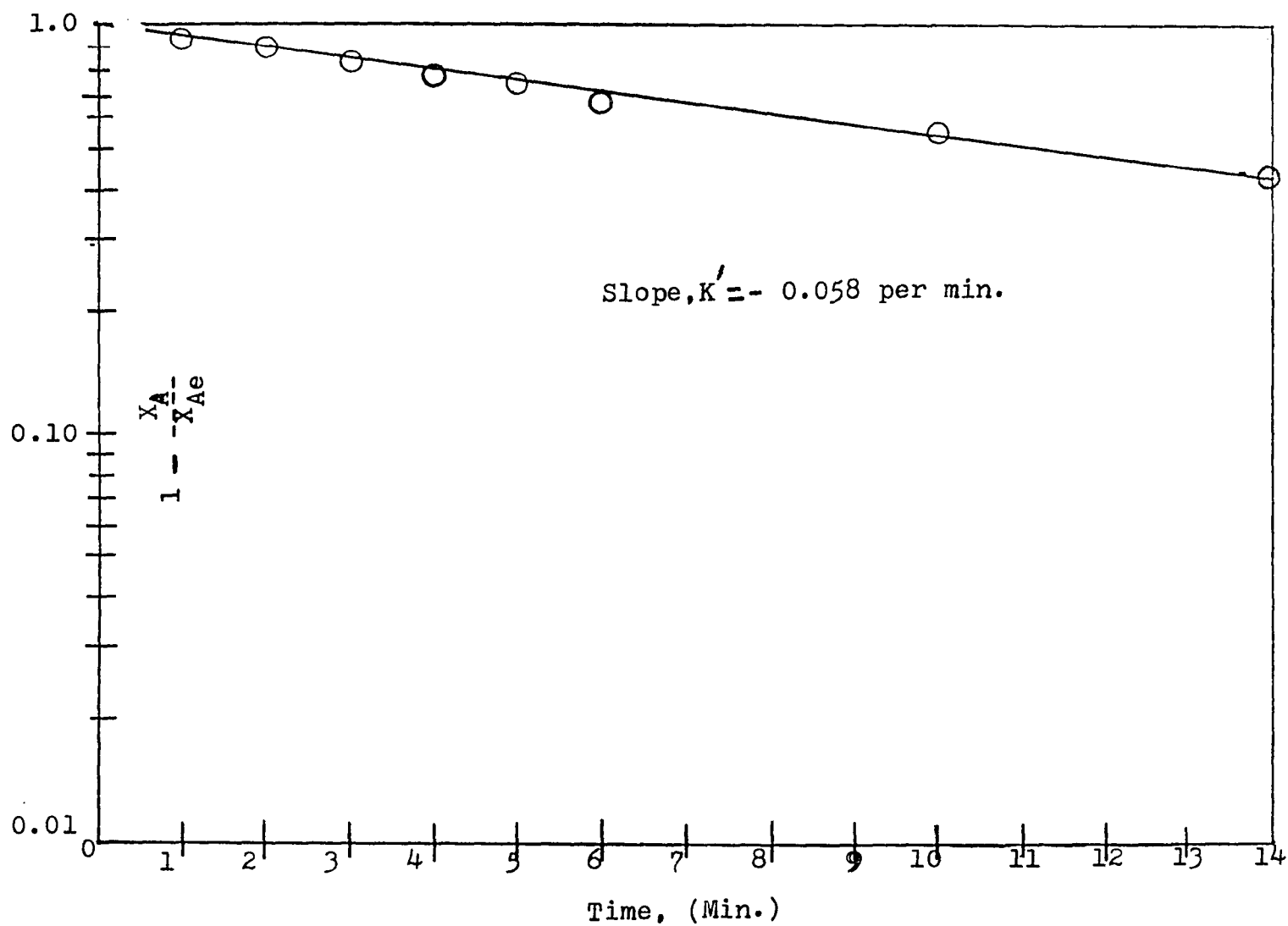
Figure B.8 First order Reversible Kinetic Fit.
o-Xylene onto Activated Carbon,(Dia.≃ 0.273 mm).

Slope, K' = - 6.16 per min.*

$1 - \dfrac{X_A}{X_{Ae}}$

Time, (Min.)
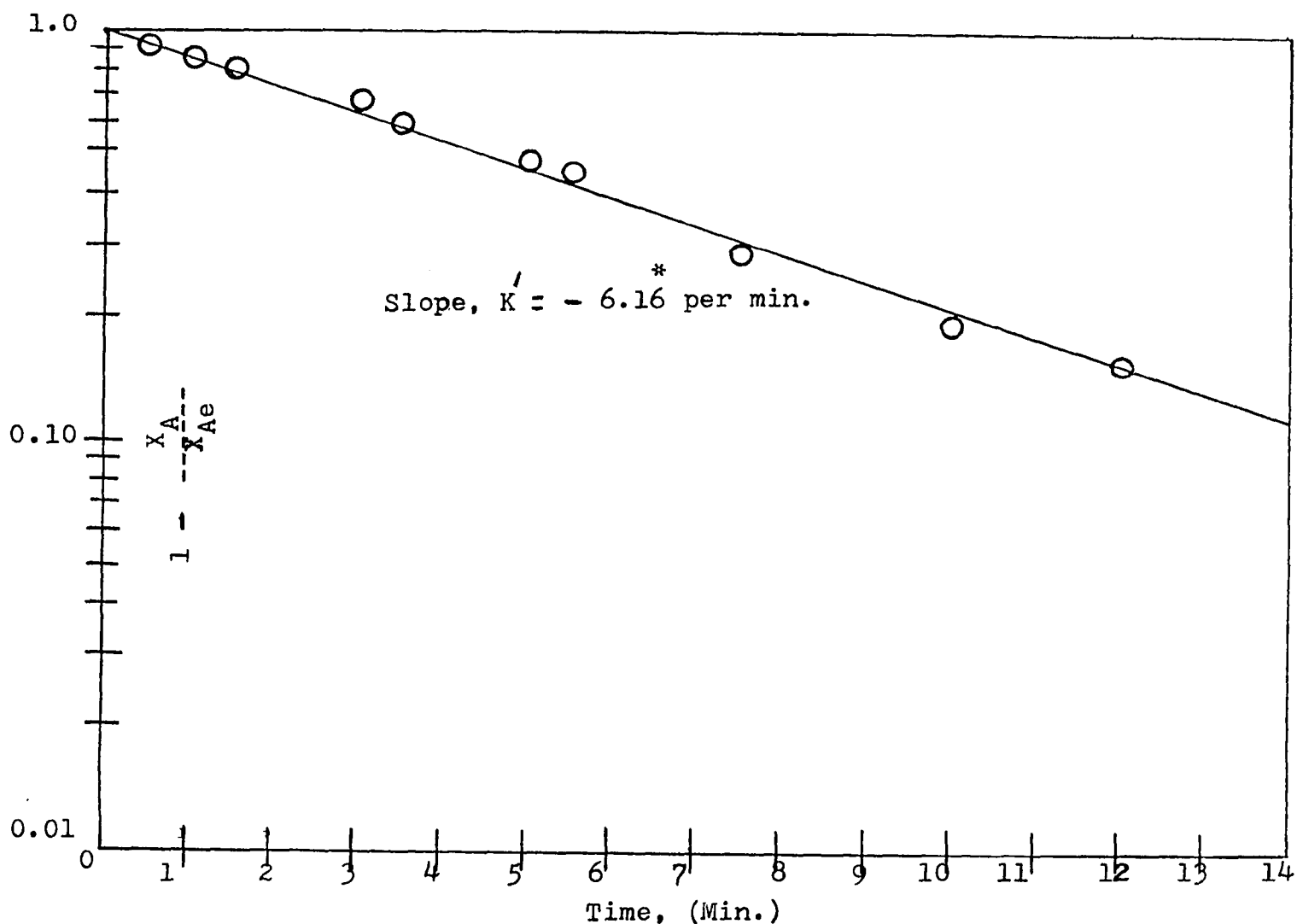
* Experiment performed using 0.5 g. of carbon per 750 ml. of Solution,
Over all rate constant≃- 0.154 per min. (based on the above Carbon
Concentration). Hence, for 20 g.of Carbon Over all rate constant
is equal to -6.16 per min.

B.8

Figure B.9 First order Reversible Kinetic Fit.
o-Xylene onto Activated Carbon,(Dia.$\simeq$ 0.150mm).

Slope, $K' = - 6.8^*$ per min.

$1 - \dfrac{X_A}{X_{Ae}}$

Time, (Min.)
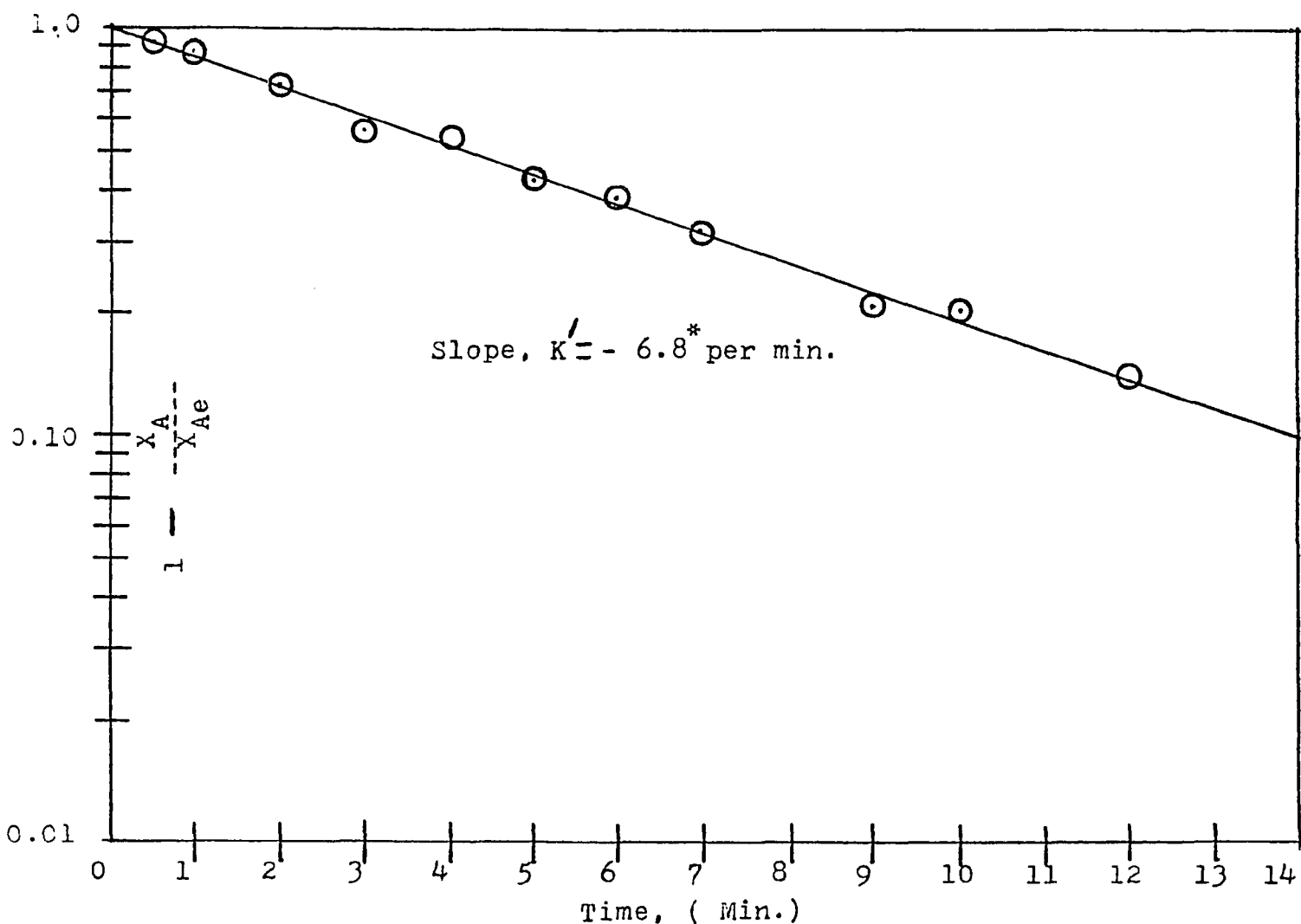
* Experiment performed using 0.50 g. of Carbon per 750 ml. of solution, Over all rate constant$\simeq$ - 0.170 per min. (based on the above concentration). Hence, for 20 g. of Carbon Over all rate constant is equal to - 6.80 per min.

APPENDIX - 'C'

SINGLE SOLUTE ADSORPTION EQUILIBRIA

Figure C.1. Adsorption Isotherm
Methyl Alcohol onto Militant Flyash

Equilibrium Concentration (mg/L)

Adsorption Capacity (ug/g)

C.1
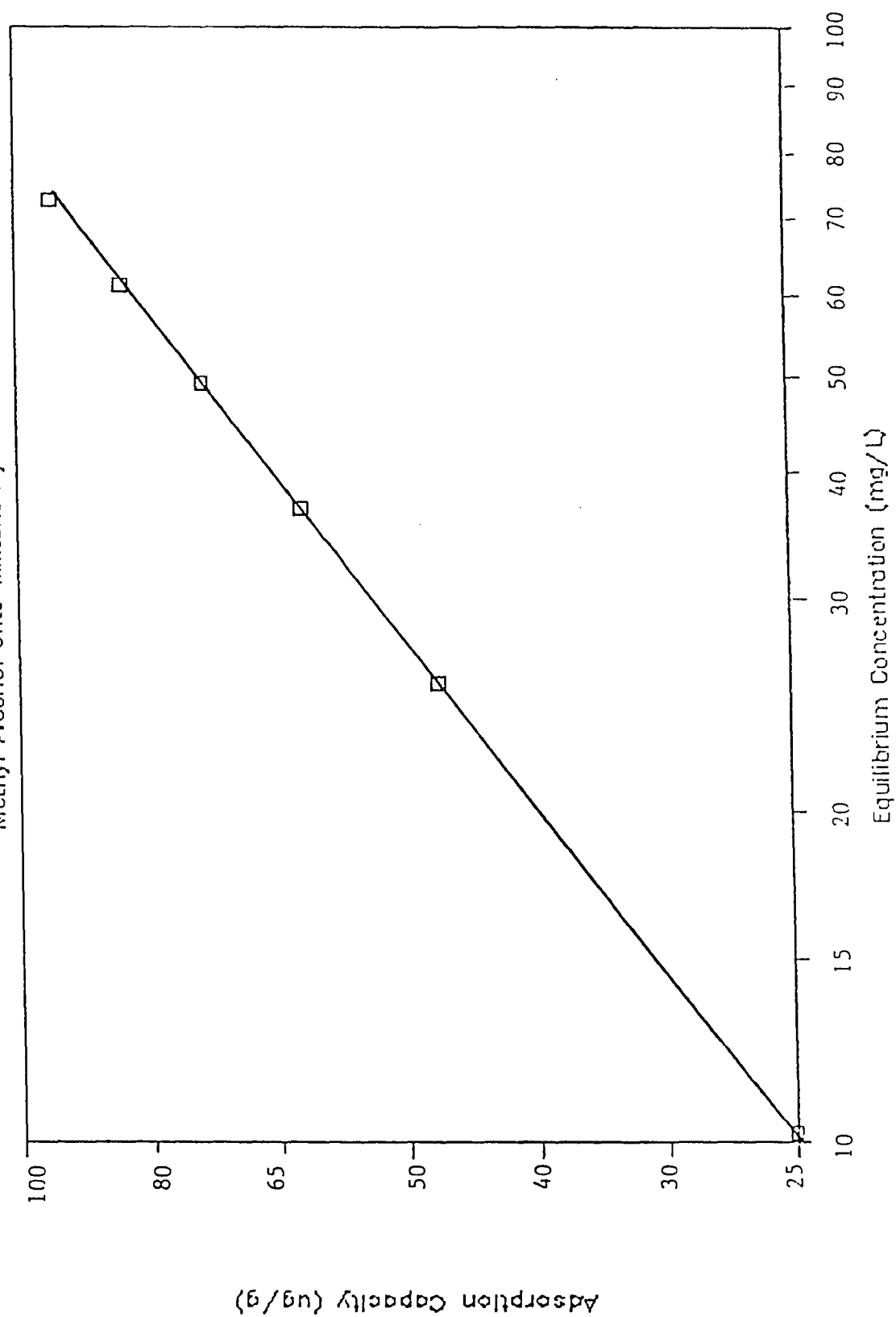
Figure C.2. Adsorption Isotherm
Ethanol onto Militant Flyash

Adsorption Capacity (ug/g)

Equilibrium Concentration (mg/L)

C.2
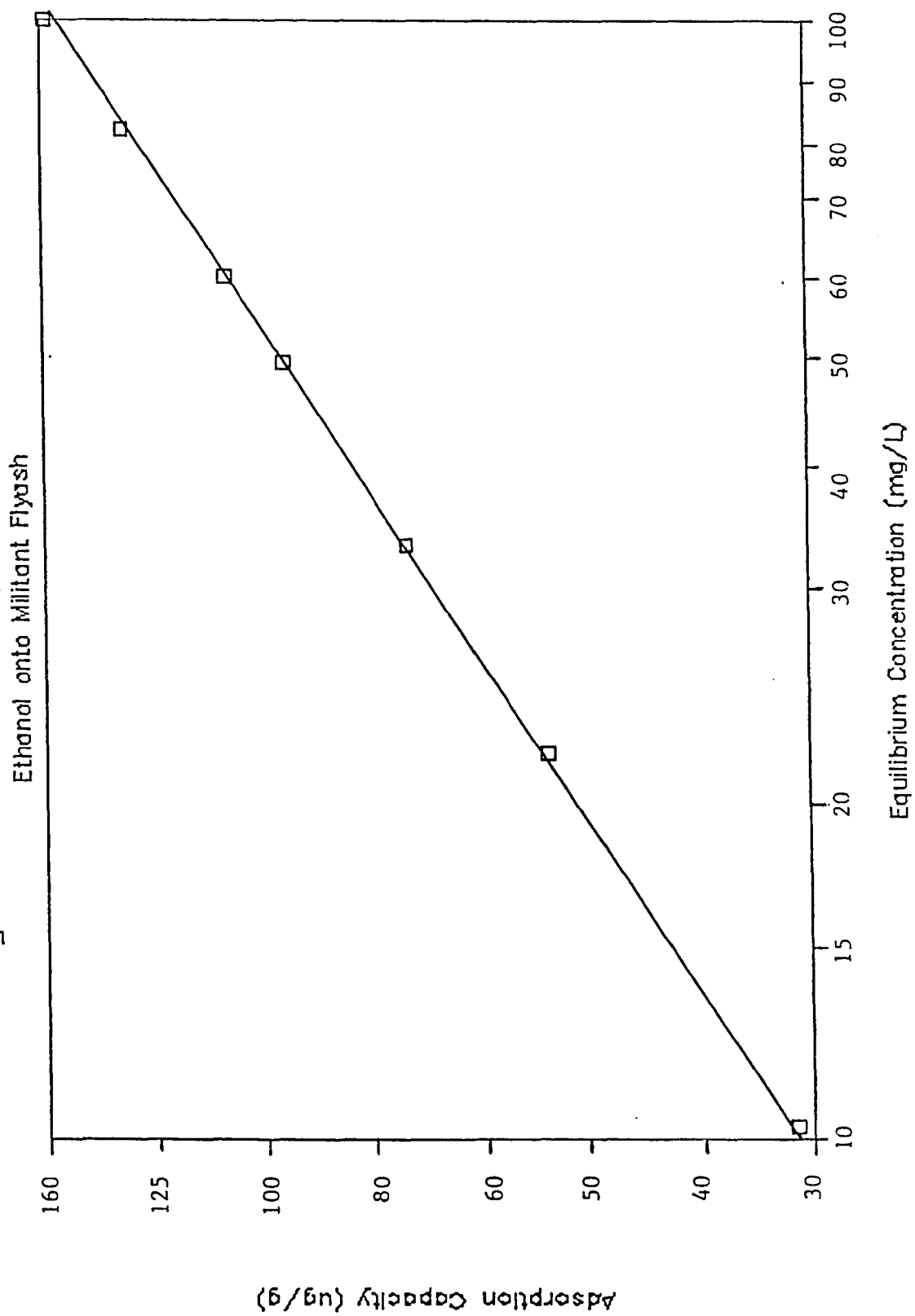
Figure C.3. Adsorption Isotherm
Propanol onto Militant Flyash

Adsorption Capacity (ug/g)

Equilibrium Concentration (mg/L)

c.3
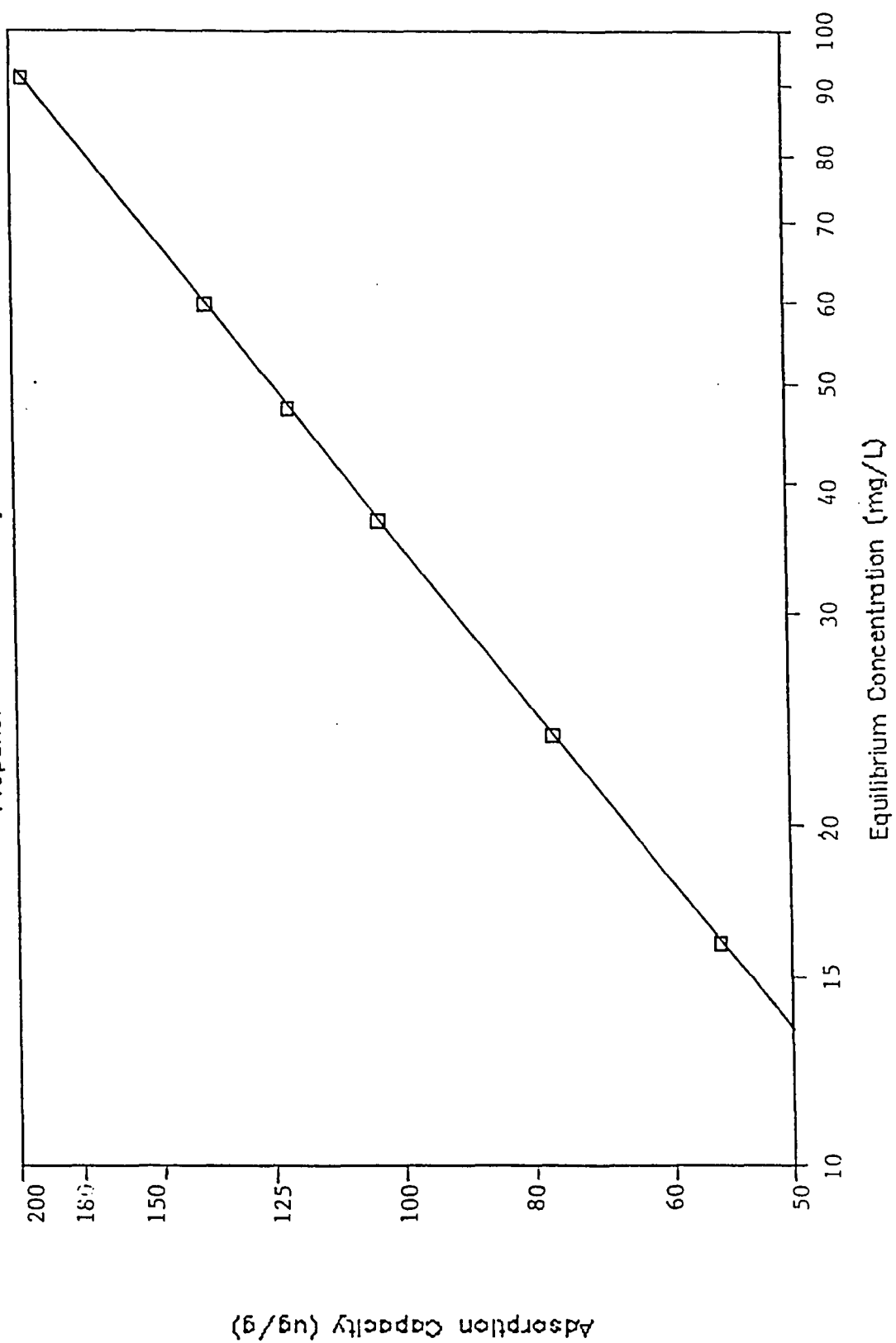
Figure C.4. Adsorption Isotherm
Butanol onto Militant Flyash

Adsorption Capacity (ug/g)

Equilibrium Concentration (mg/L)

c.4
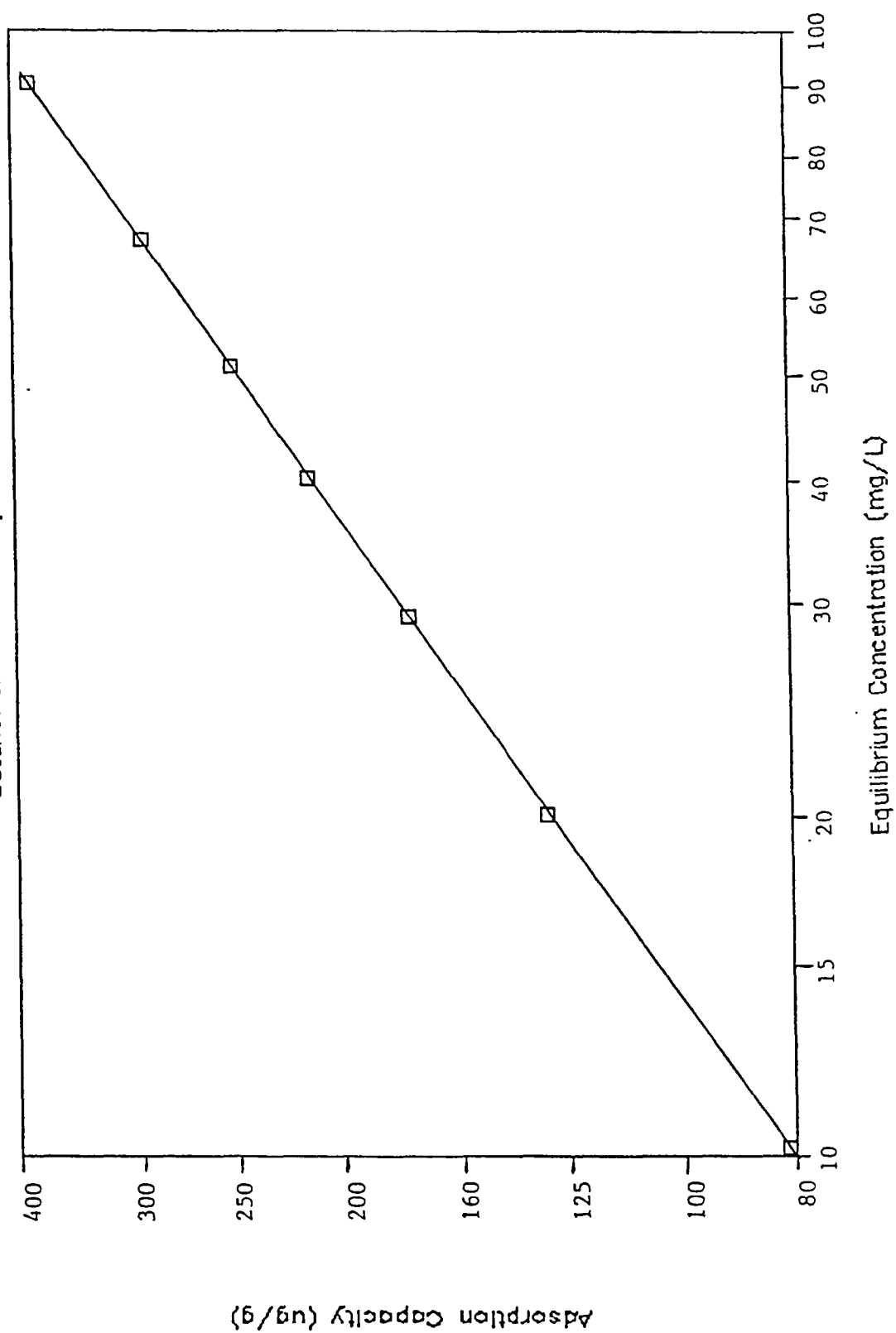
Figure C.5. Adsorption Isotherm
Iso-Propanol onto Militant Flyash

Equilibrium Concentration (mg/L)

Adsorption Capacity (ug/g)
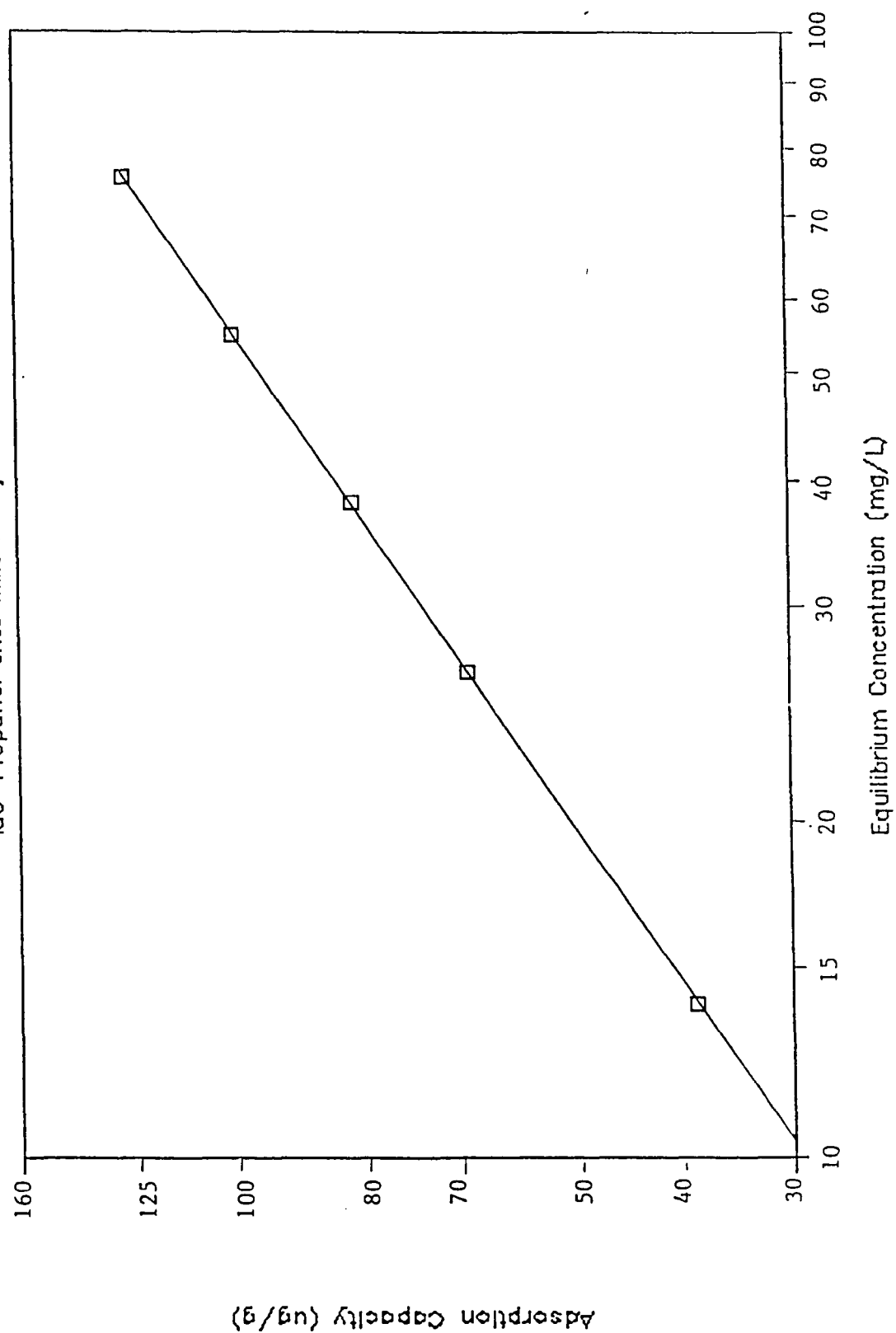
Figure C.6.Adsorption Isotherm
s-Butanol onto Militant Flyash

Adsorption Capacity (ug/g)

Equilibrium Concentration (mg/L)

c.6
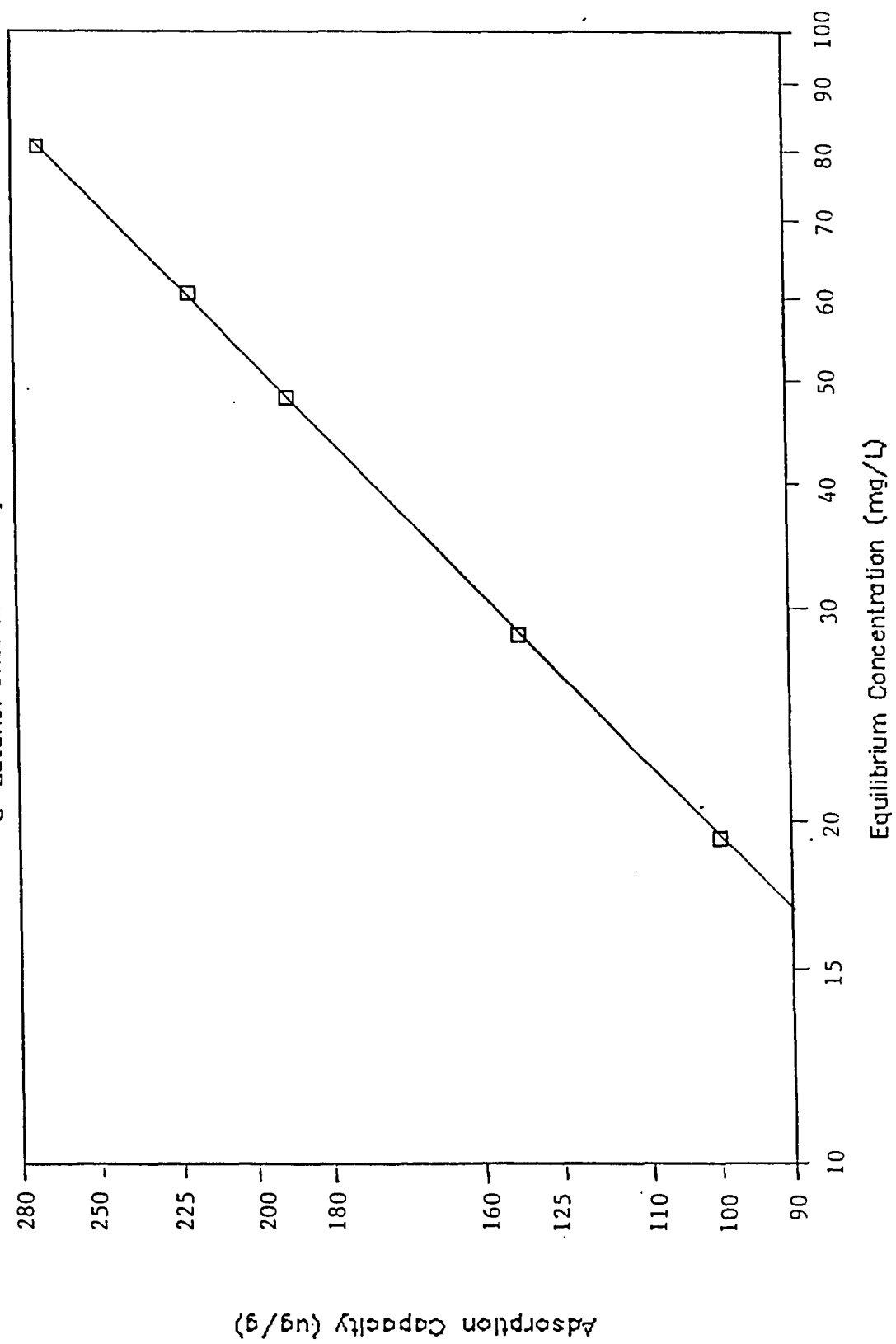
Figure C.7. Adsorption Isotherm
Phenol onto Militant Flyash

Equilibrium Concentration (mg/L)

Adsorption Capacity (ug/g)
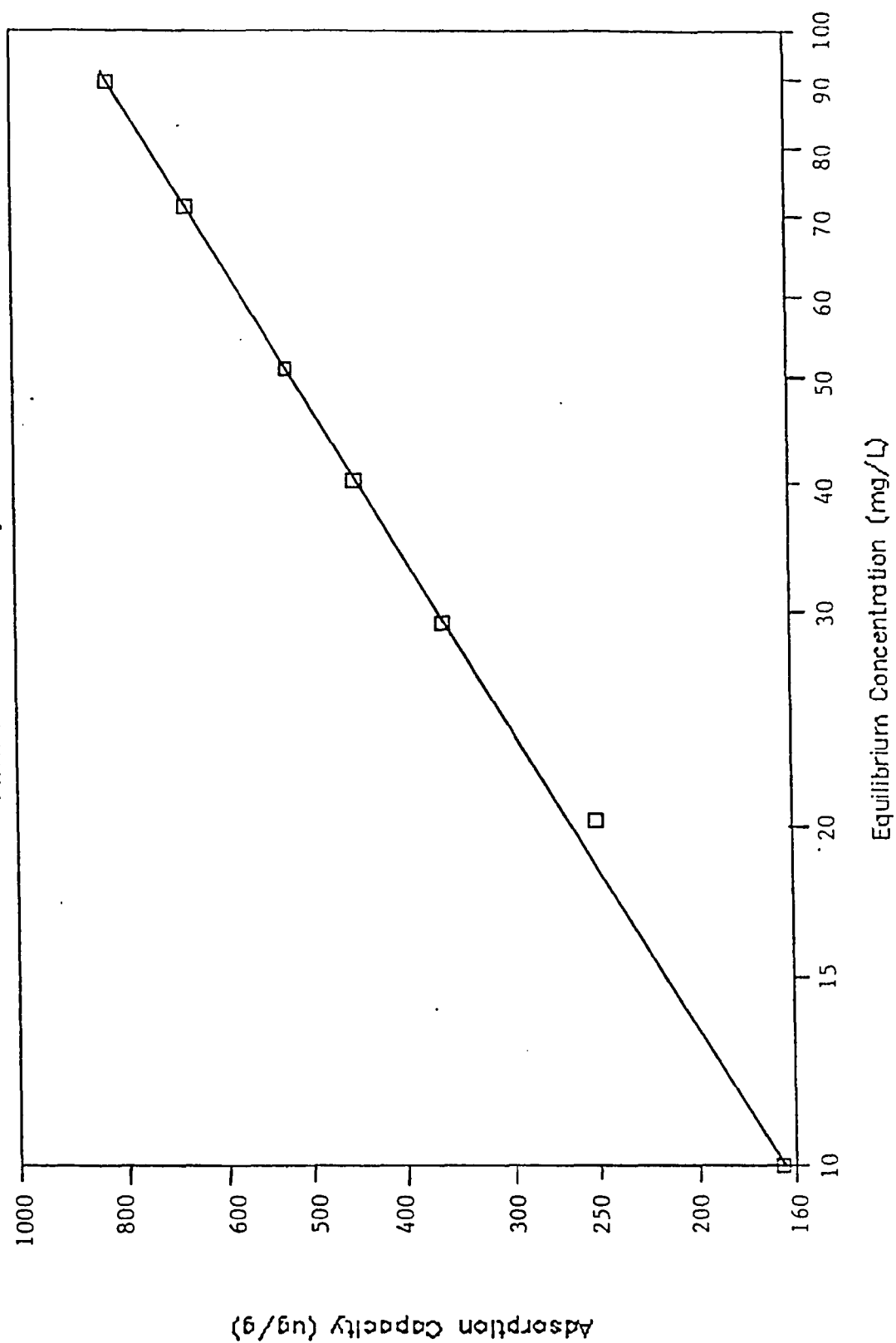
Figure C.8. Adsorption Isotherm
Acetone onto Militant Flyash

Equilibrium Concentration (mg/L)

Adsorption Capacity (ug/g)

c.8
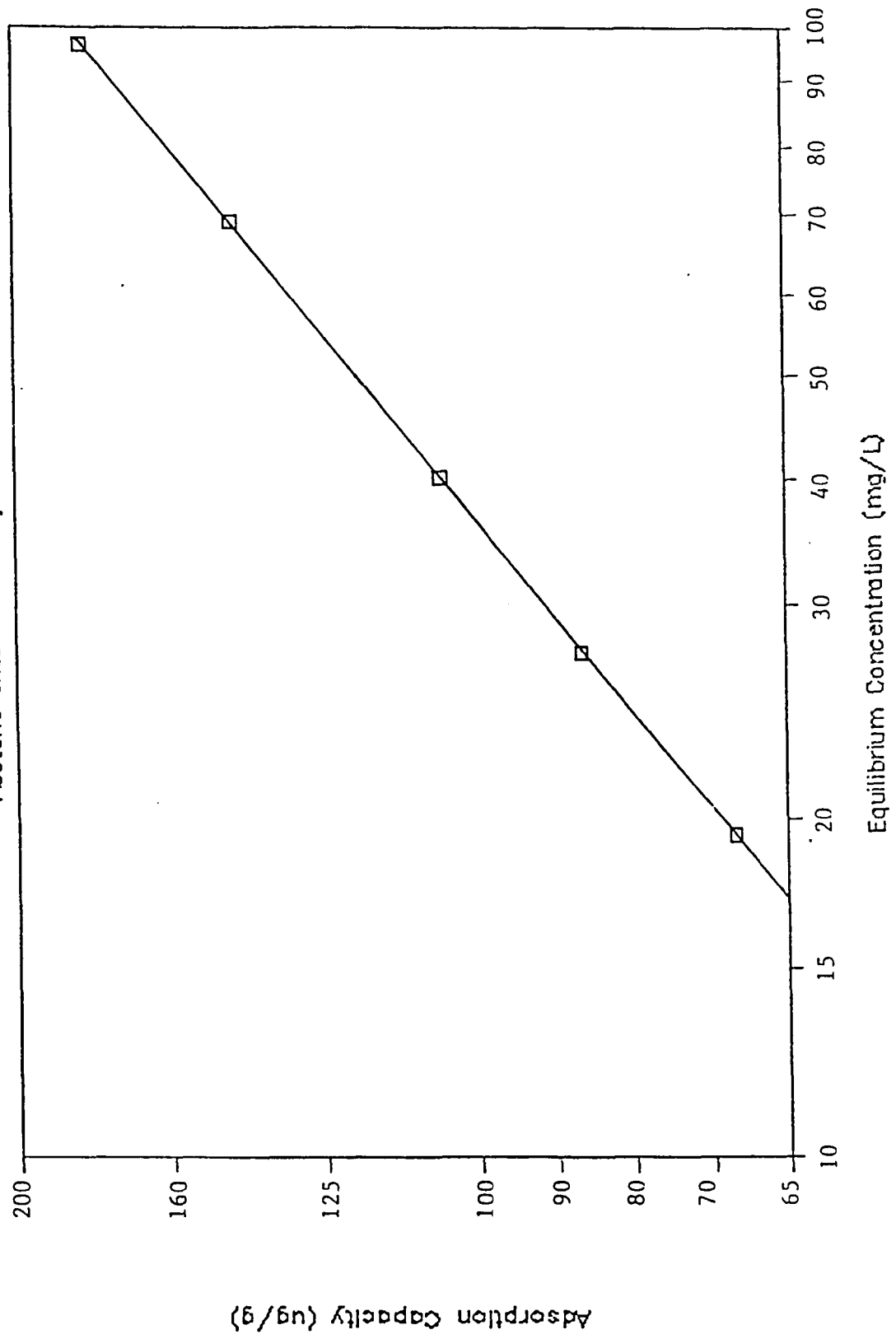
Figure C.9. Adsorption Isotherm
MEK onto Militant Flyash

Equilibrium Concentration (mg/L)

Adsorption Capacity (ug/g)

C.9
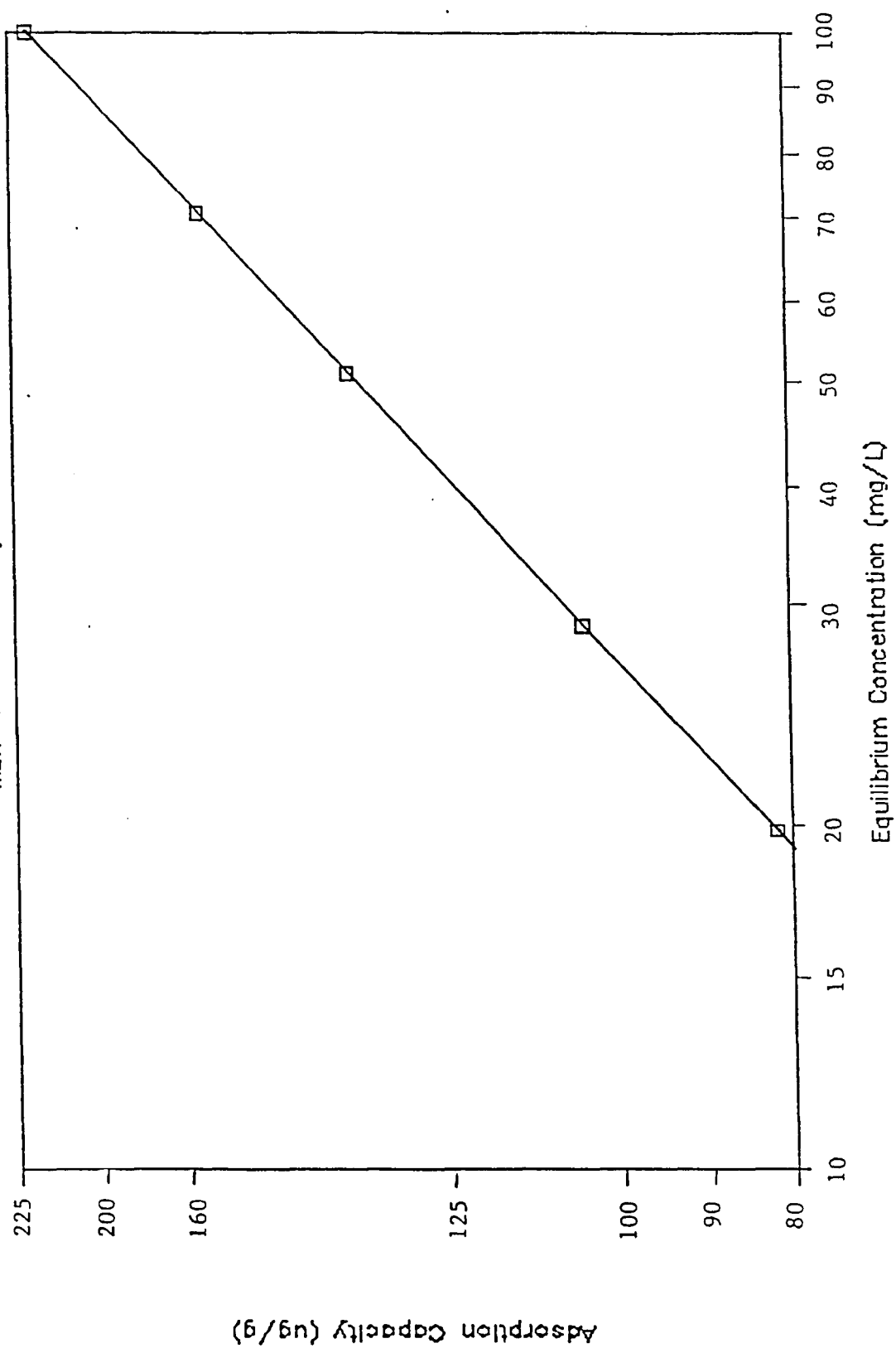
FigureC.10 Adsorption Isotherm

MIBK onto Militant Flyash

Equilibrium Concentration (mg/L)

Adsorption Capacity (ug/g)

c.10
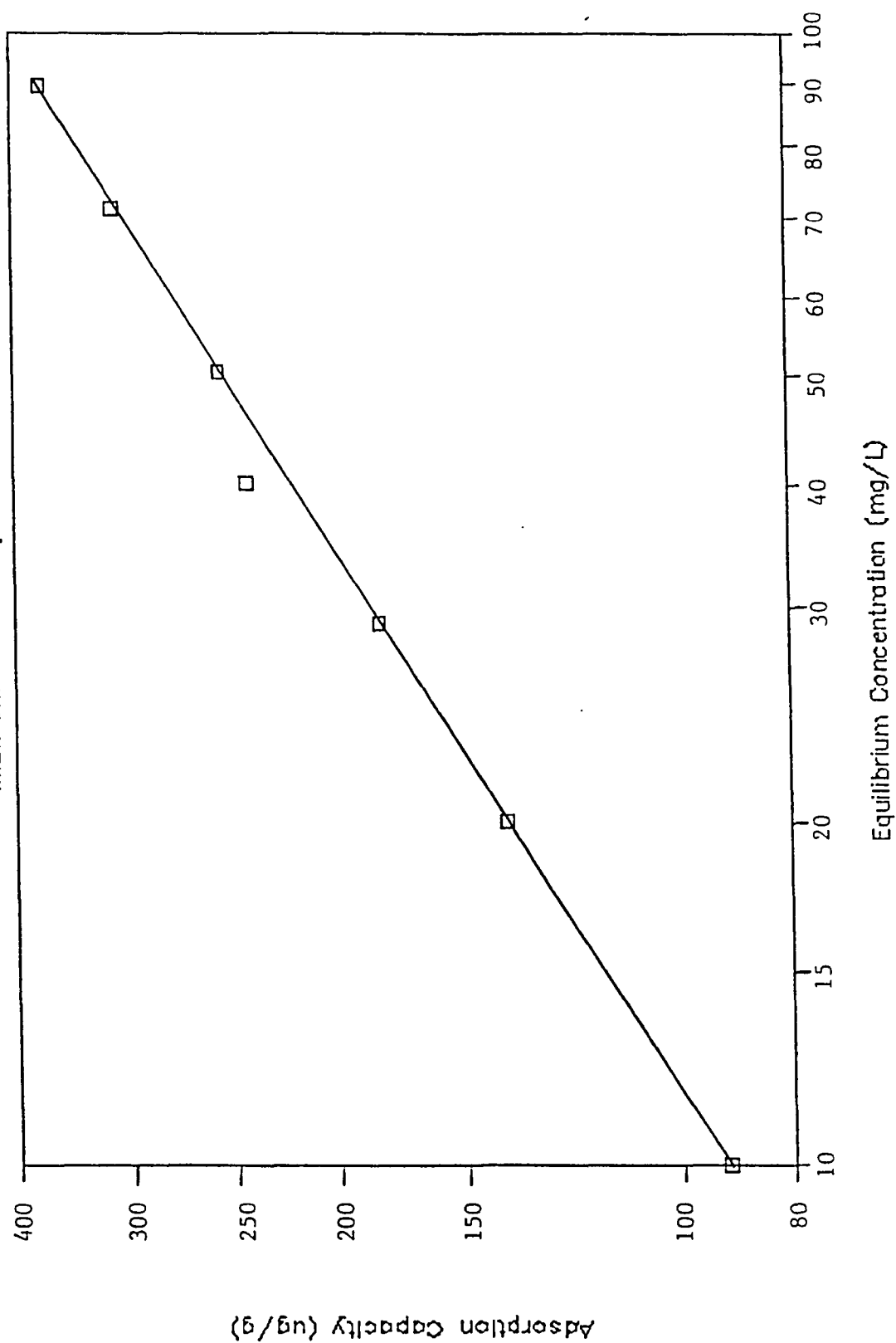
FigureC.11Adsorption Isotherm
Cyclohexanone onto Militant Flyash

Adsorption Capacity (ug/g)

Equilibrium Concentration (mg/L)

C.11
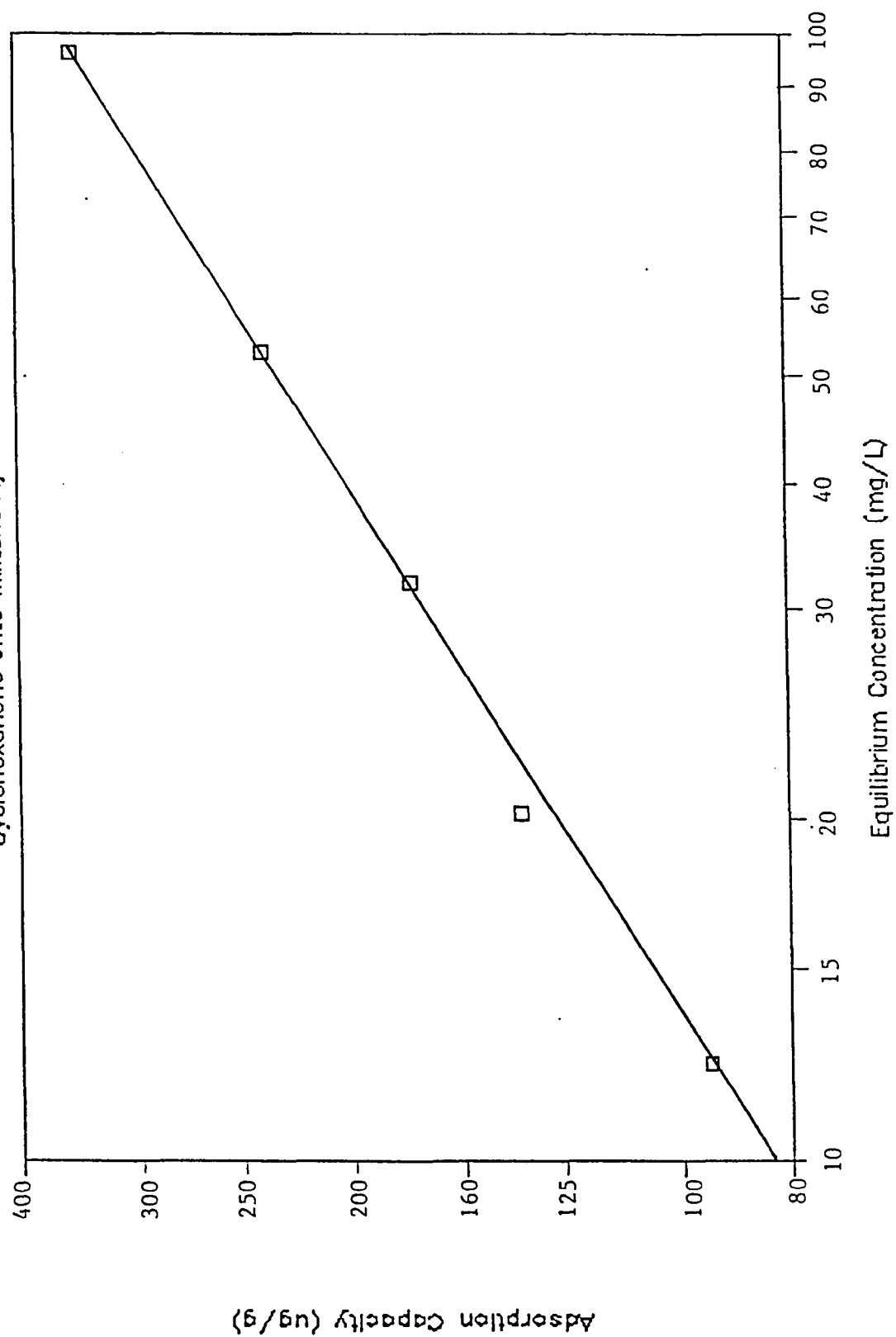
Figure C.12 Adsorption Isotherm
Formaldehyde onto Militant Flyash
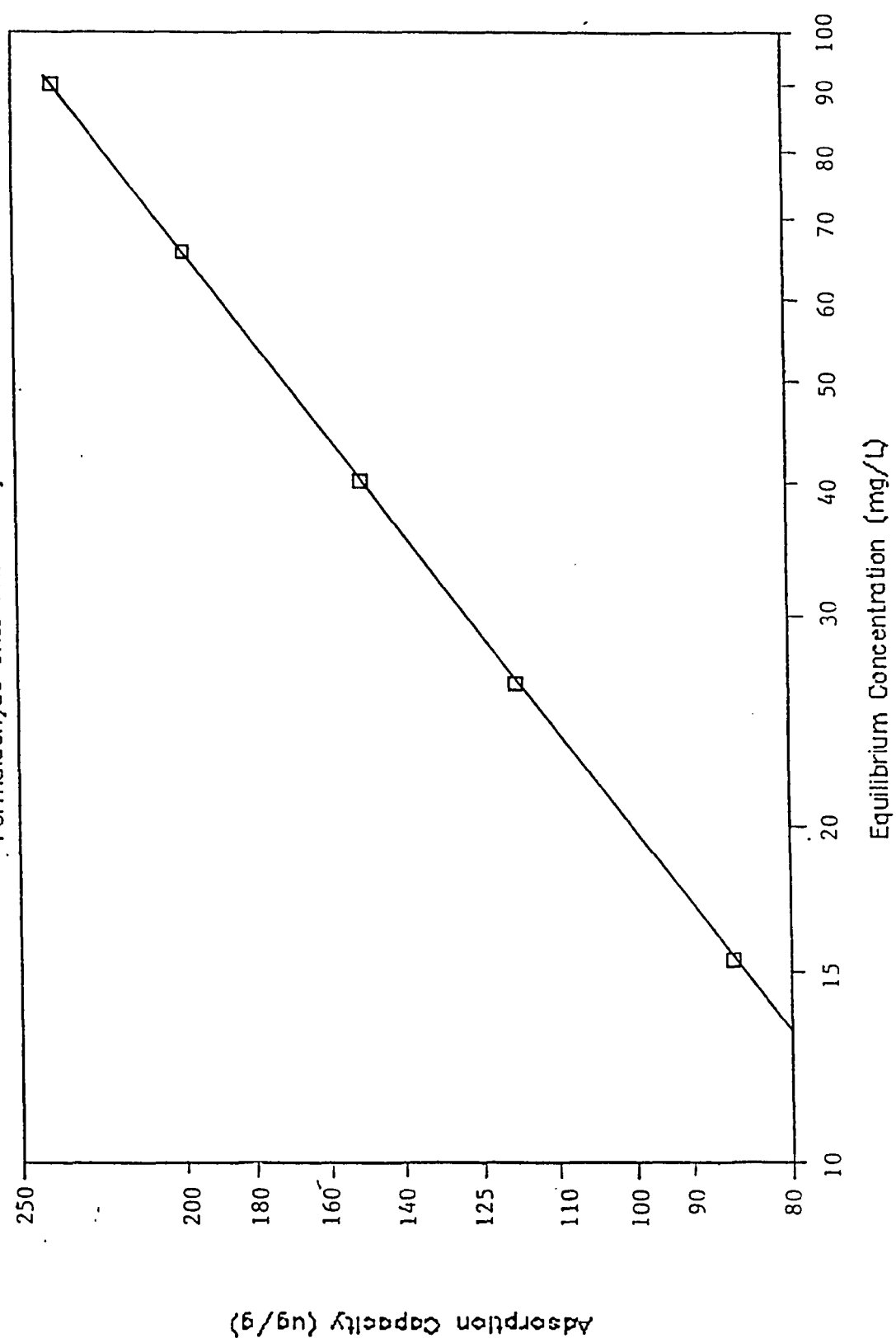
Figure C.13 Adsorption Isotherm
Acetaldehyde onto Militant Flyash

Adsorption Capacity (ug/g) vs Equilibrium Concentration (mg/L)
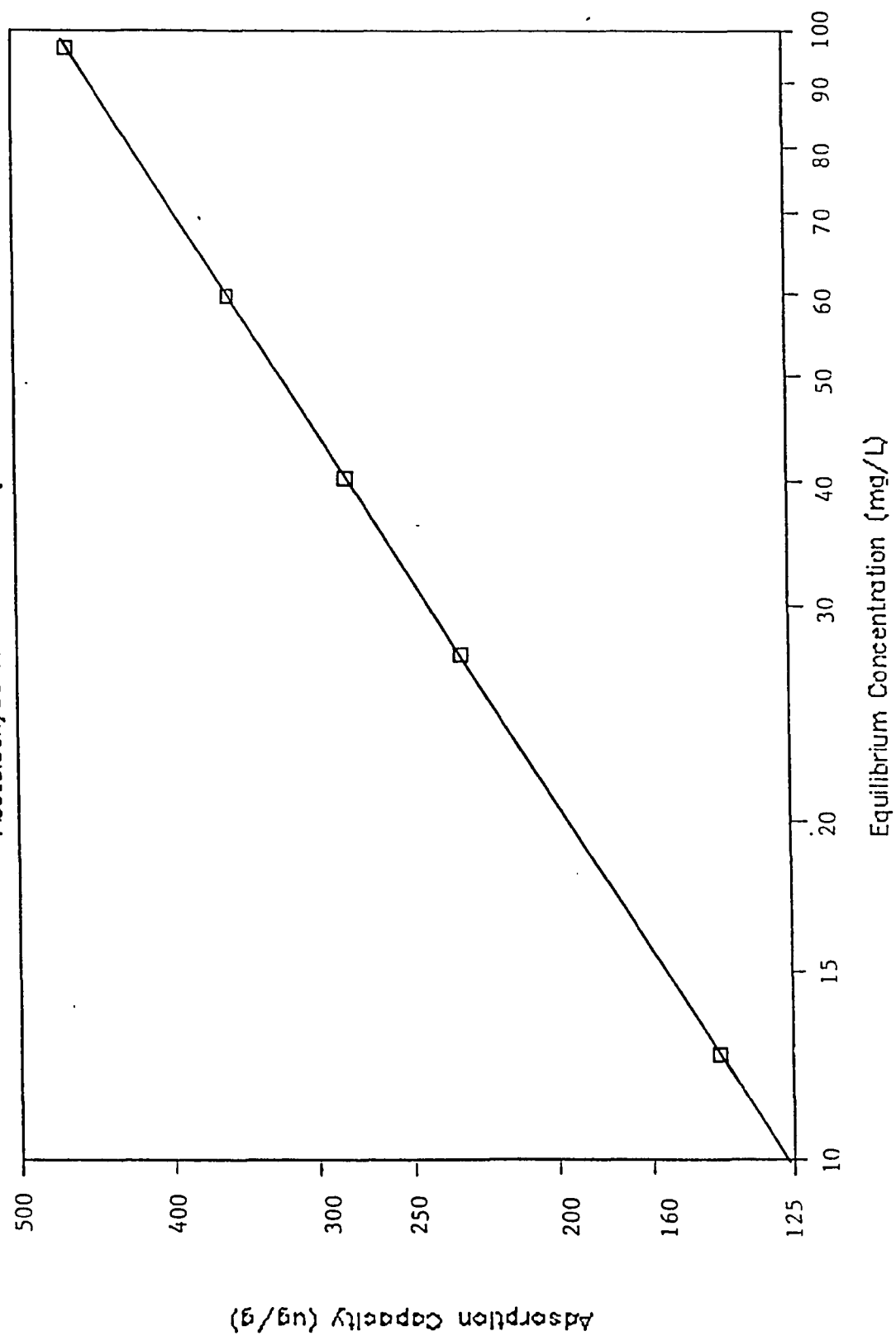
Figure C.14 Adsorption Isotherm
Butyraldehyde onto Militant Flyash

Equilibrium Concentration (mg/L)

Adsorption Capacity (ug/g)

C.14
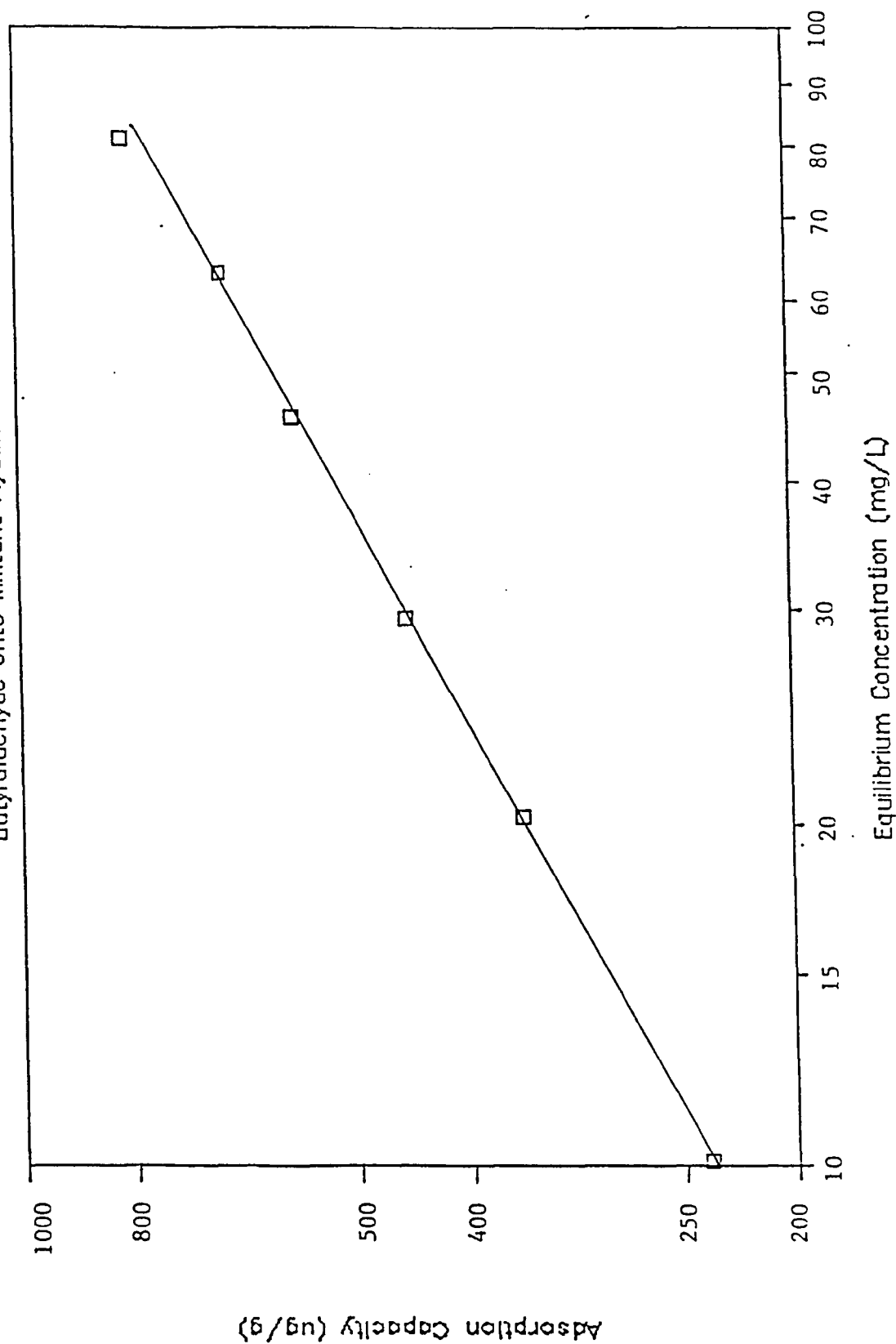
Figure C.15 Adsorption Isotherm
Benzene onto Militant Flyash
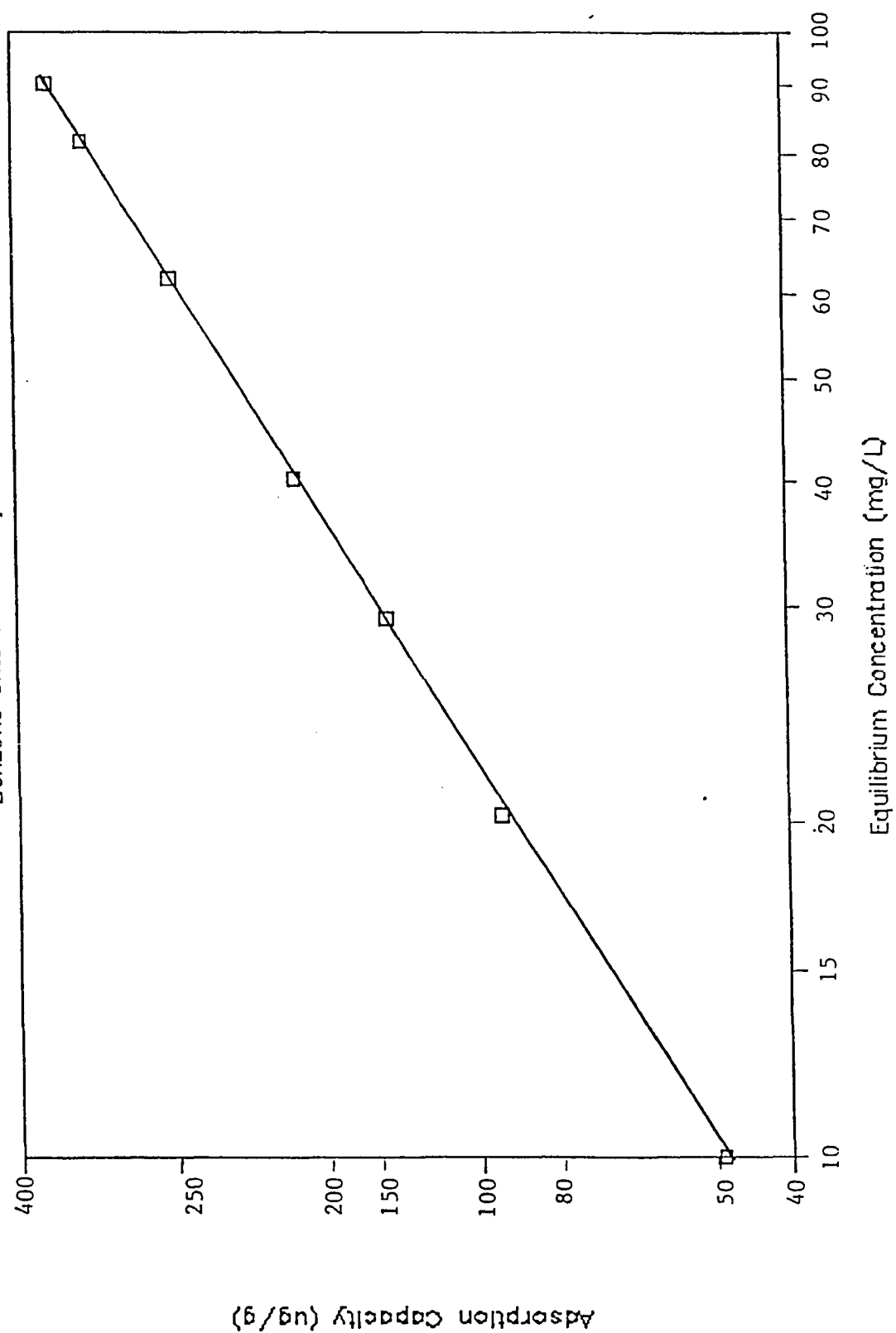
FigureC.16Adsorption Isotherm

Aniline onto Militant Flyash

Adsorption Capacity (ug/g) vs Equilibrium Concentration (mg/L)

C.16
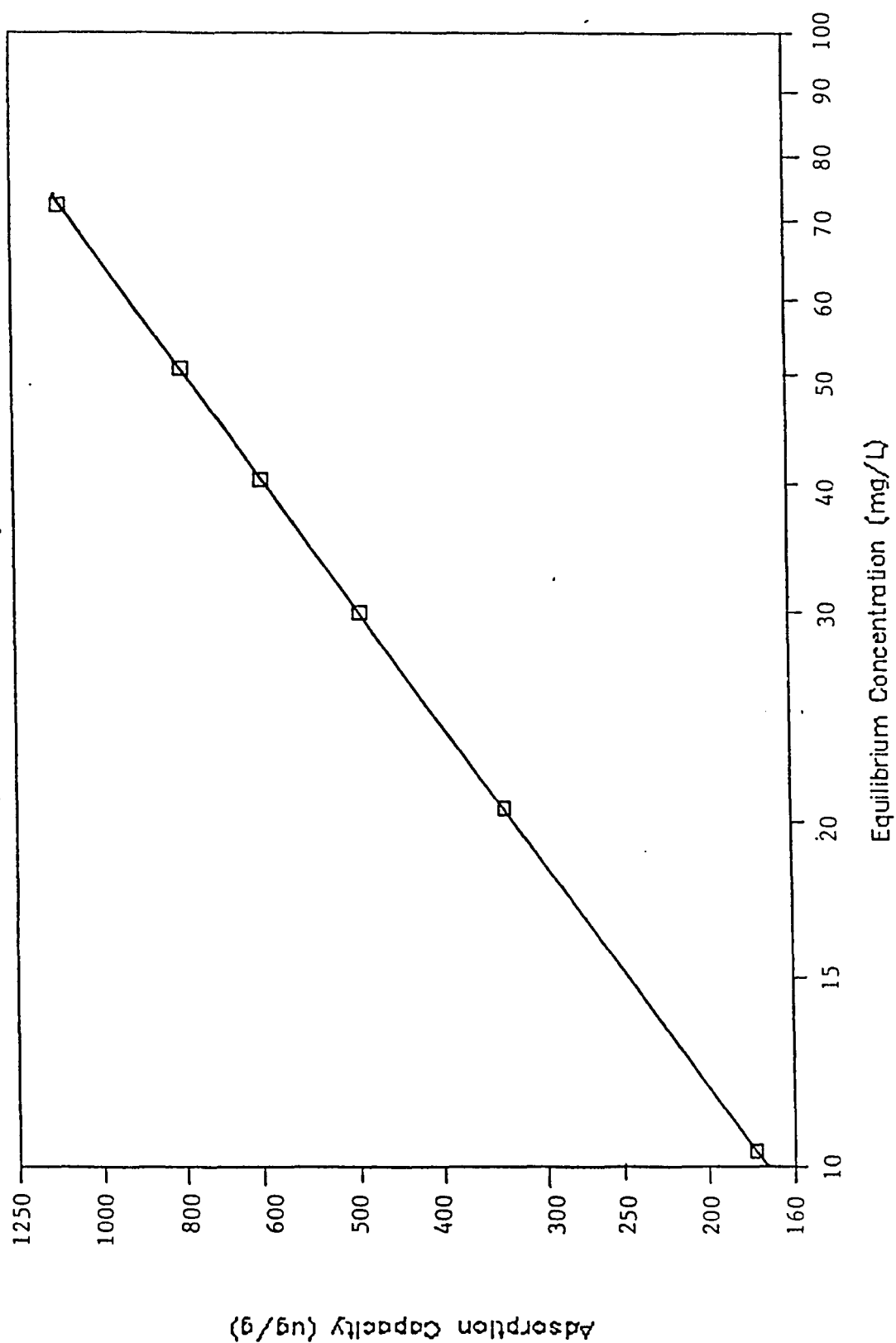
Figure C.17 Adsorption Isotherm
meta-Cresol onto Militant Flyash

Equilibrium Concentration (mg/L)

Adsorption Capacity (ug/g)

c.17
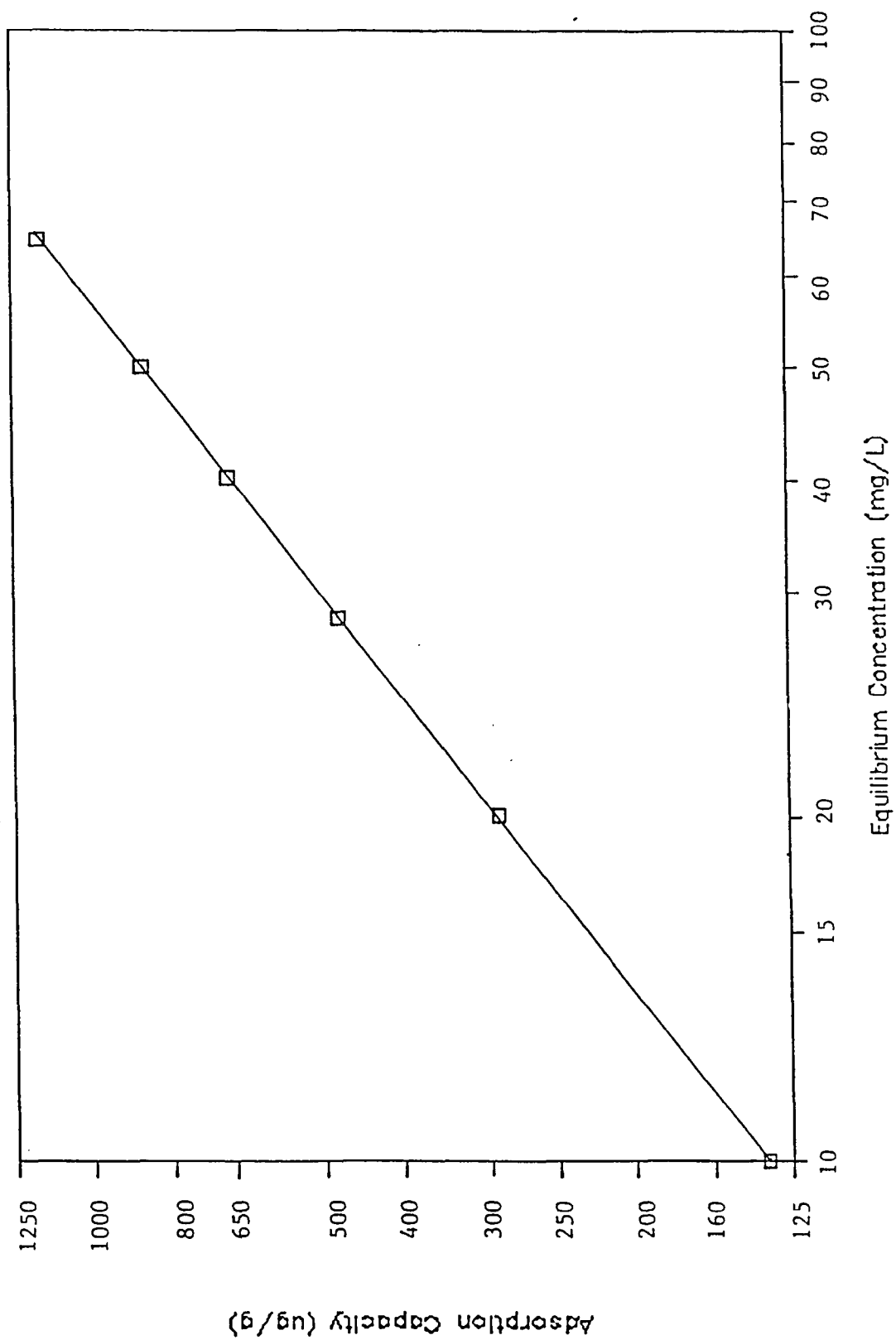
Figure C.18 Adsorption Isotherm
Ethyl Benzene onto Militant Flyash

Adsorption Capacity (ug/g)

Equilibrium Concentration (mg/L)

C.18
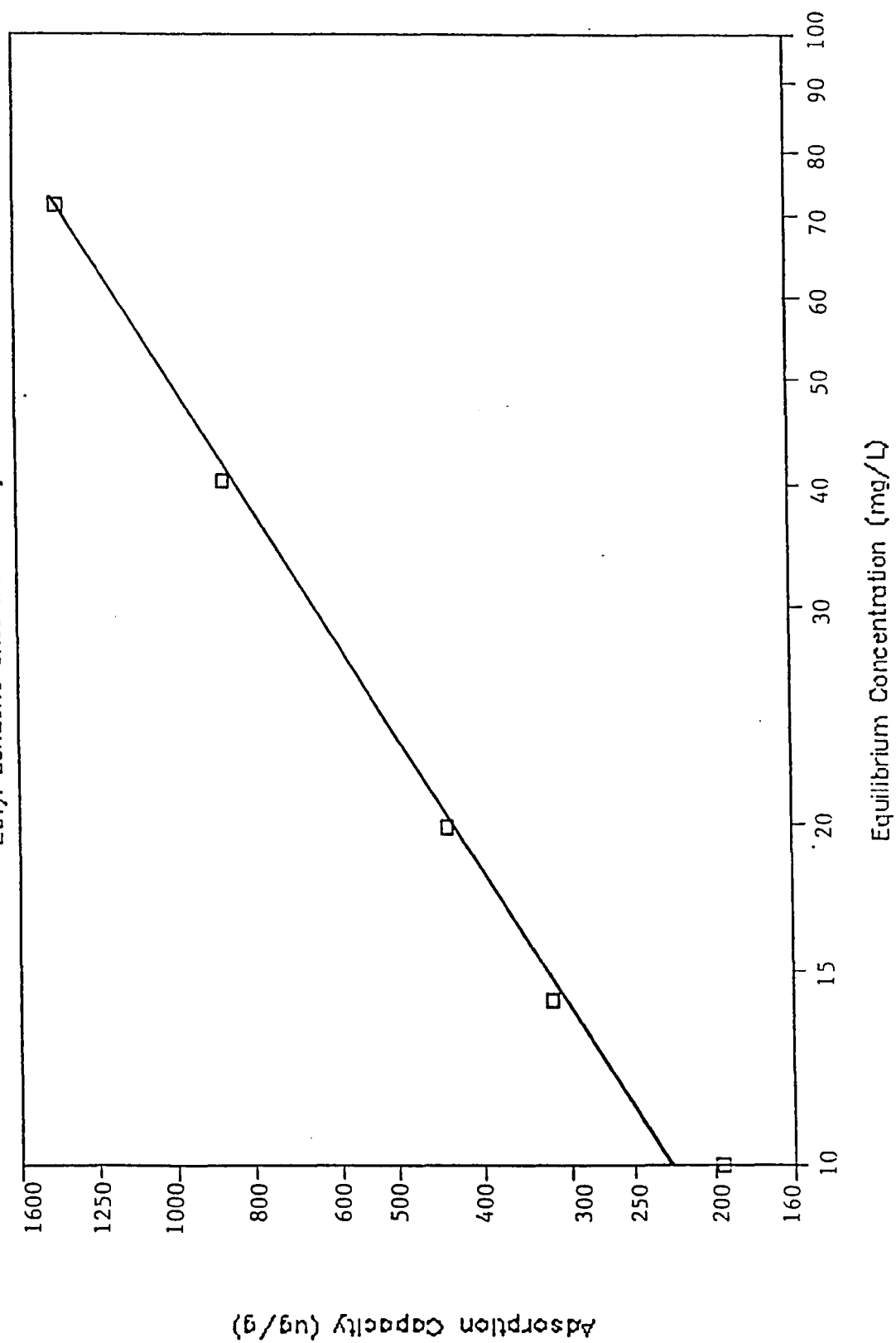
Figure C.19 Adsorption Isotherm
ortho-Xylene onto Militant Flyash
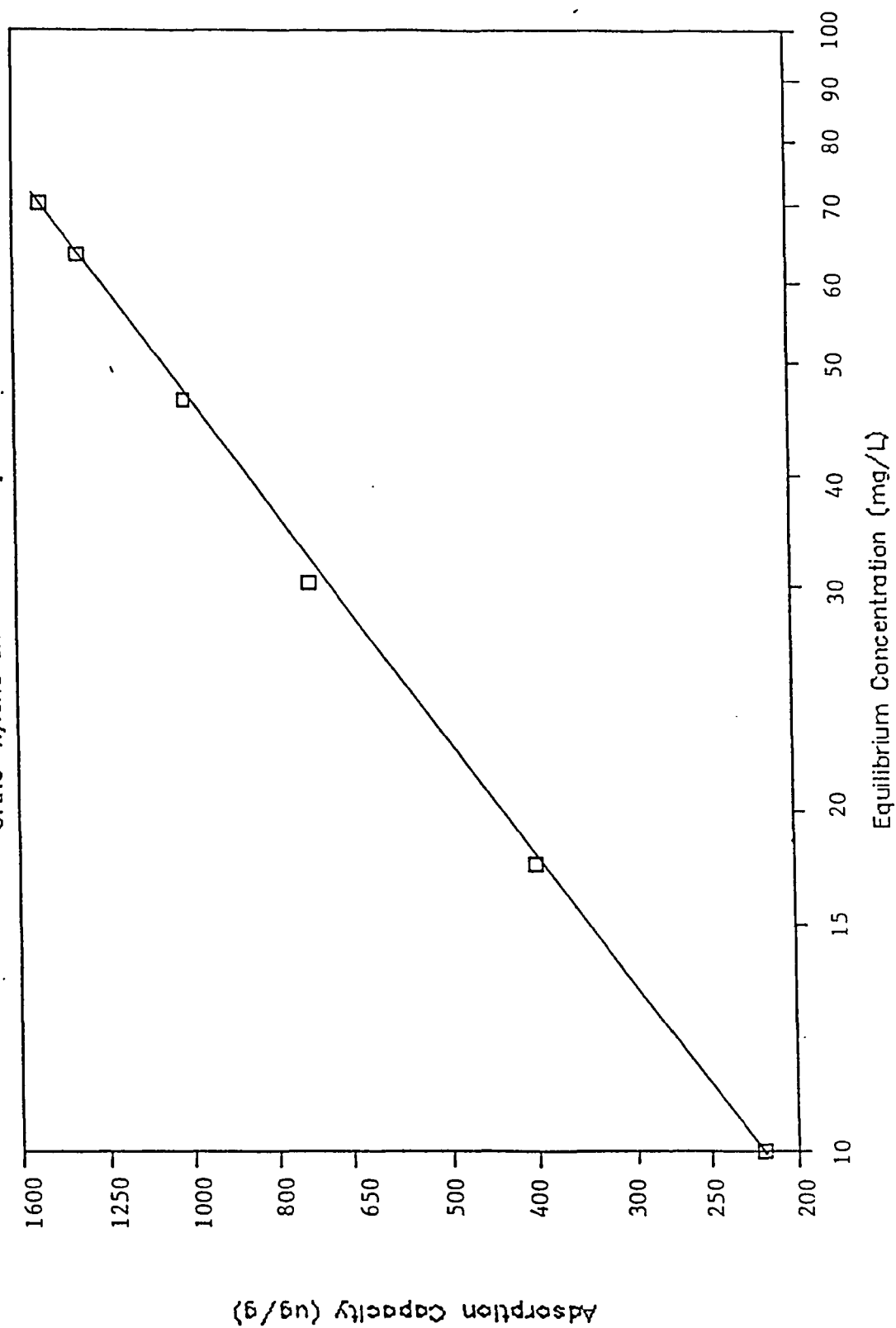
Figure C.20 Adsorption Isotherm
Methanol onto Activated Carbon

Equilibrium Concentration (mg/L)

Adsorption Capacity (mg/g)

C.20
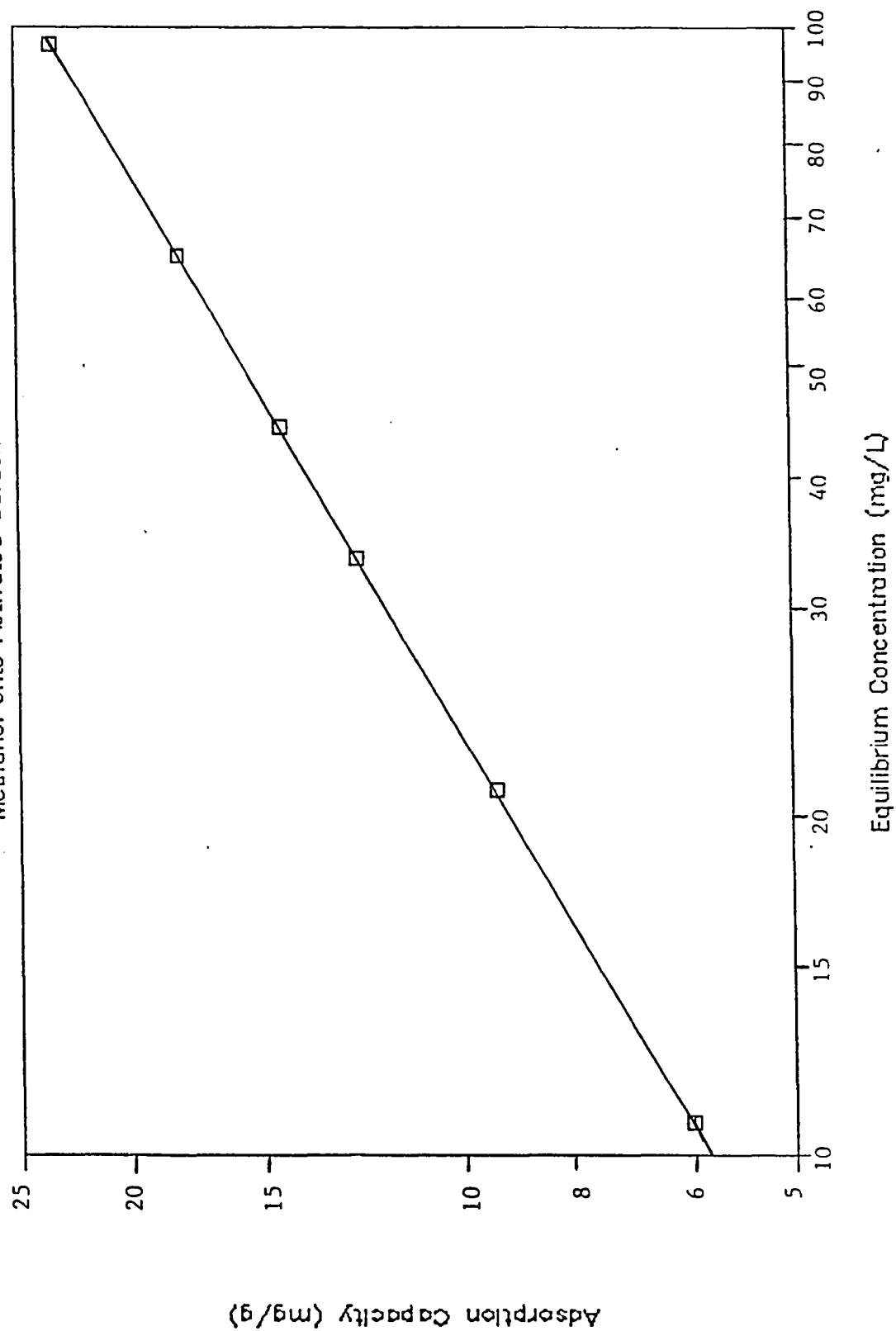
Figure C.21 Adsorption Isotherm
Ethanol onto Activated Carbon

Adsorption Capacity (mg/g)

Equilibrium Concentration (mg/L)

C.21
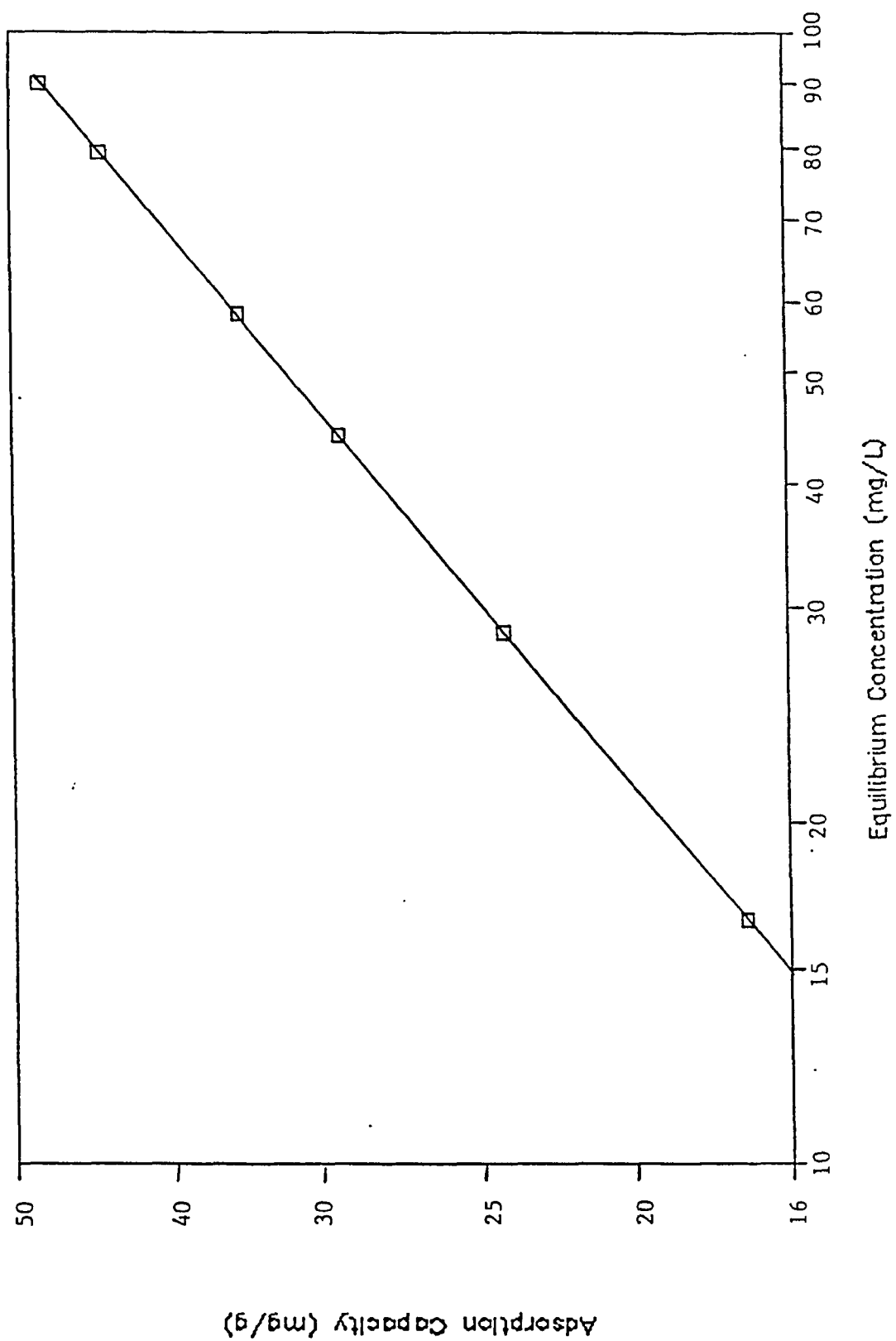
Figure C.22 Adsorption Isotherm
Propanol onto Activated Carbon

Equilibrium Concentration (mg/L)

Adsorption Capacity (mg/g)

C.22
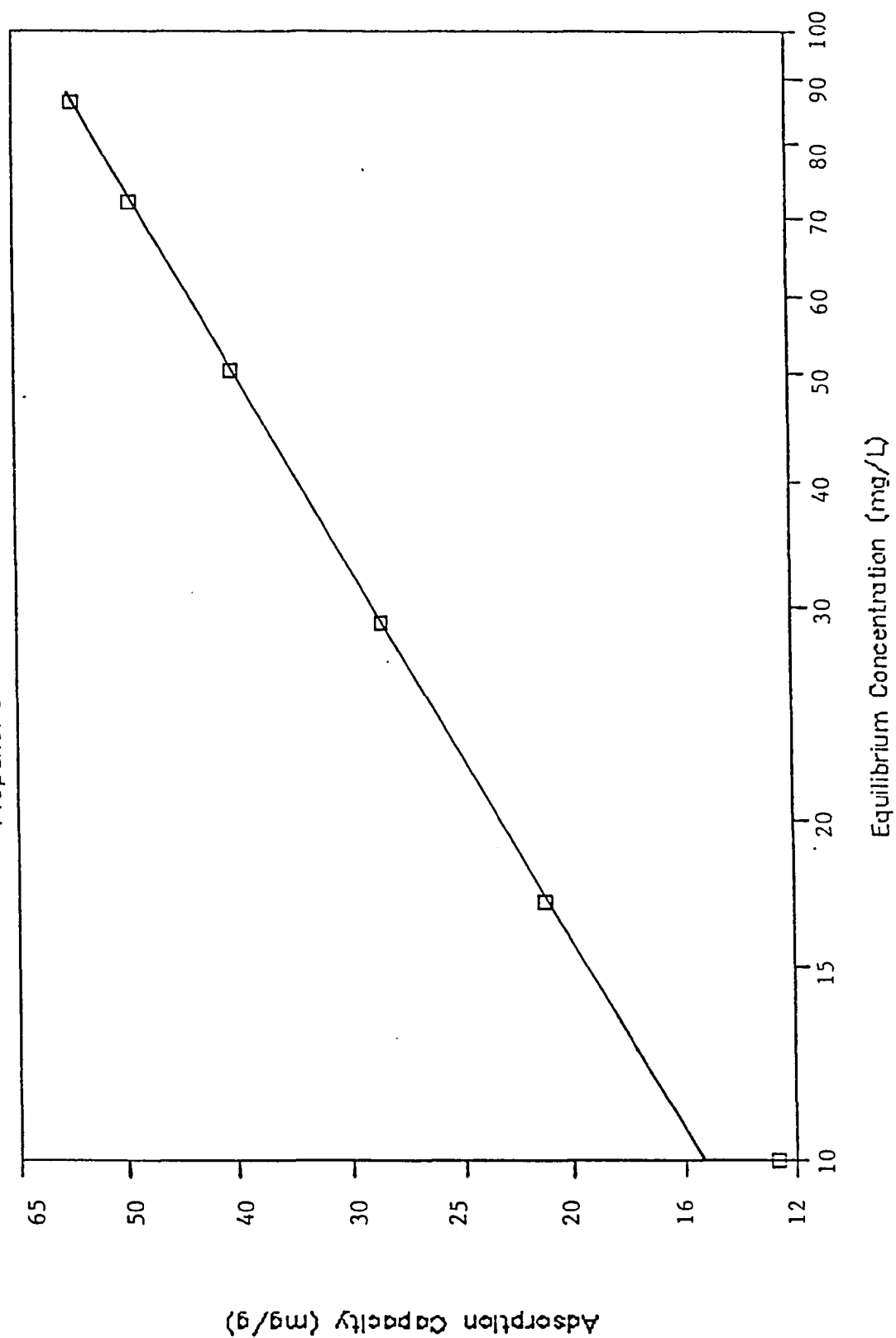
Figure C.23 Adsorption Isotherm
Butanol onto Activated Carbon

C.23
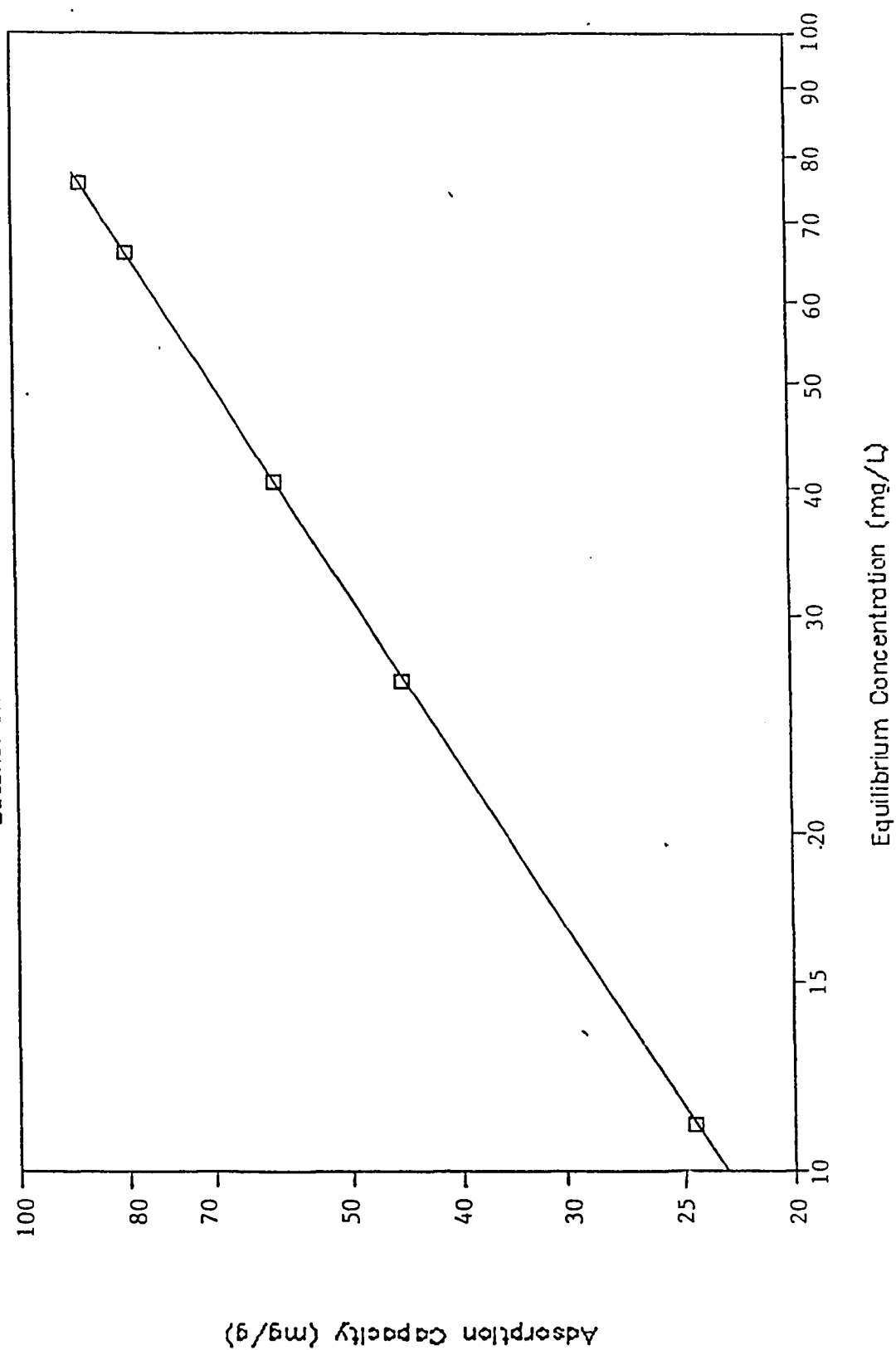
FigureC.24 Adsorption Isotherm

Iso-Propanol onto Activated Carbon

Adsorption Capacity (mg/g)

Equilibrium Concentration (mg/L)

c.24
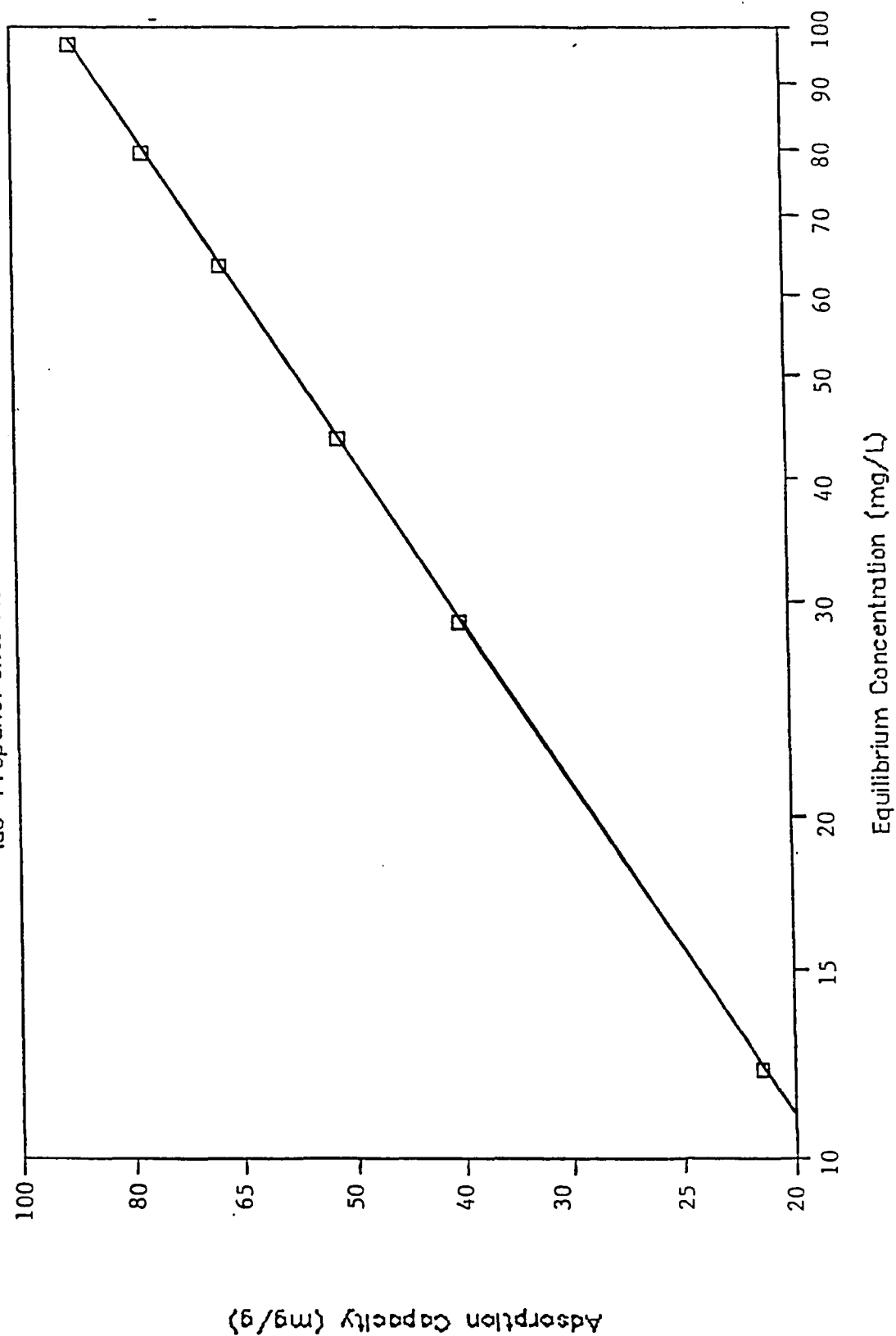
Figure C.25 Adsorption Isotherm
s-Butanol onto Activated Carbon

Equilibrium Concentration (mg/L)

Adsorption Capacity (mg/g)

C.25
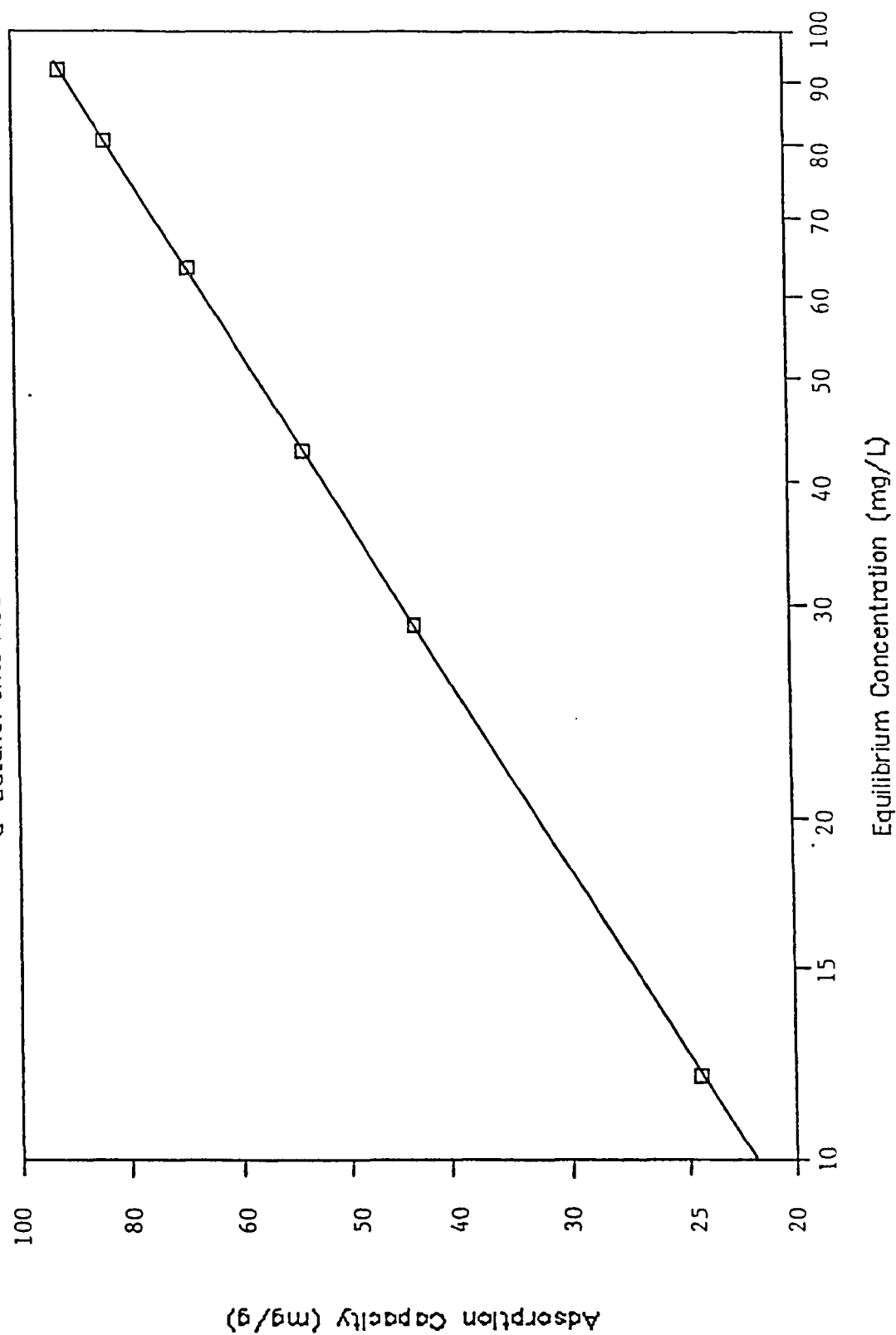
Figure C.26 Adsorption Isotherm
Acetone onto Activated Carbon

Adsorption Capacity (mg/g)

Equilibrium Concentration (mg/L)
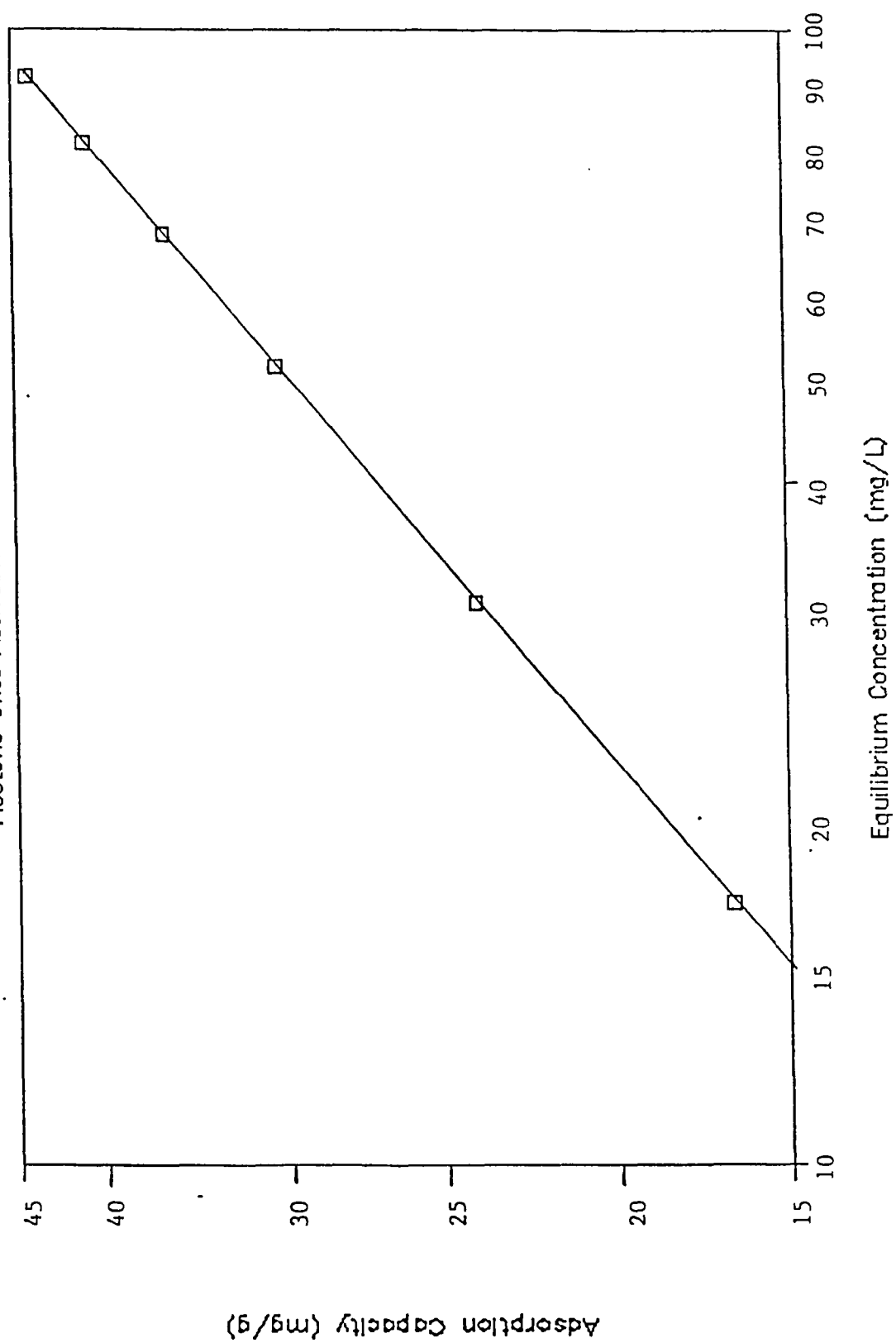
Figure C.27 Adsorption Isotherm
MEK onto Activated Carbon

Adsorption Capacity (mg/g)

Equilibrium Concentration (mg/L)

C.27
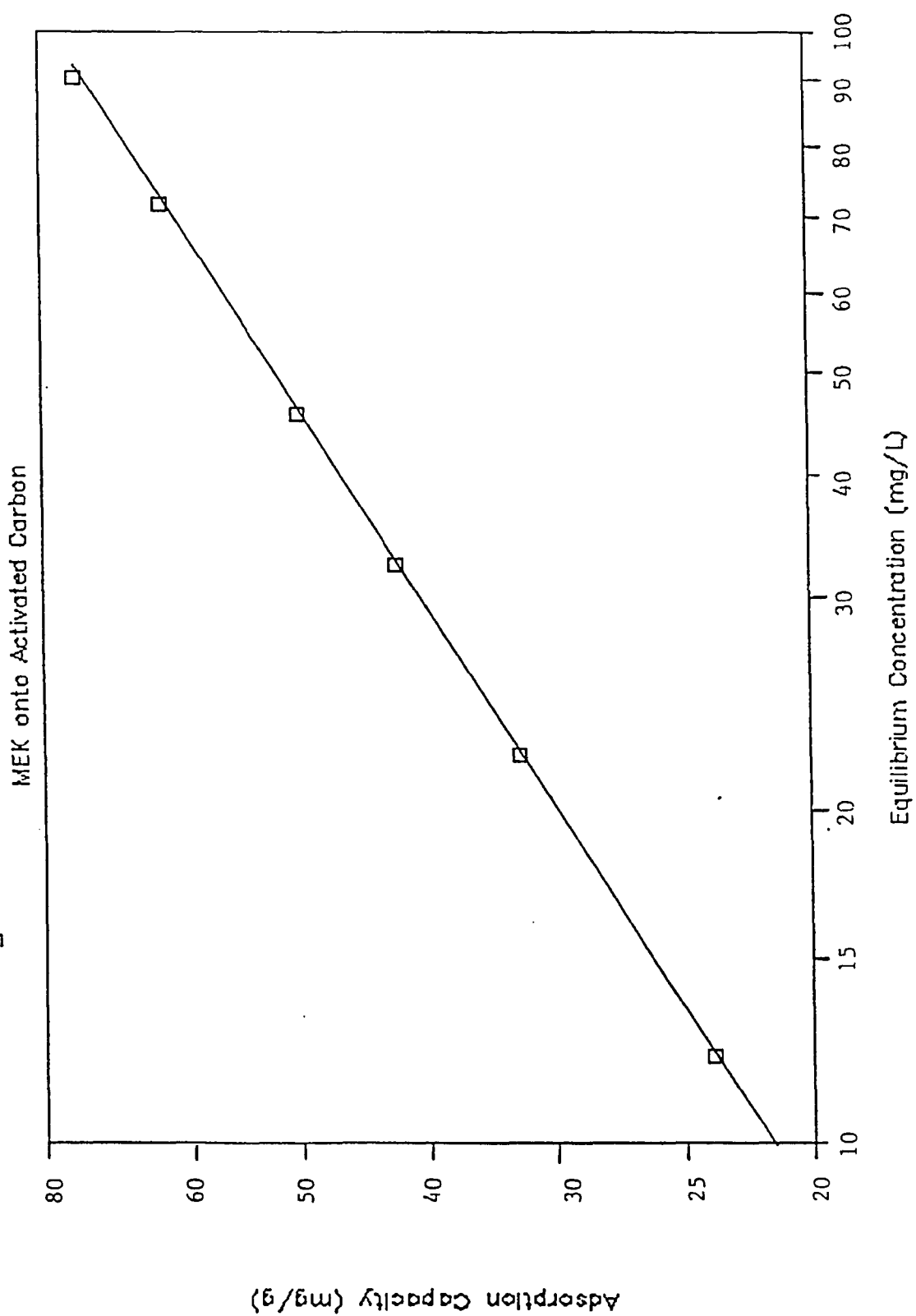
Figure C.28 Adsorption Isotherm

MIBK onto Activated Carbon

Equilibrium Concentration (mg/L)

Adsorption Capacity (mg/g)

C.28
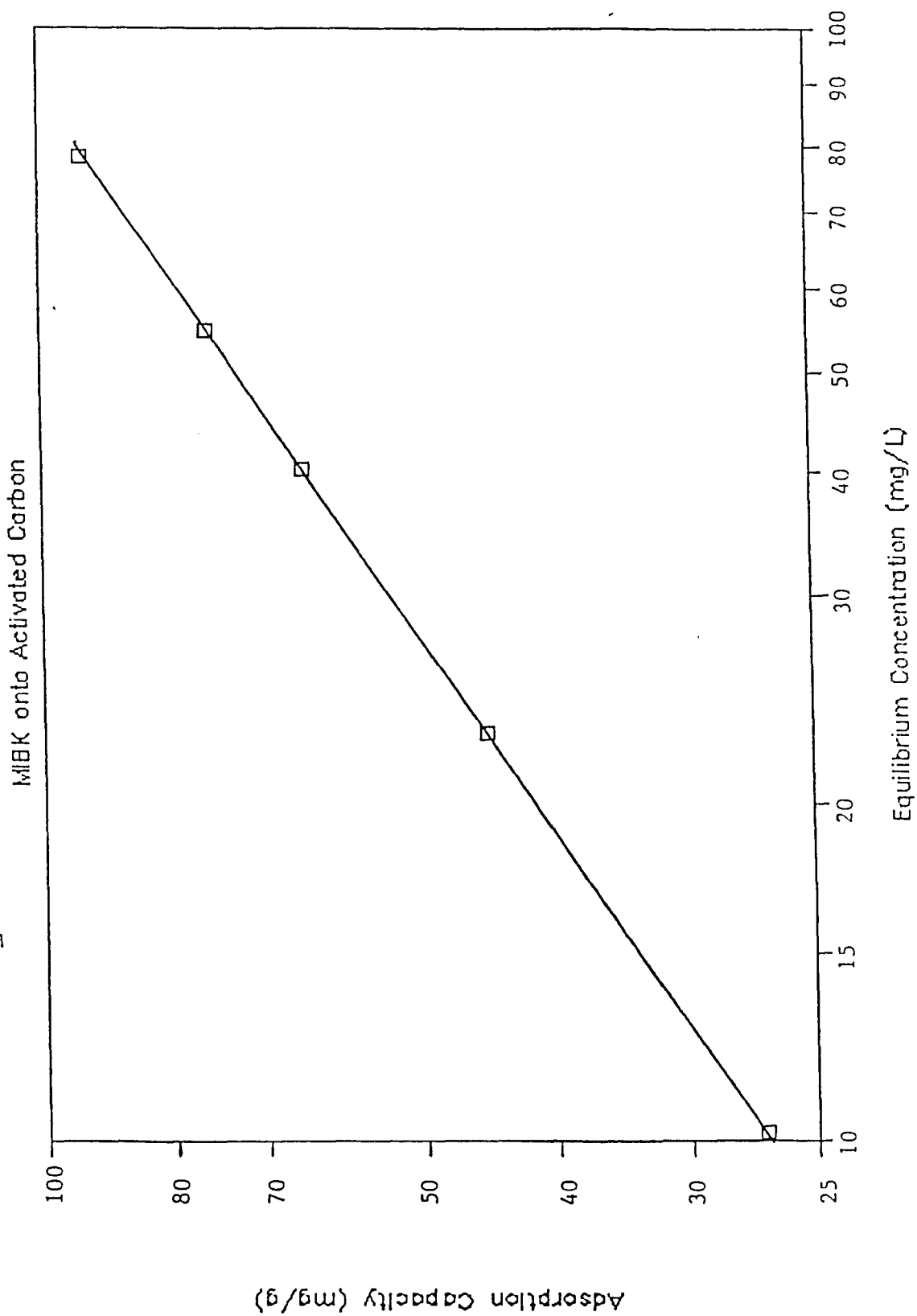
Figure C.29 Adsorption Isotherm
Cyclohexanone onto Activated Carbon

C.29
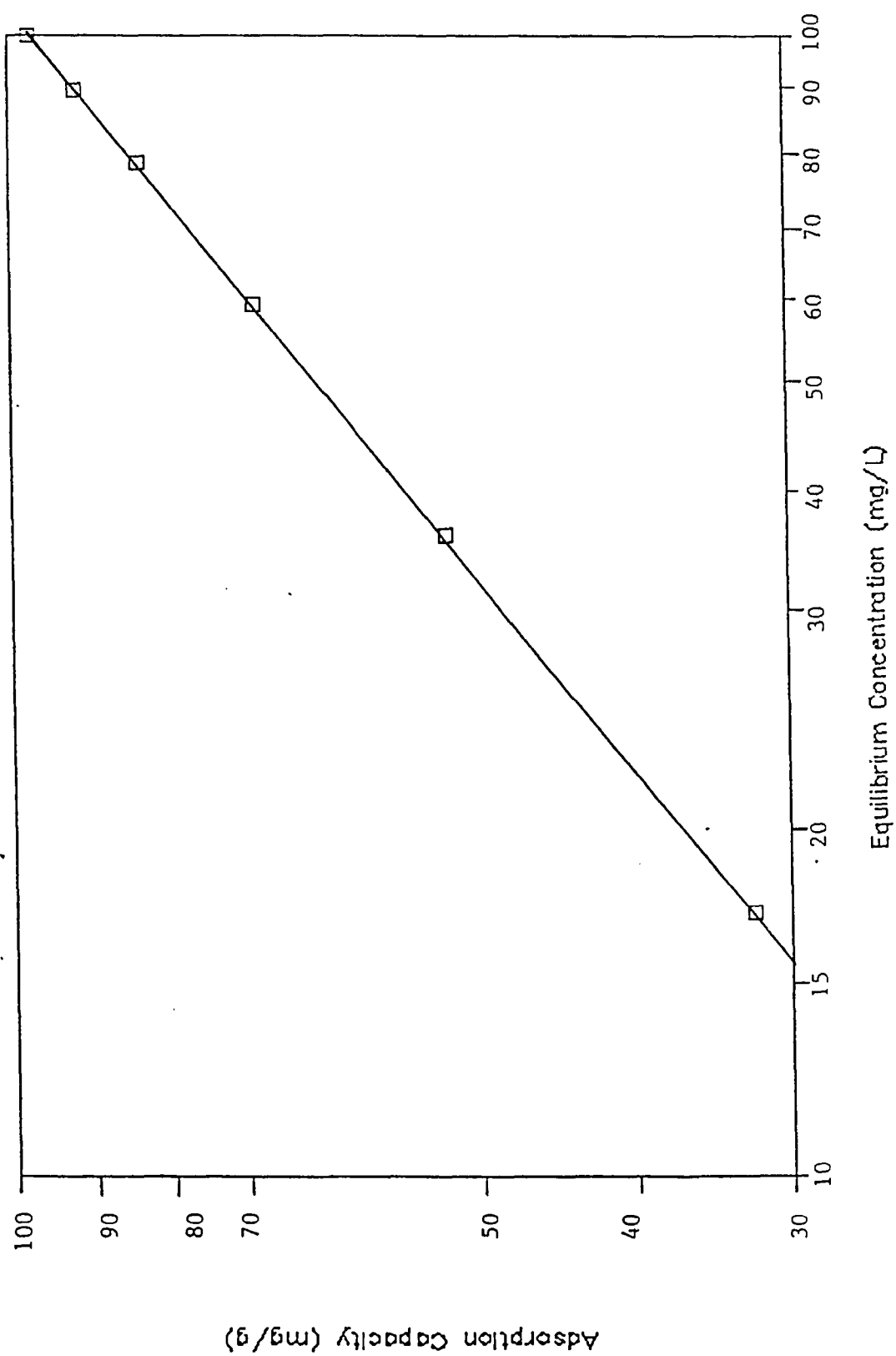
Figure C.30 Adsorption Isotherm
Formaldehyde onto Activated Carbon

Equilibrium Concentration (mg/L)

Adsorption Capacity (mg/g)

C.30
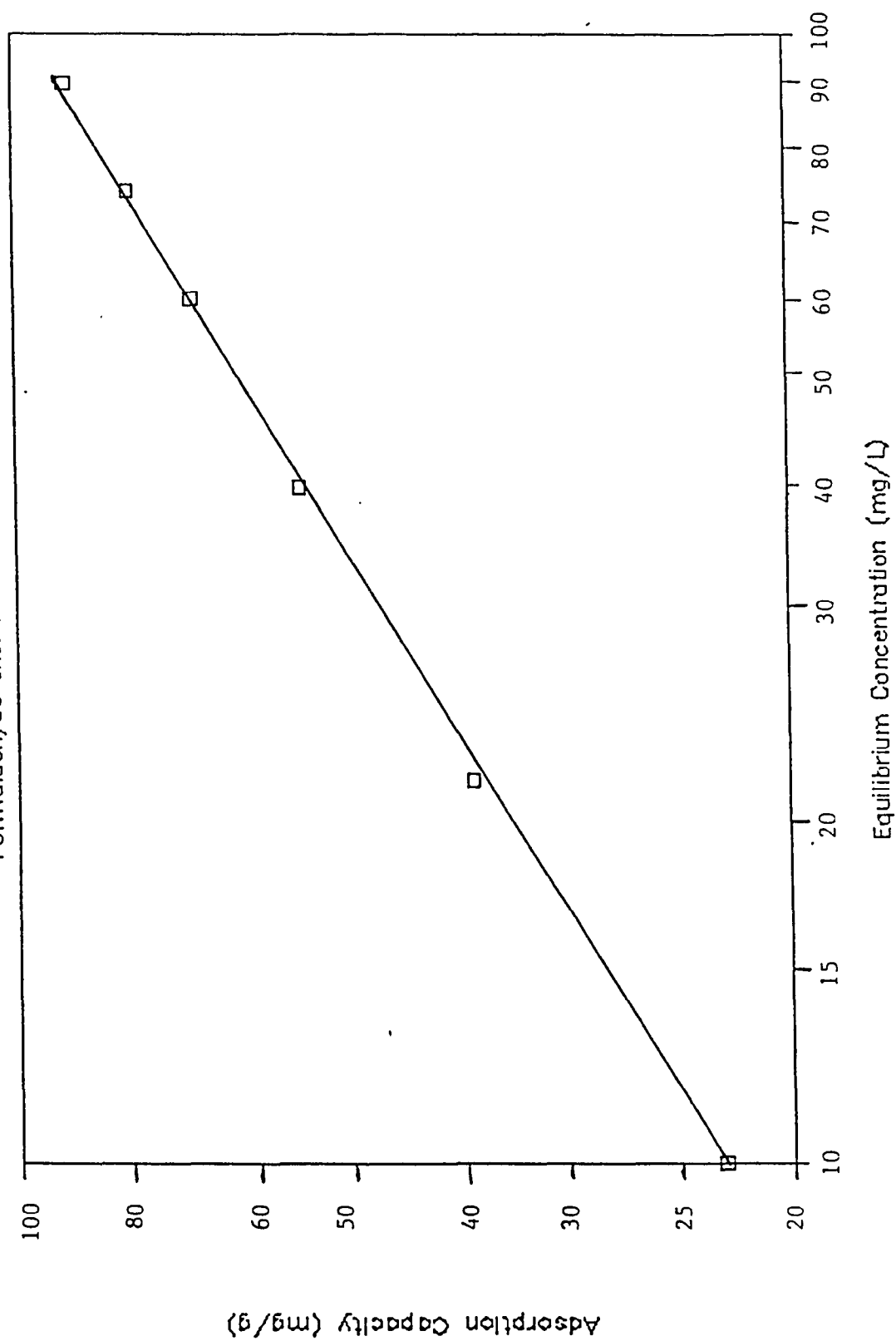
Figure C.31 Adsorption Isotherm
Acetaldehyde onto Activated Carbon

Equilibrium Concentration (mg/L)

Adsorption Capacity (mg/g)
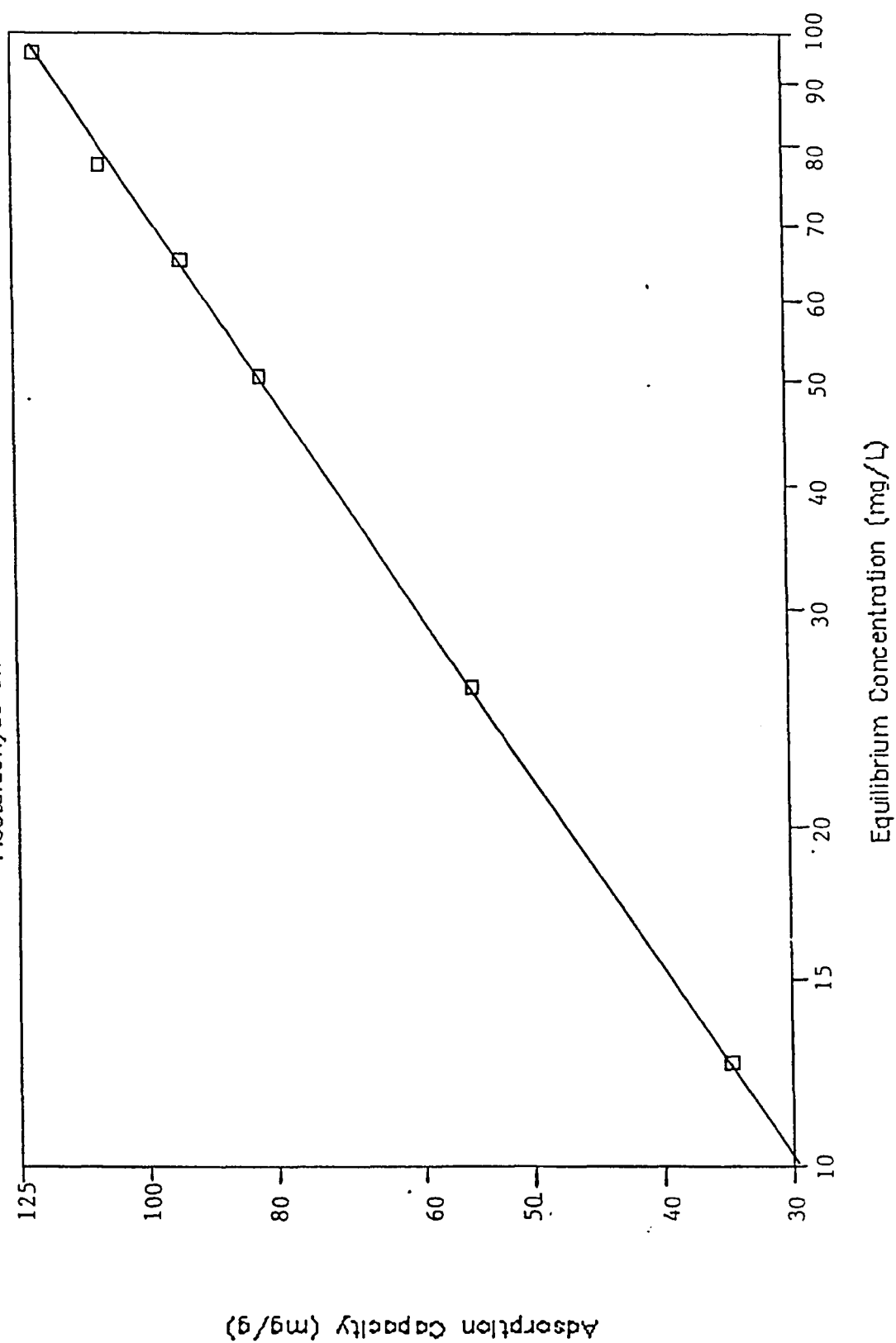
FigureC.32 Adsorption Isotherm

Butyraldehyde onto Activated Carbon

Adsorption Capacity (mg/g)

Equilibrium Concentration (mg/L)

C.32
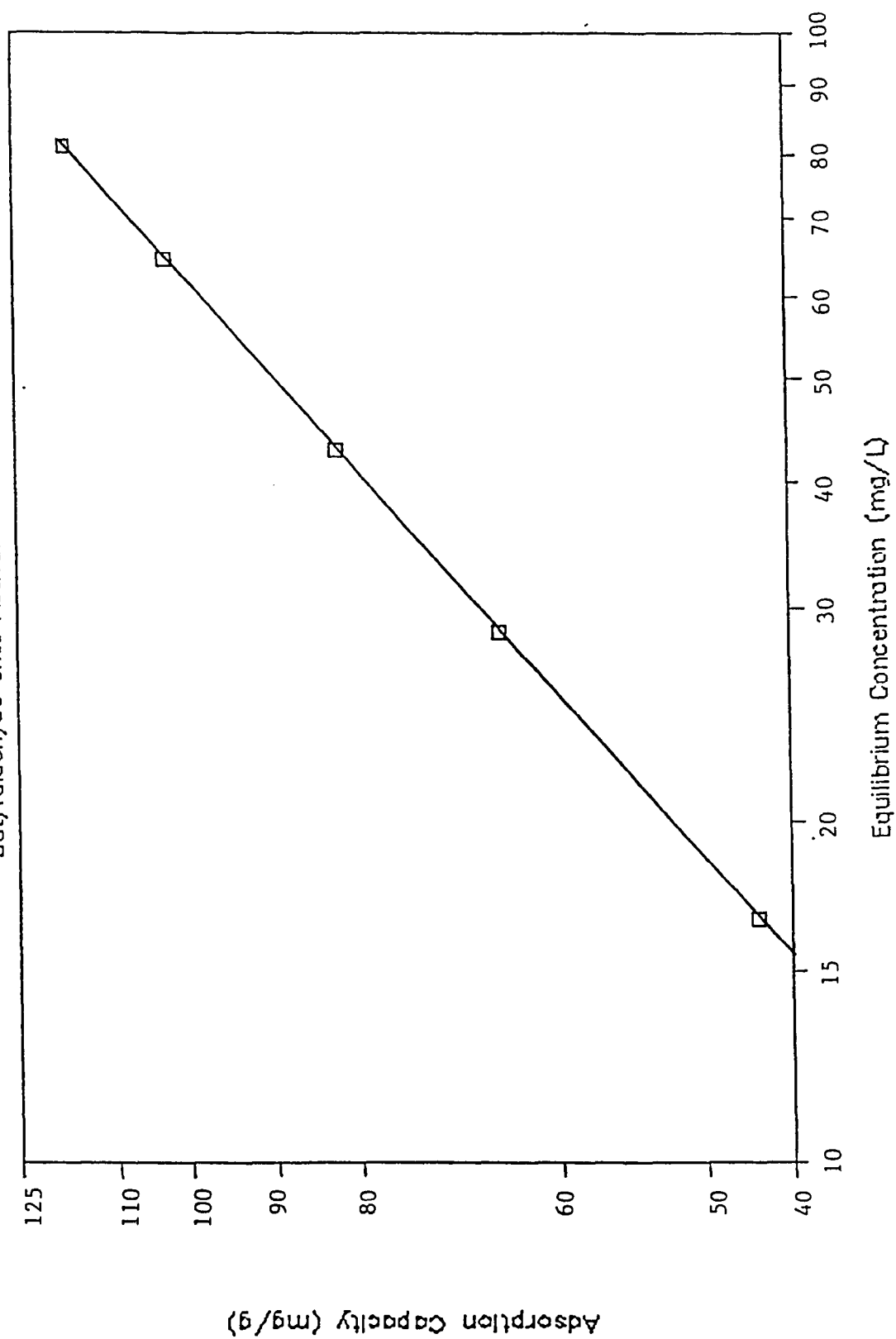
Figure C.33 Adsorption Isotherm
Benzene onto Activated Carbon

C.33
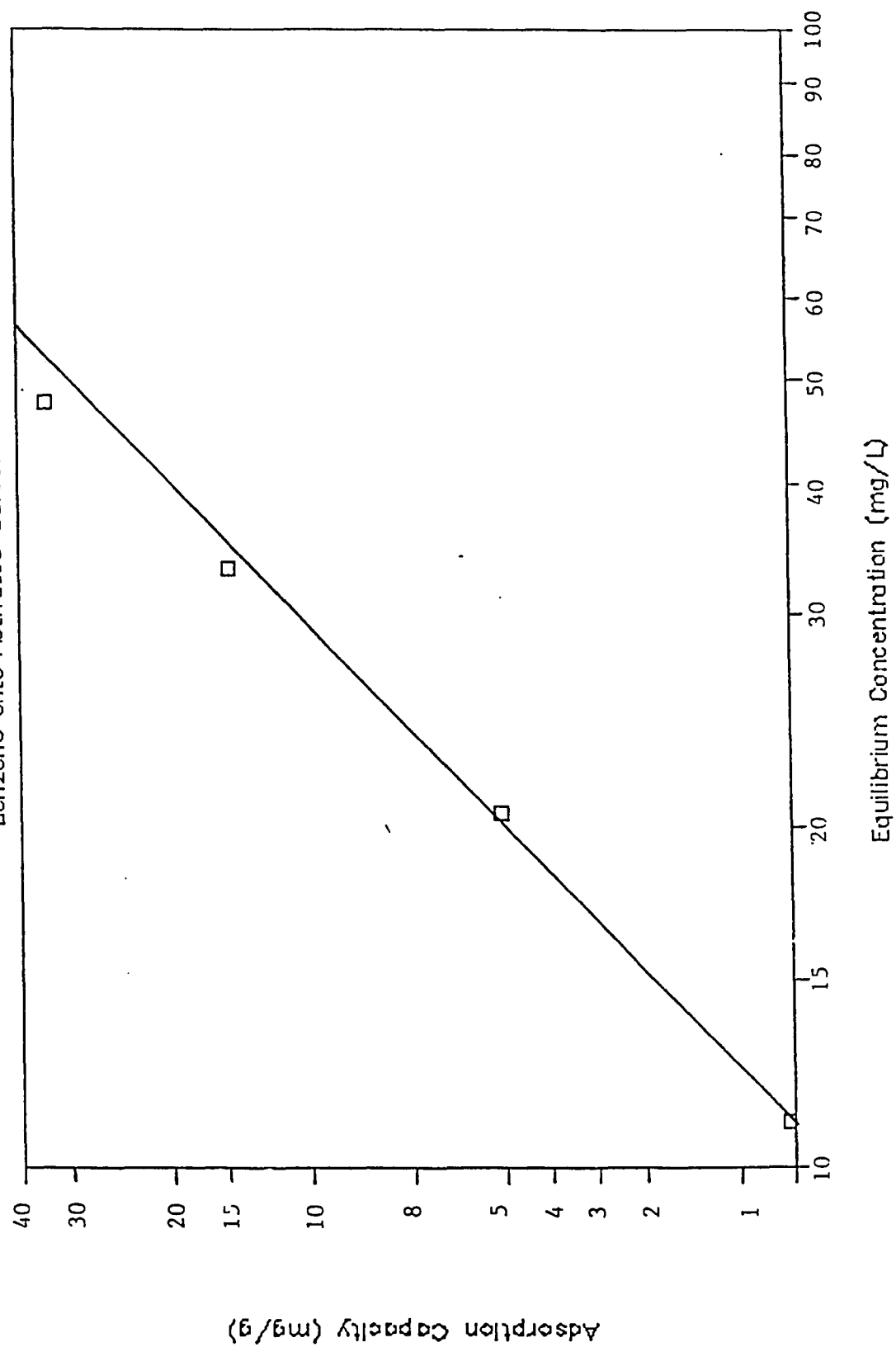
Figure C.34 Adsorption Isotherm
Phenol onto Activated Carbon

C.34
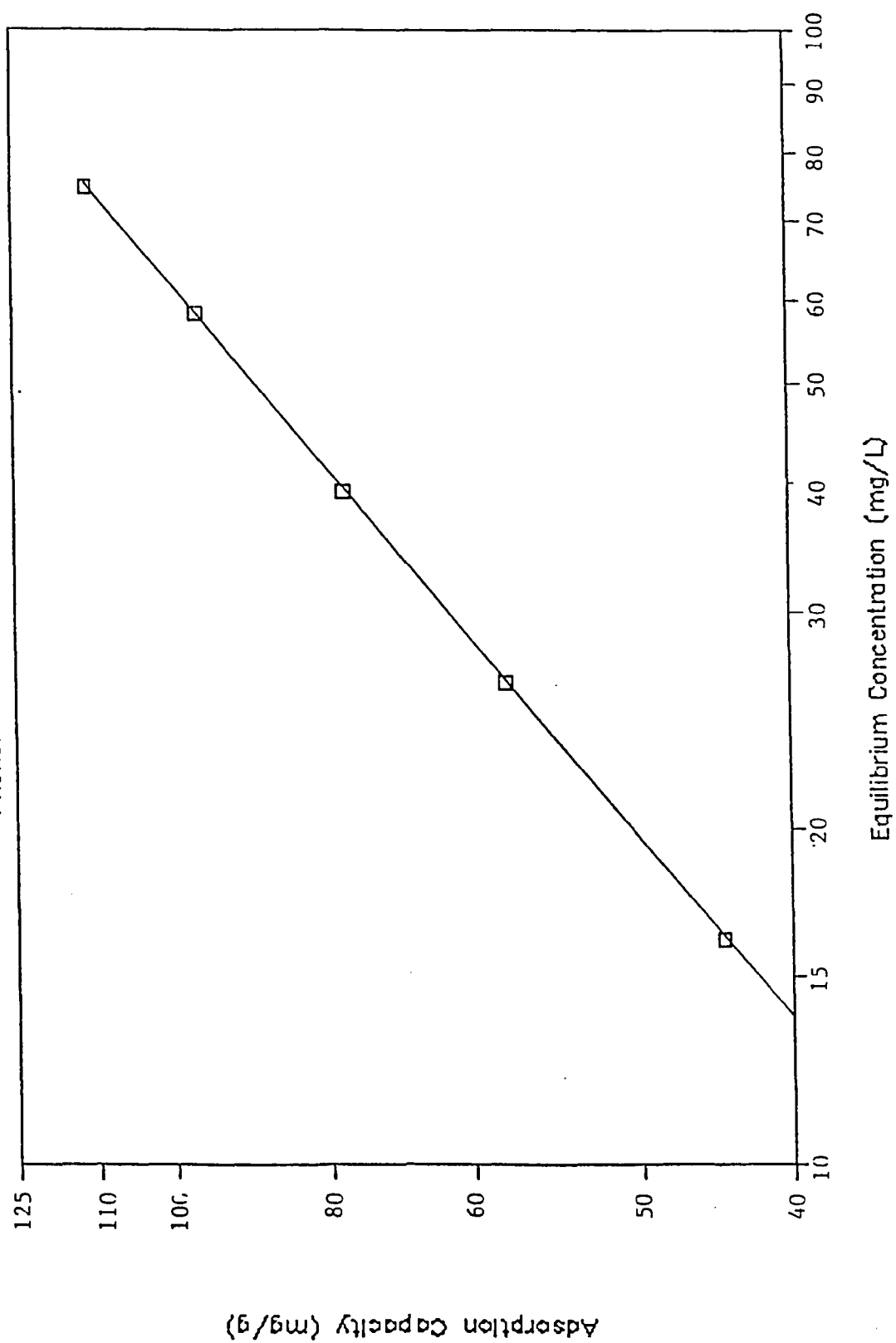
Figure C.35 Adsorption Isotherm
meta-Cresol onto Activated Carbon

Equilibrium Concentration (mg/L)

Adsorption Capacity (mg/g)

C.35
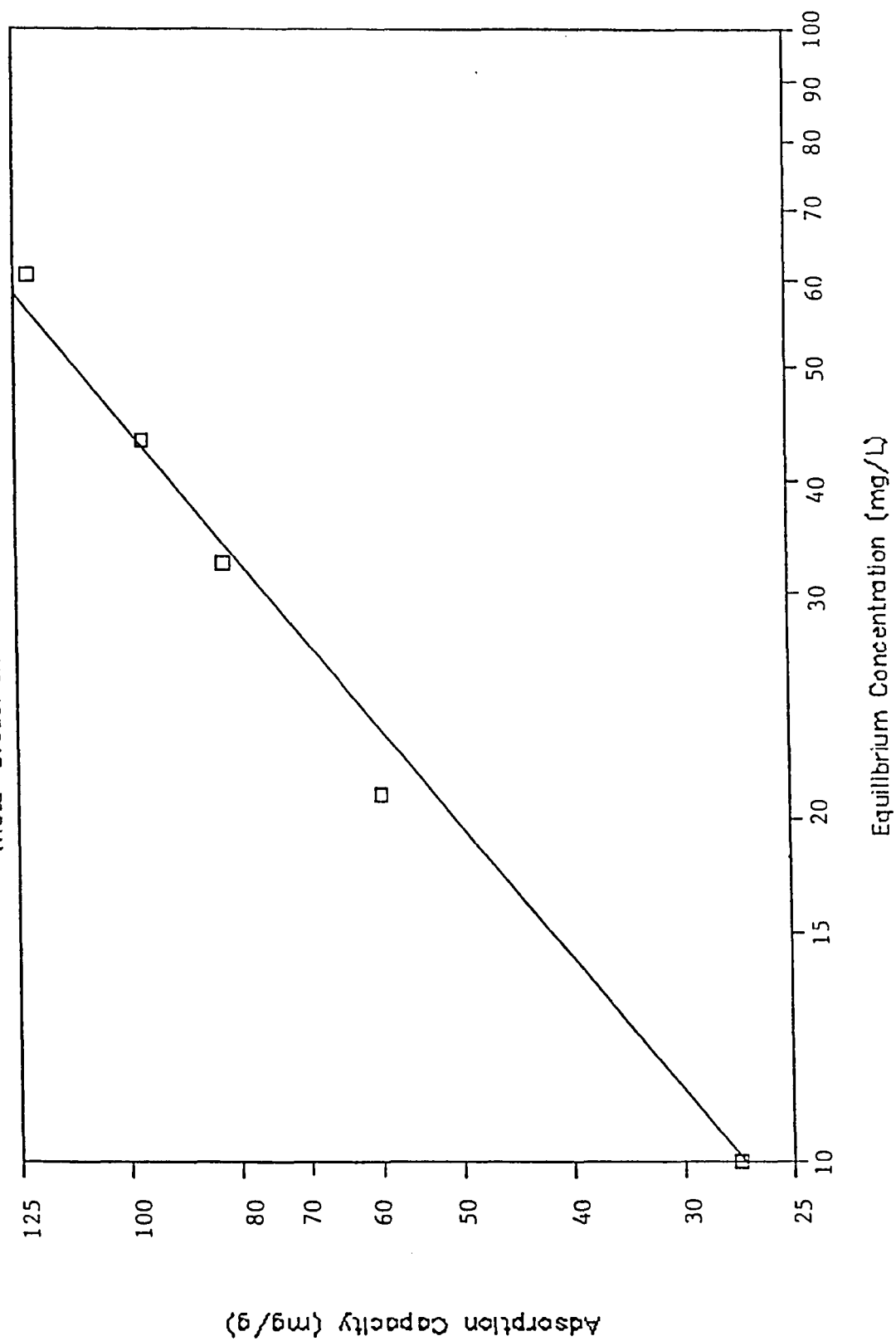
Figure C.36 Adsorption Isotherm

Ethyl Benzene onto Activated Carbon

Adsorption Capacity (mg/g)

Equilibrium Concentration (mg/L)

c.36
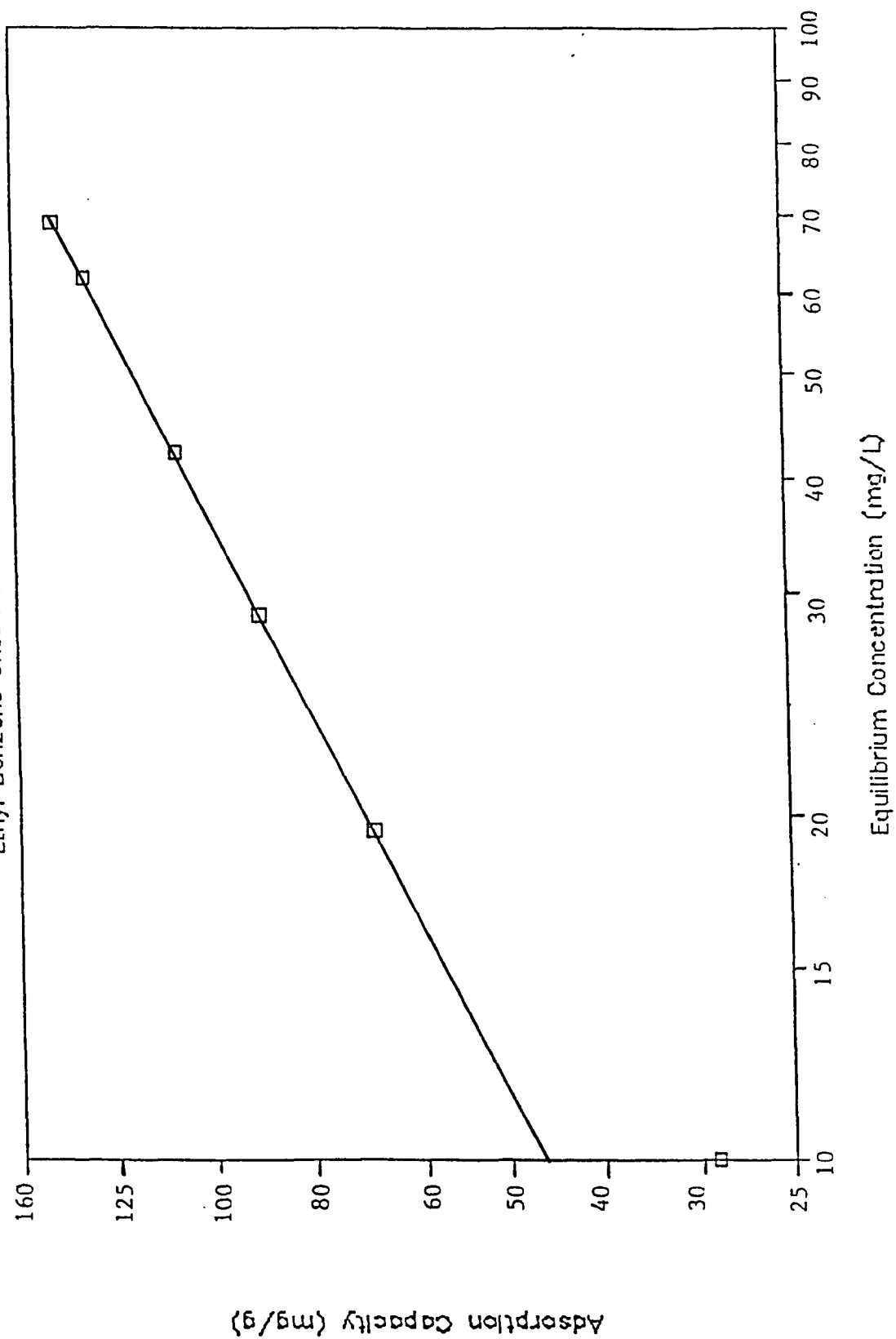
Figure C.37 Adsorption Isotherm
ortho-Xylene onto Activated Carbon

Adsorption Capacity (mg/g)

Equilibrium Concentration (mg/L)

c.37
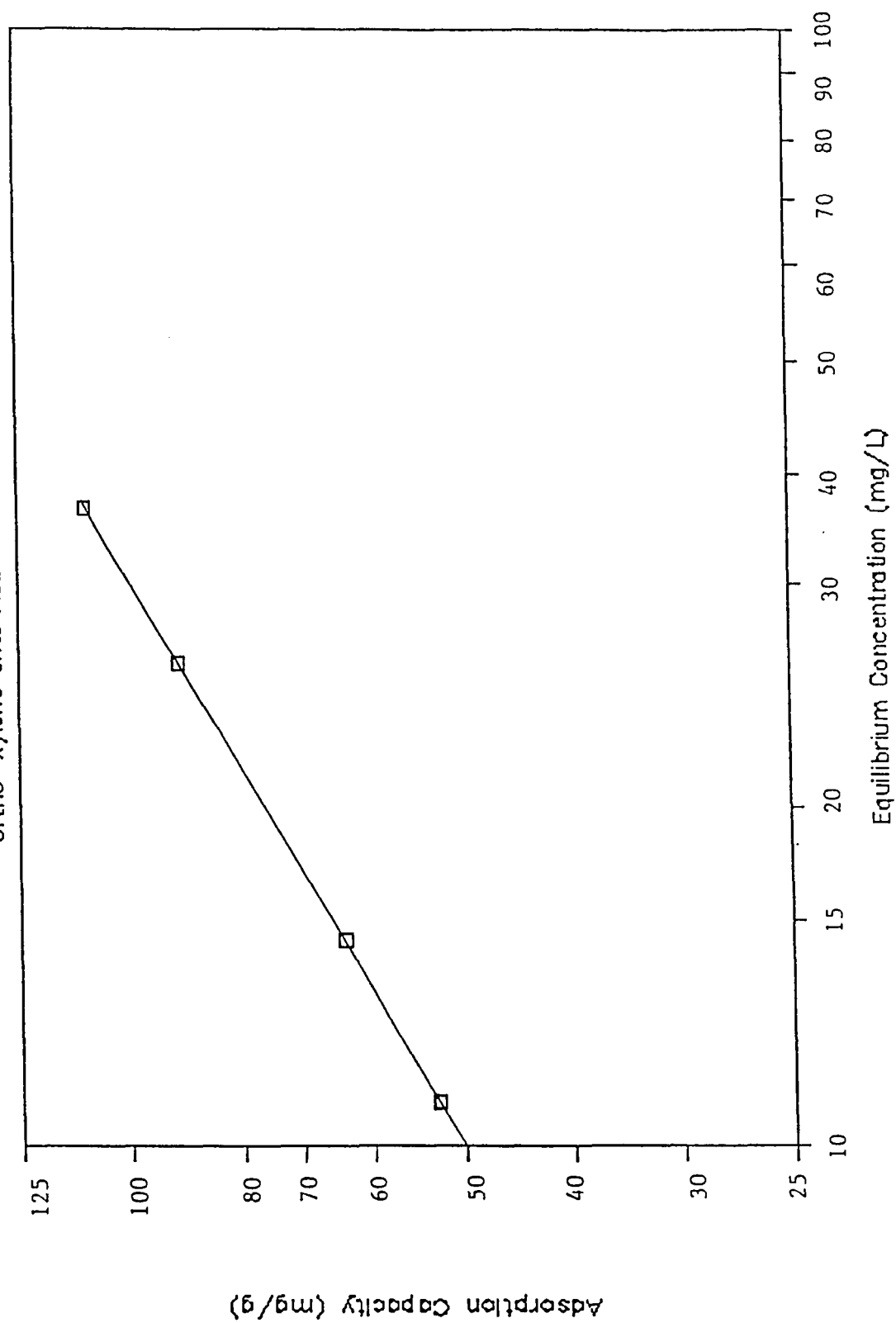
APPENDIX - 'D'

MULTI SOLUTE ADSORPTION EQUILIBRIA

Figure D.1. Two Component Equilibria
Butanol onto Militant Flyash

X/M (ug/g)

Effluent Concentration (mg/L)

□   Single Solute   +   Two Component

D.1
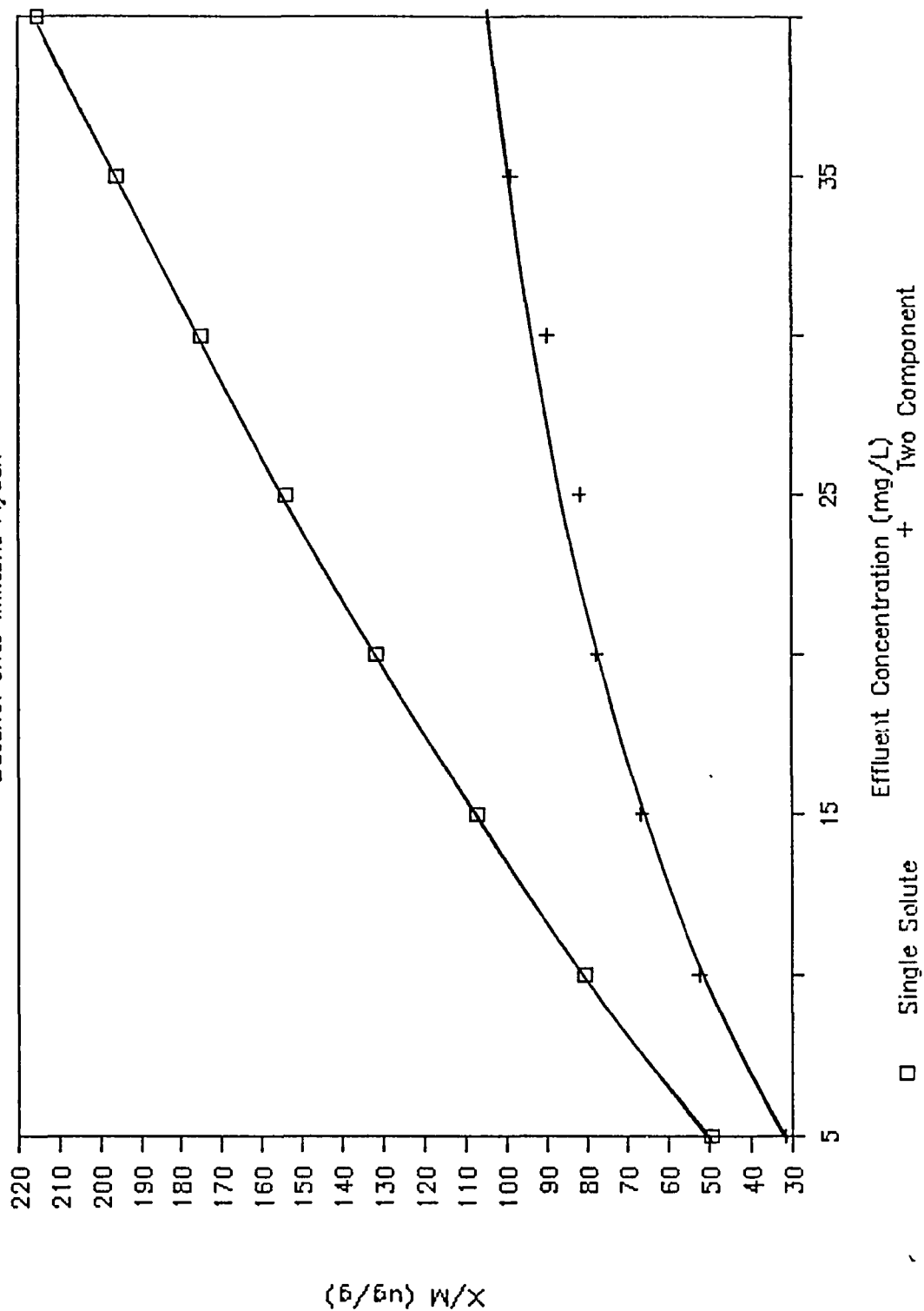
Figure D.2. Two Component Equilibria
o-Xylene onto Militant Flyash
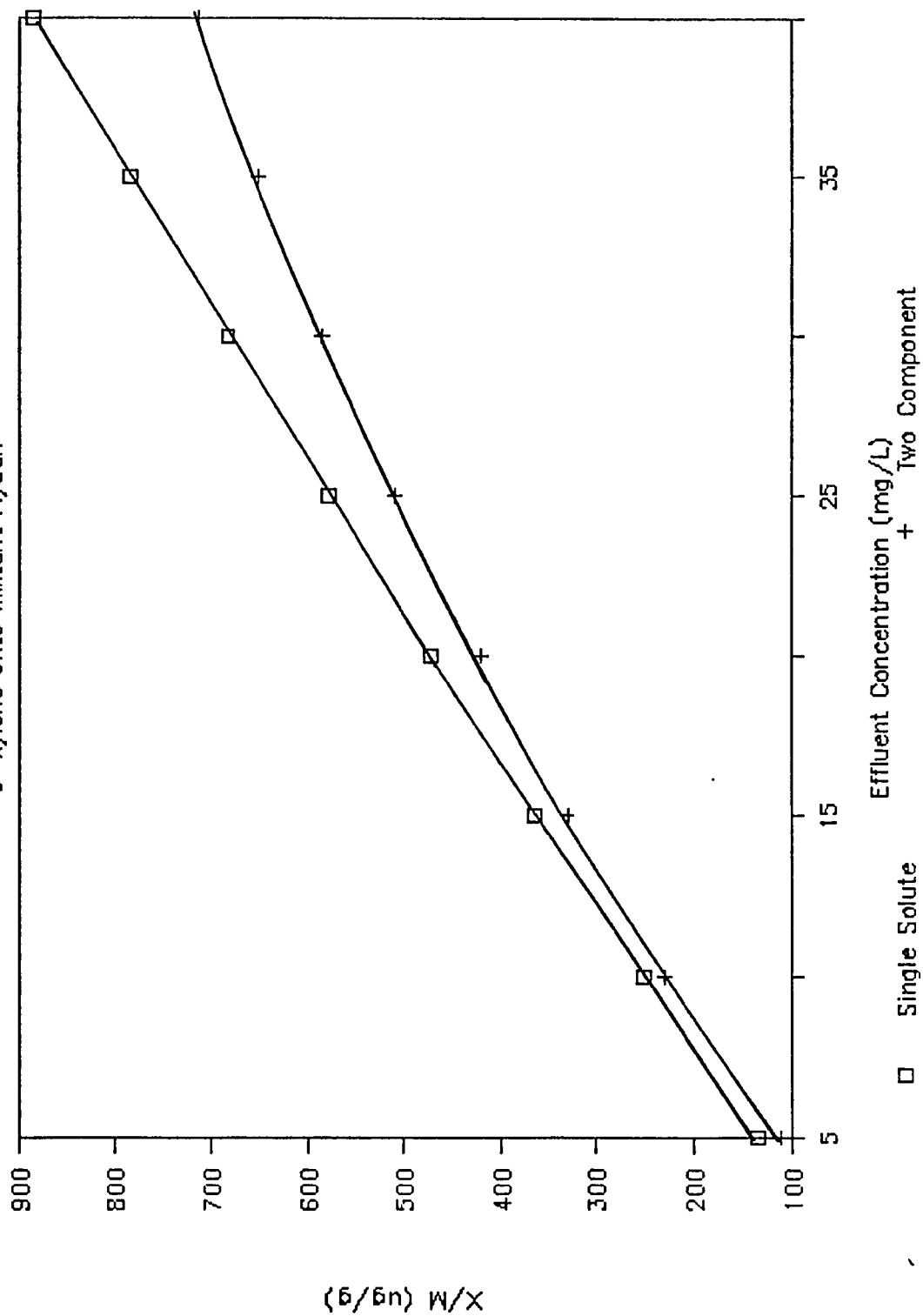
Figure D.3. Two Component Equilibria
Butyraldehyde onto Militant Flyash

X/M (ug/g)

Effluent Concentration (mg/L)

□ Single Solute
+ Two Component

D.3
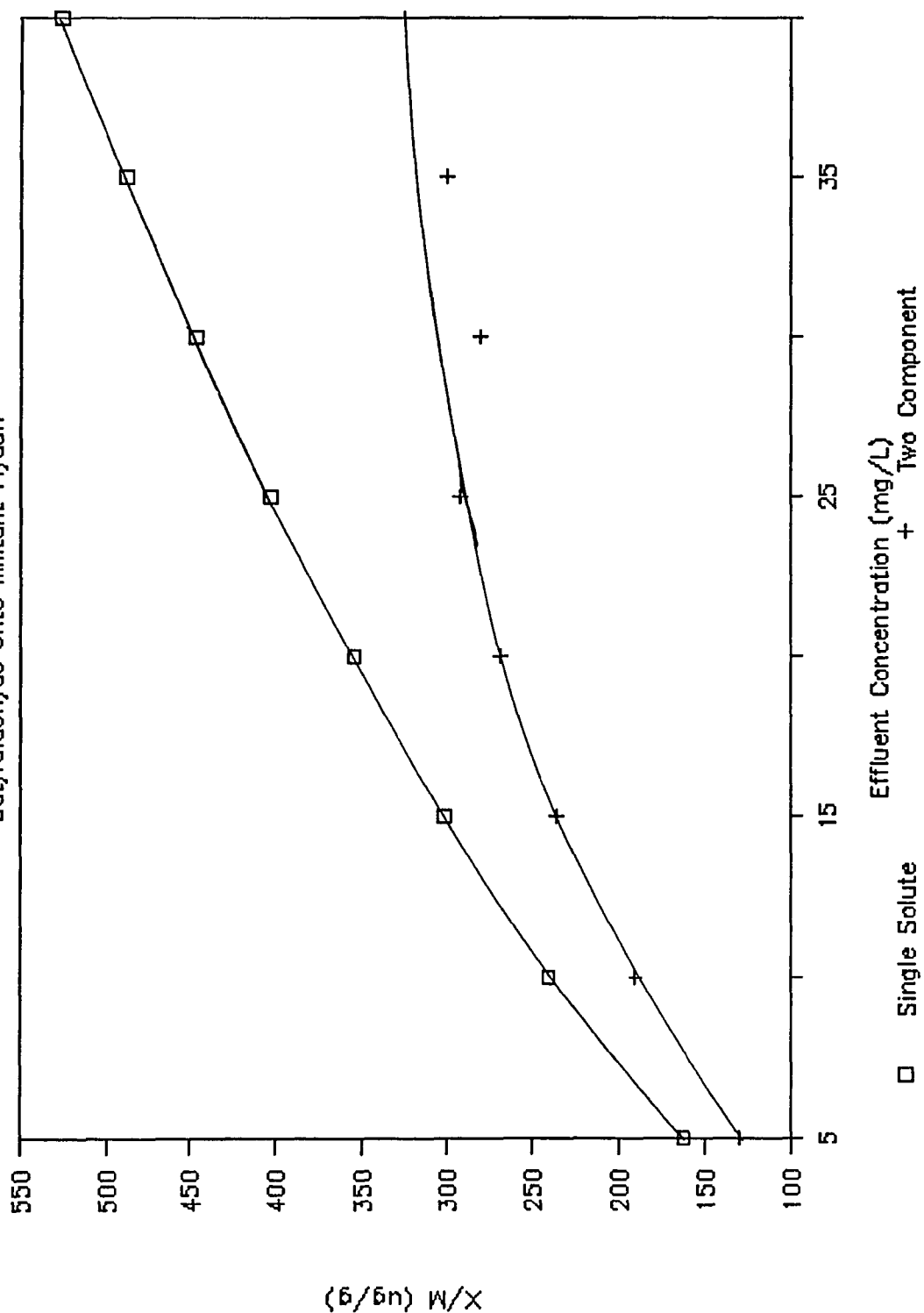
Figure D.4. Two Component Equilibria
o-Xylene onto Militant Flyash

X/M (ug/g)

Effluent Concentration (mg/L)

□   Single Solute   +   Two Component
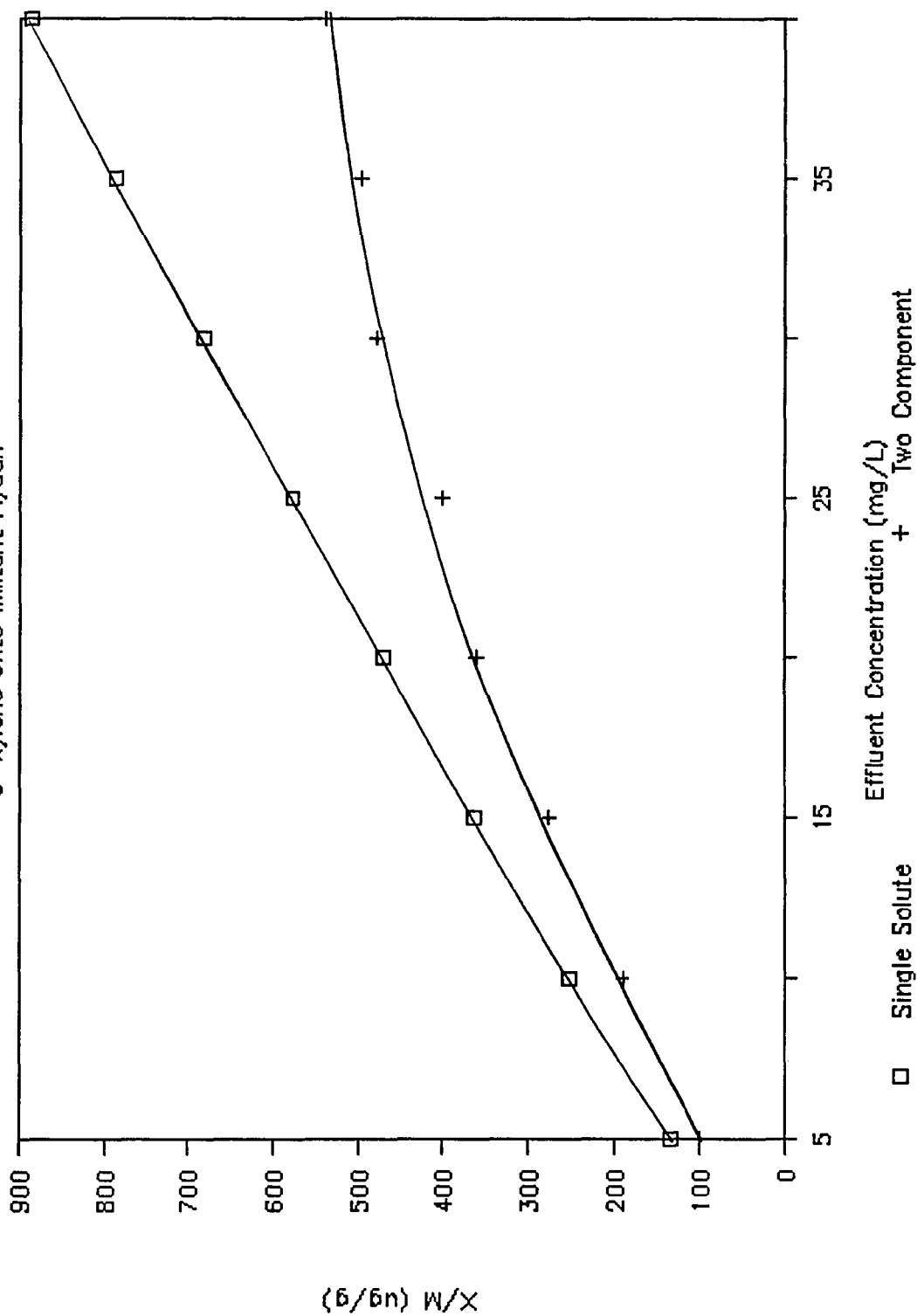
Figure D.5. Four Component Equilibria

Butanol onto Militant Flyash

Effluent Concentration (mg/L)

□ Single Solute   + Four Component

X/M (ug/g)

D.5
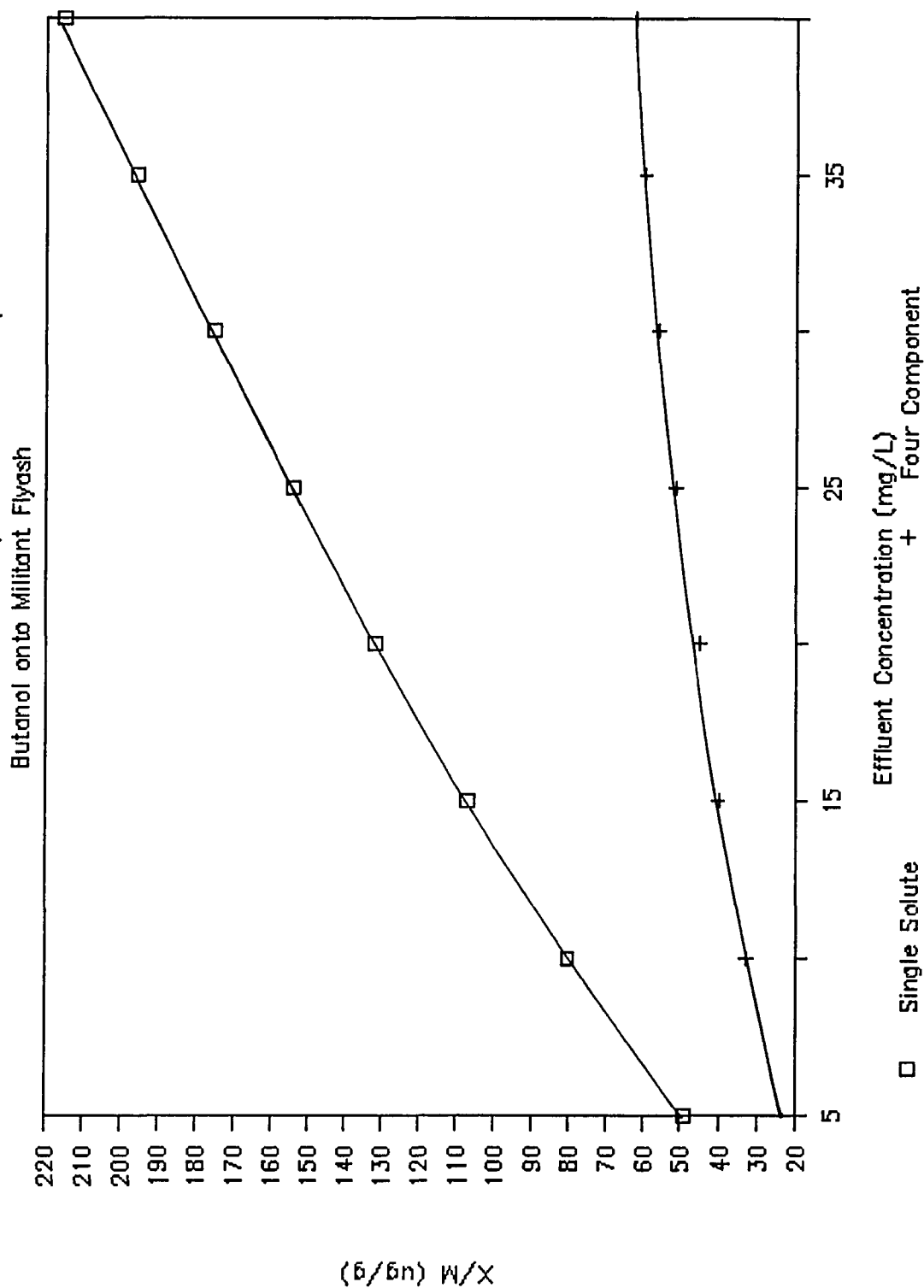
Figure D. . Four Component Equilibria

o-Xylene onto Militant Flyash

Effluent Concentration (mg/L)

□ Single Solute   + Four Component

X/M (ug/g)

D.6
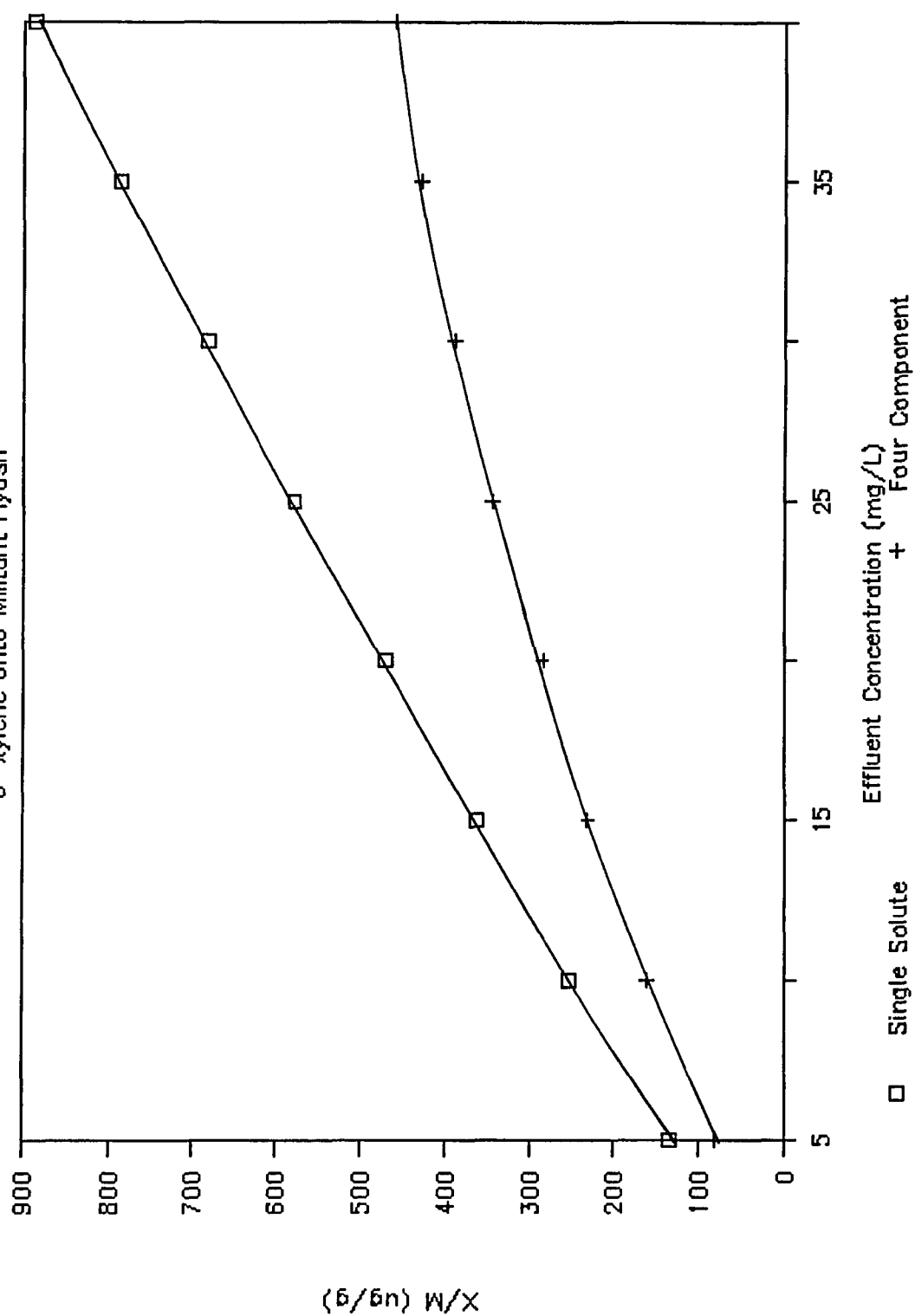
Figure D.7. Four Component Equilibria

Butyraldehyde onto Militant Flyash

X/M (ug/g)

Effluent Concentration (mg/L)

□   Single Solute   +   Four Component

D.7
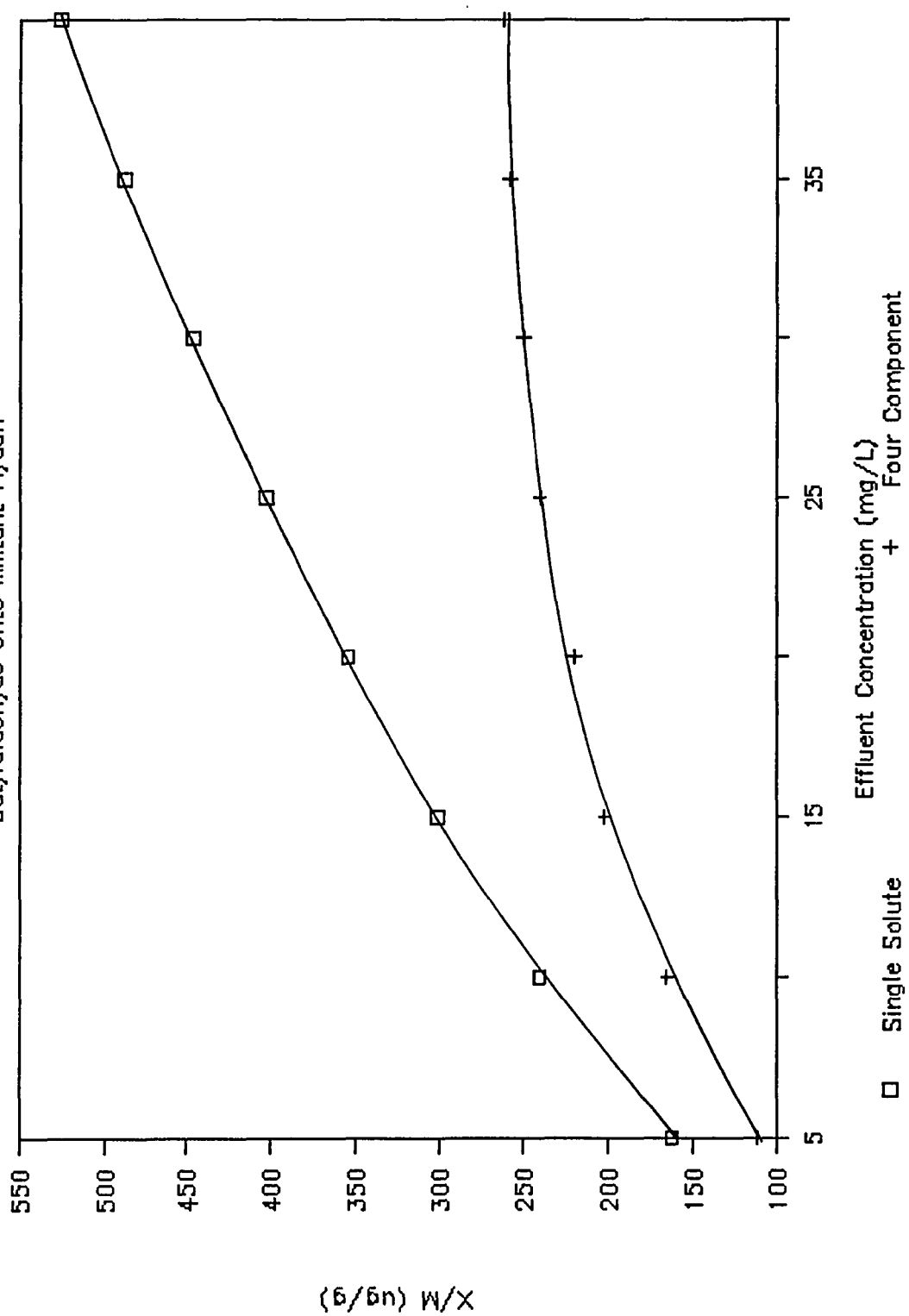
Figure D.8. Four Component Equilibria

MIBK onto Militant Flyash

X/M (ug/g)

Effluent Concentration (mg/L)

□ Single Solute   + Four Component

D.8
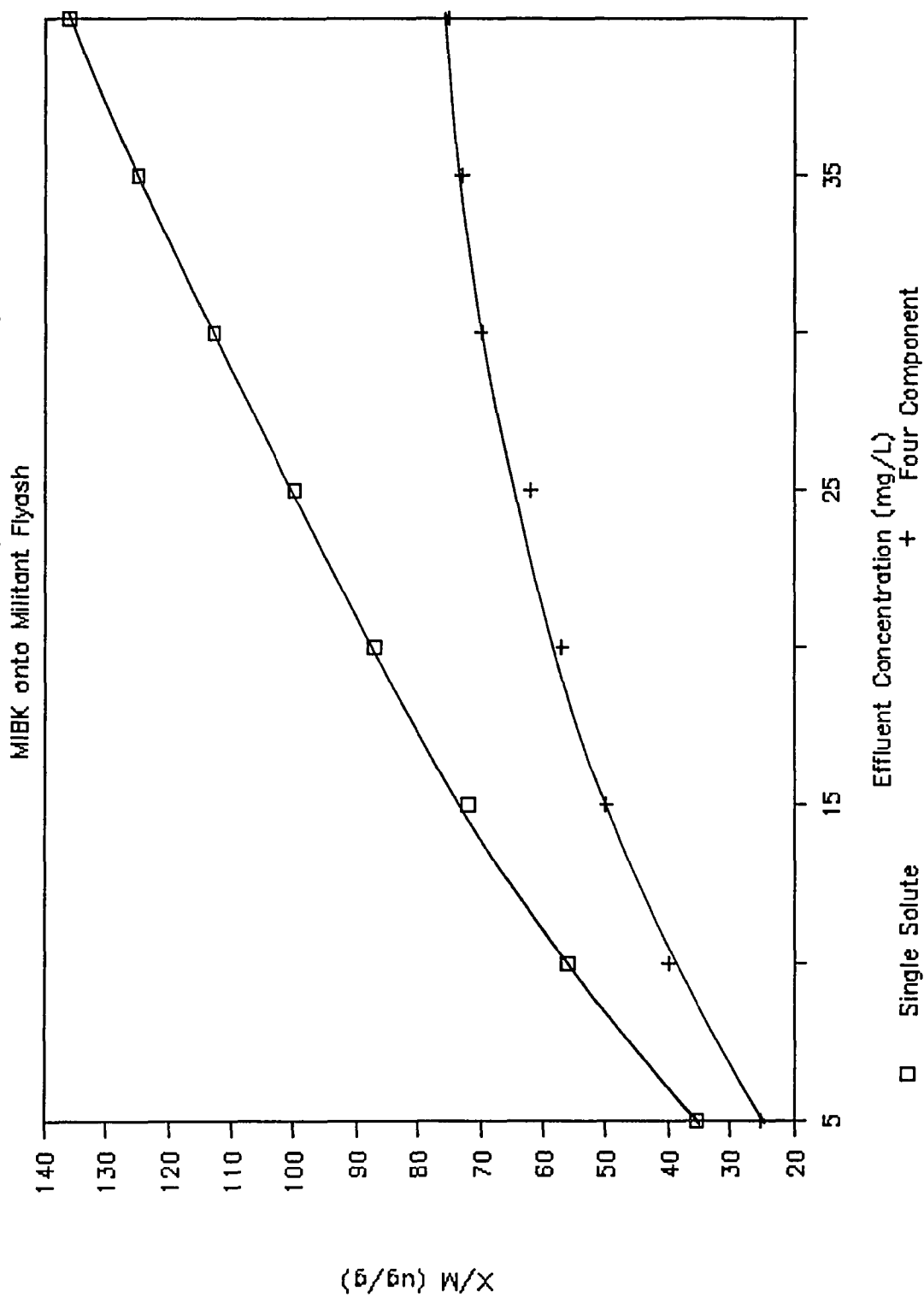
Figure D.9. Four Component Equilibria

o-Xylene onto Militant Flyash

X/M (ug/g)

Effluent Concentration (mg/L)

□ Single Solute   + Four Component
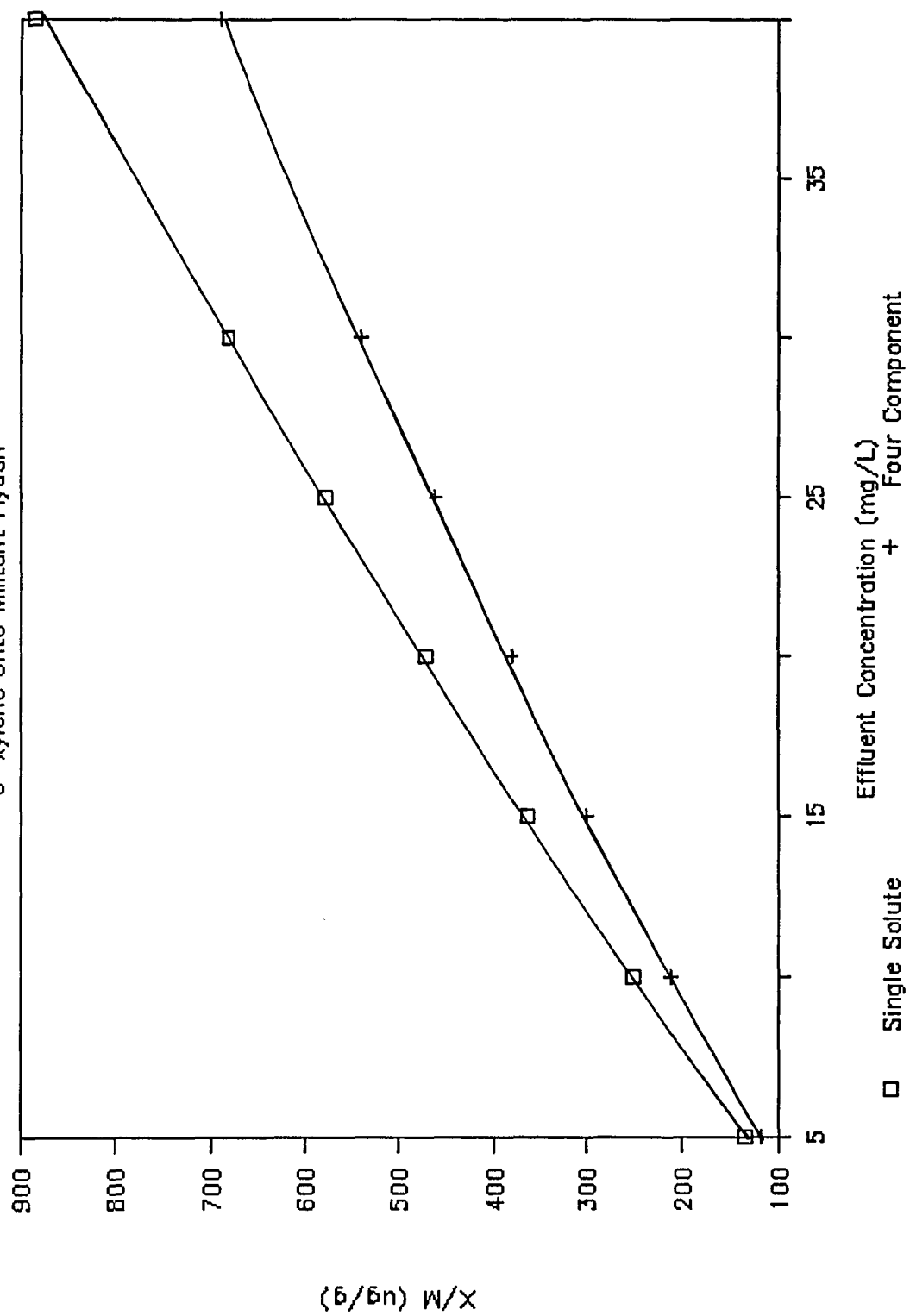
Figure D.10. Four Component Equilibria

m-Cresol onto Militant Flyash

Effluent Concentration (mg/L)

□ Single Solute   + Four Component

X/M (ug/g)

D.10
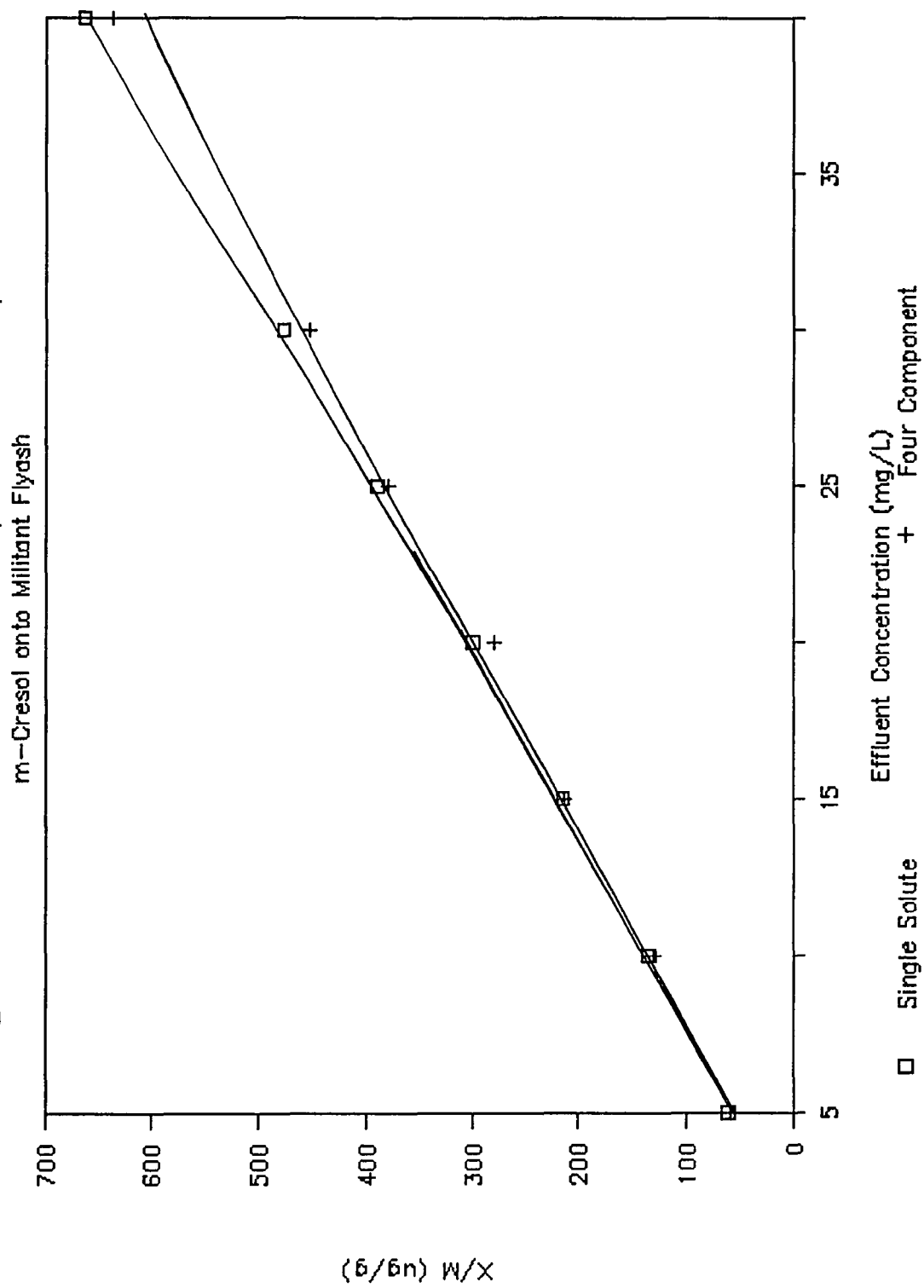
Figure D.11. Four Component Equilibria
Aniline onto Militant Flyash

X/M (ug/g)

Effluent Concentration (mg/L)

□ Single Solute   + Four Component
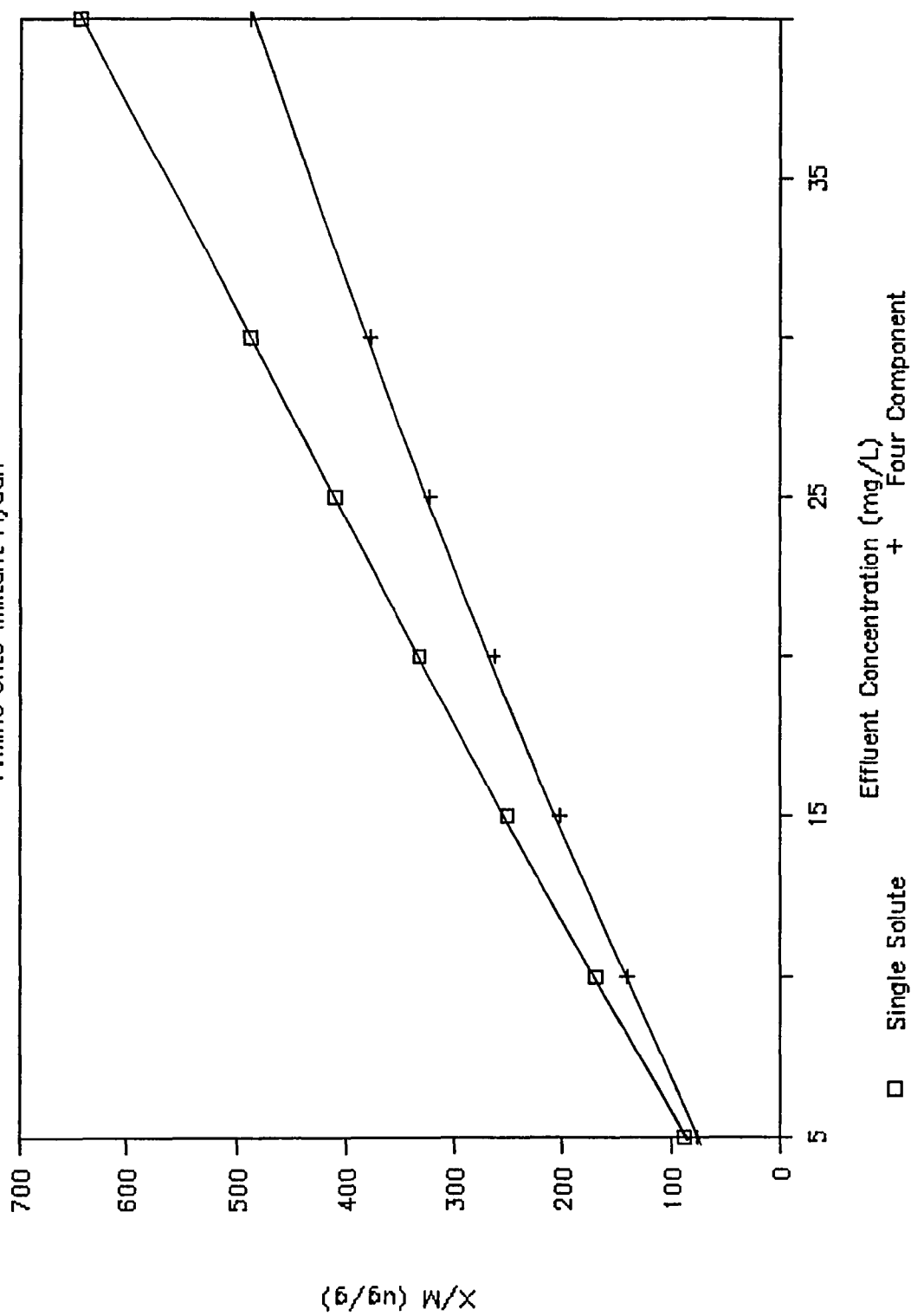
Figure D.12. Four Component Equilibria
Phenol onto Militant Flyash

X/M (ug/g)

Effluent Concentration (mg/L)

□ Single Solute   + Four Component
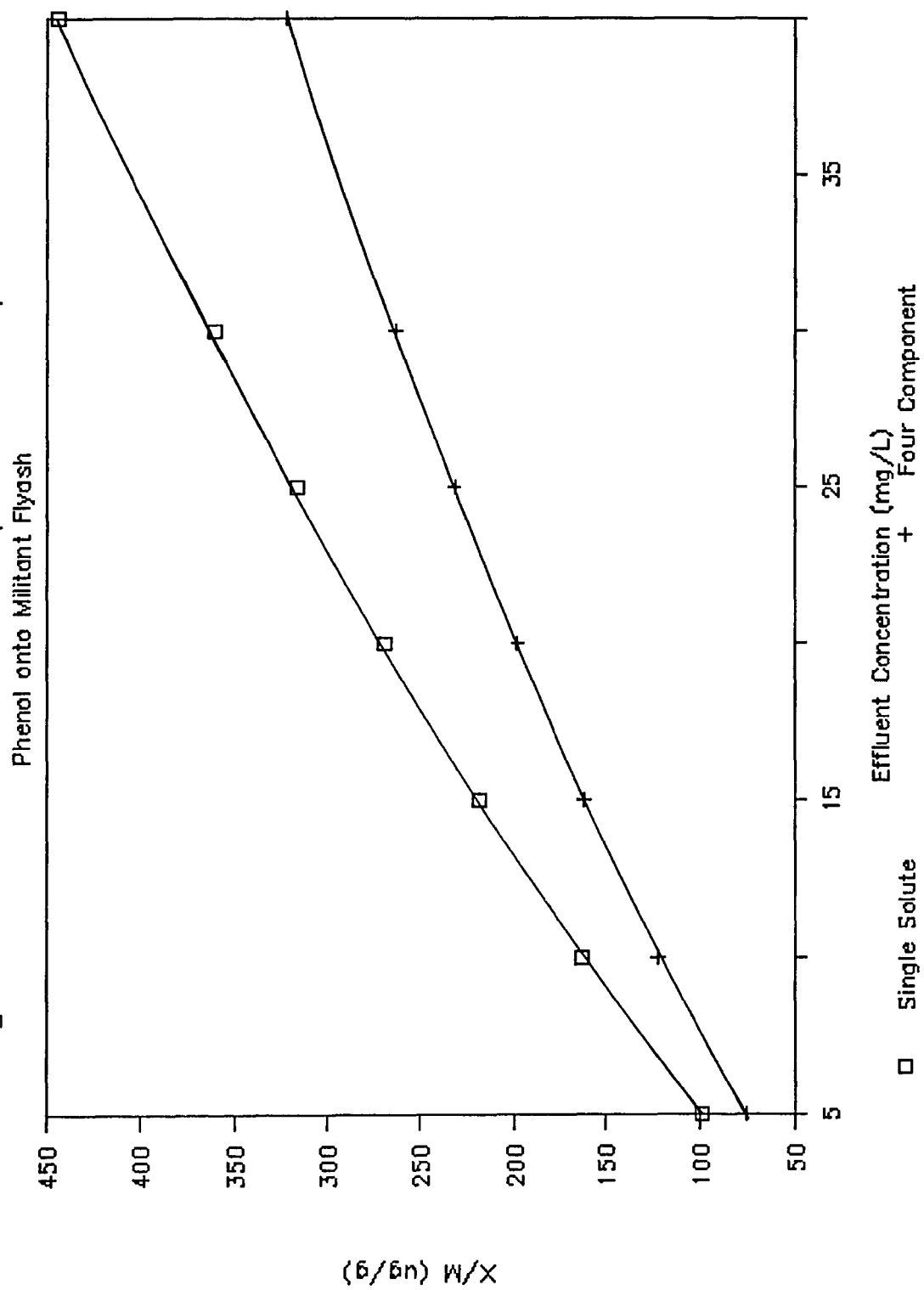
Figure D.13 Two Component Equilibria
Butanol onto Activated Carbon

X/M (mg/g)

Concentration (mg/L)

□ Single solute   + Two Component

D.13
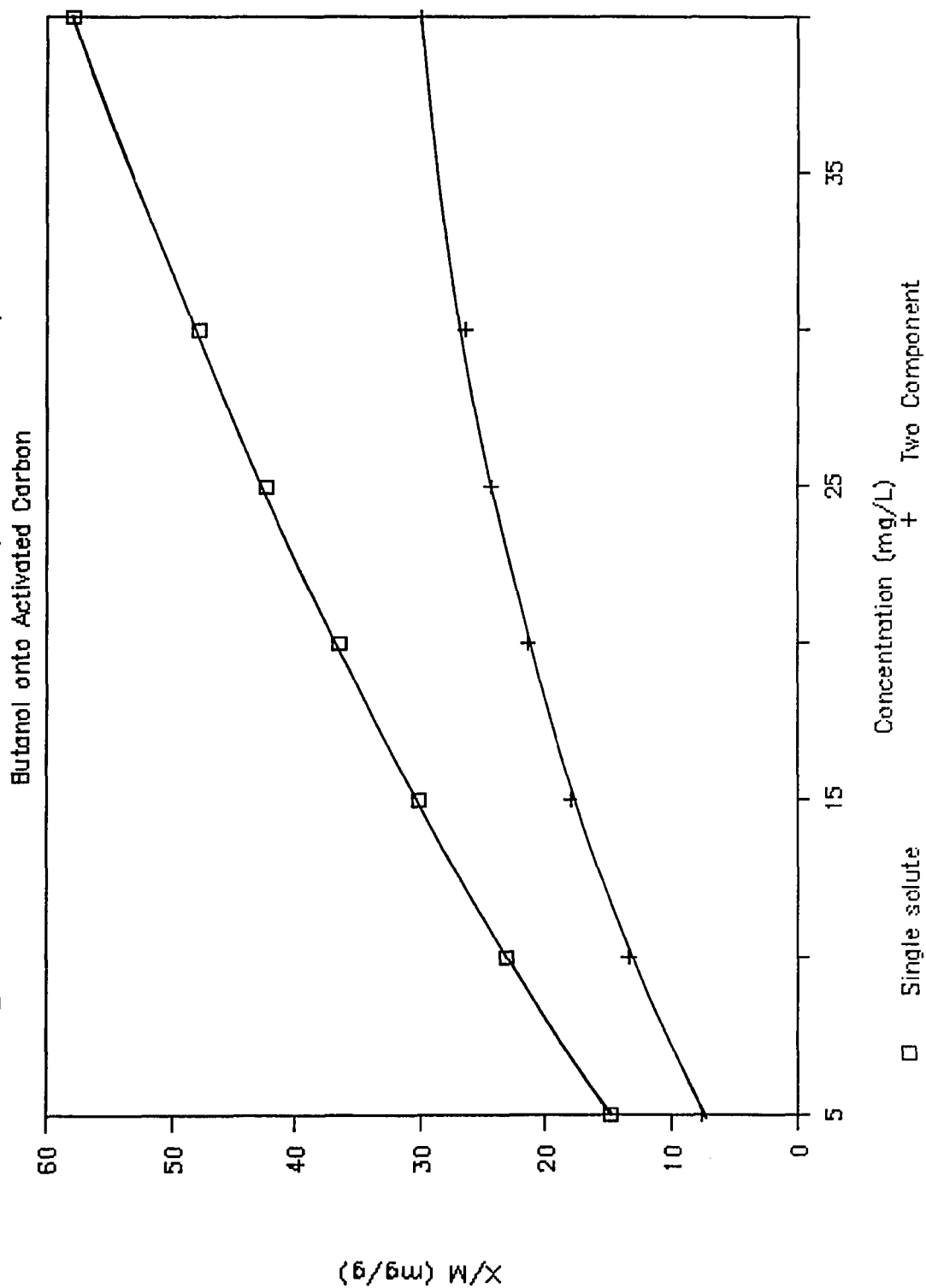
Figure D.14 Two Component Equilibria
o-Xylene onto Activated Carbon

D.14
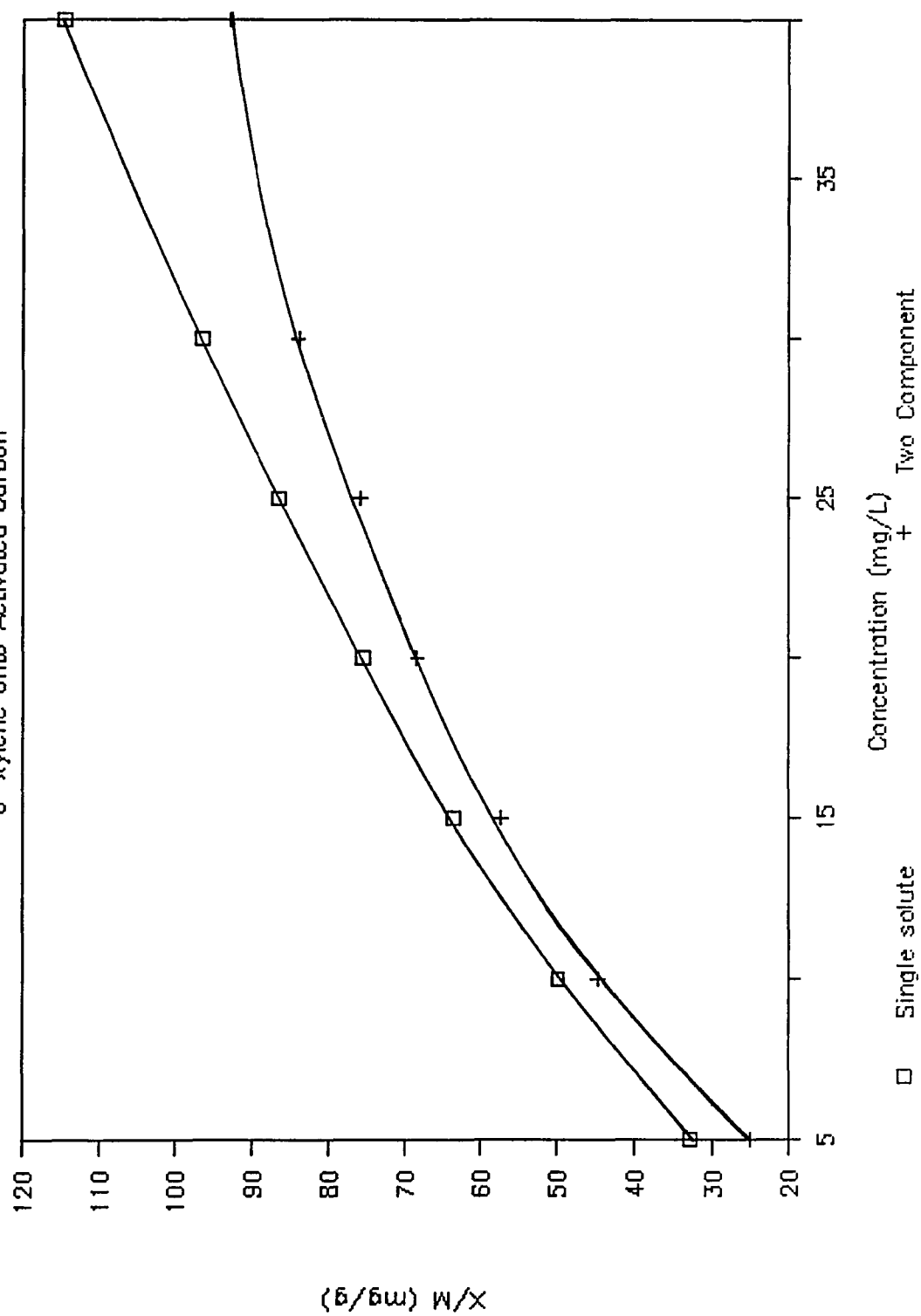
Figure D.15 Two Component Equilibria
o-Xylene onto Activated Carbon

Concentration (mg/L)

X/M (mg/g)

□   Single solute   +   Two Component

D.15
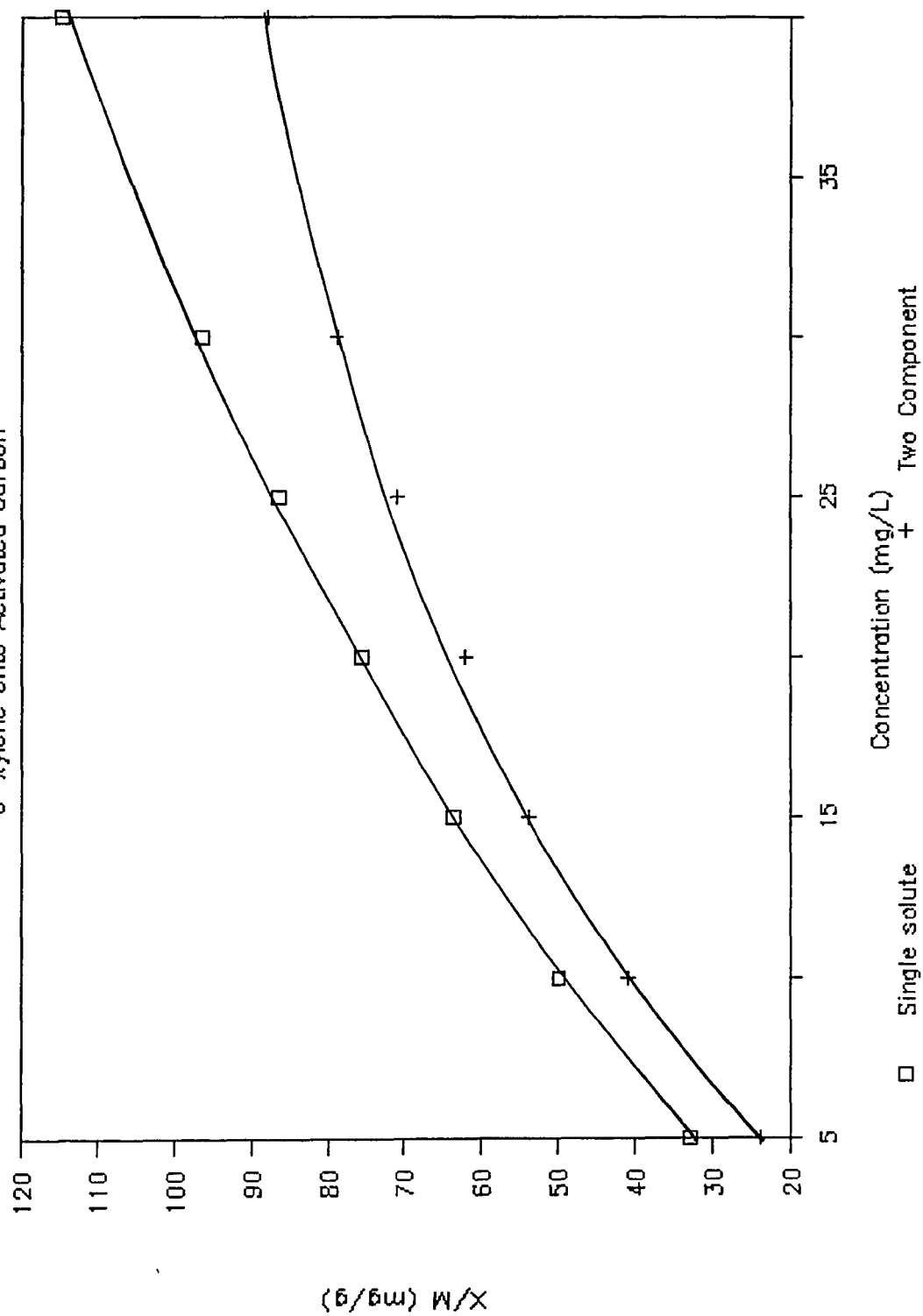
Figure D.16 Two Component Equilibria

Butyraldehyde onto Activated Carbon

X/M (mg/g)

Concentration (mg/L)

□   Single solute   +   Two Component

D.16
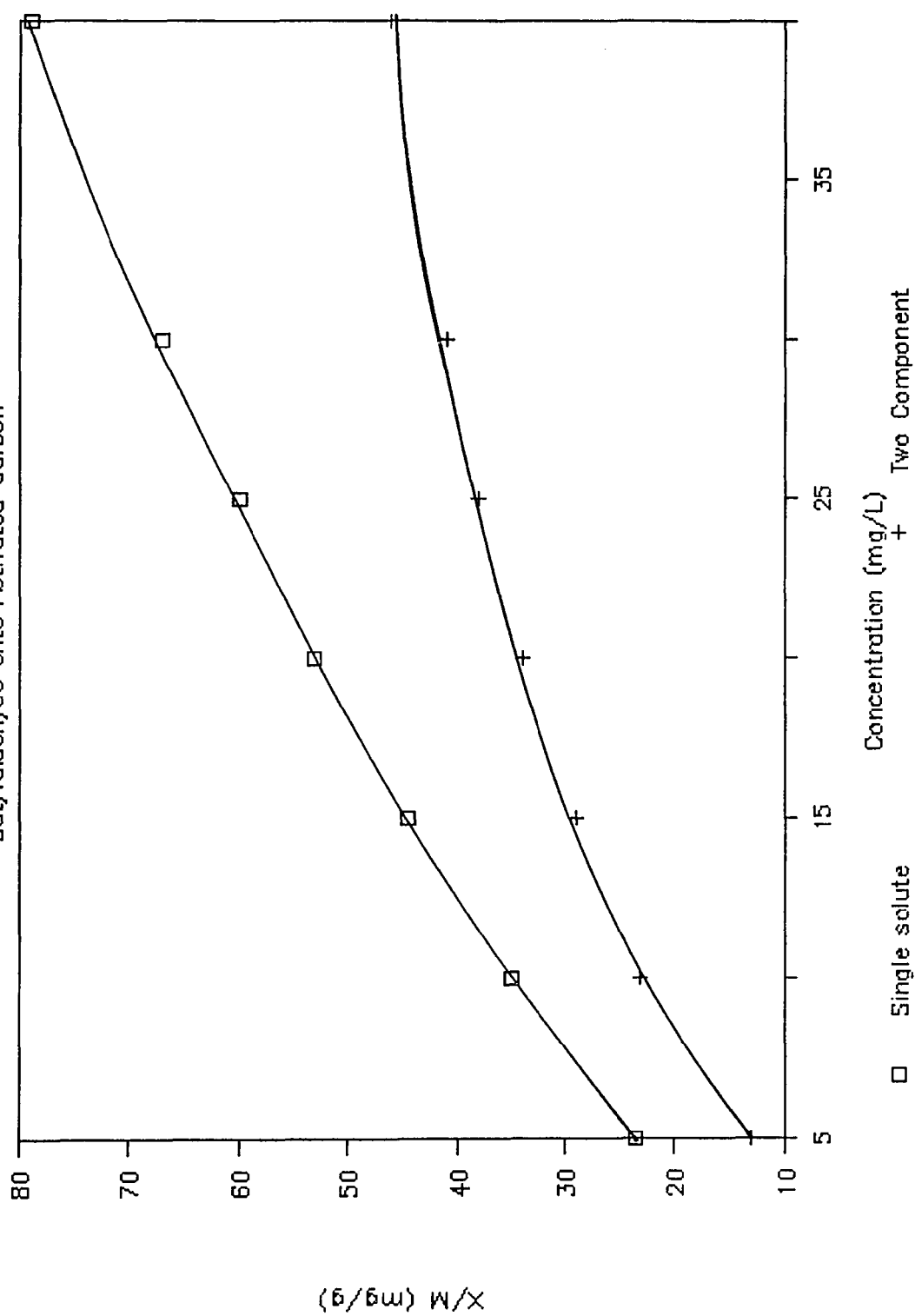
Figure D.17 Four Component Equilibria
o-Xylene onto Activated Carbon

Concentration (mg/L)

X/M (mg/g)

□ Single solute   + Four Component

D.17
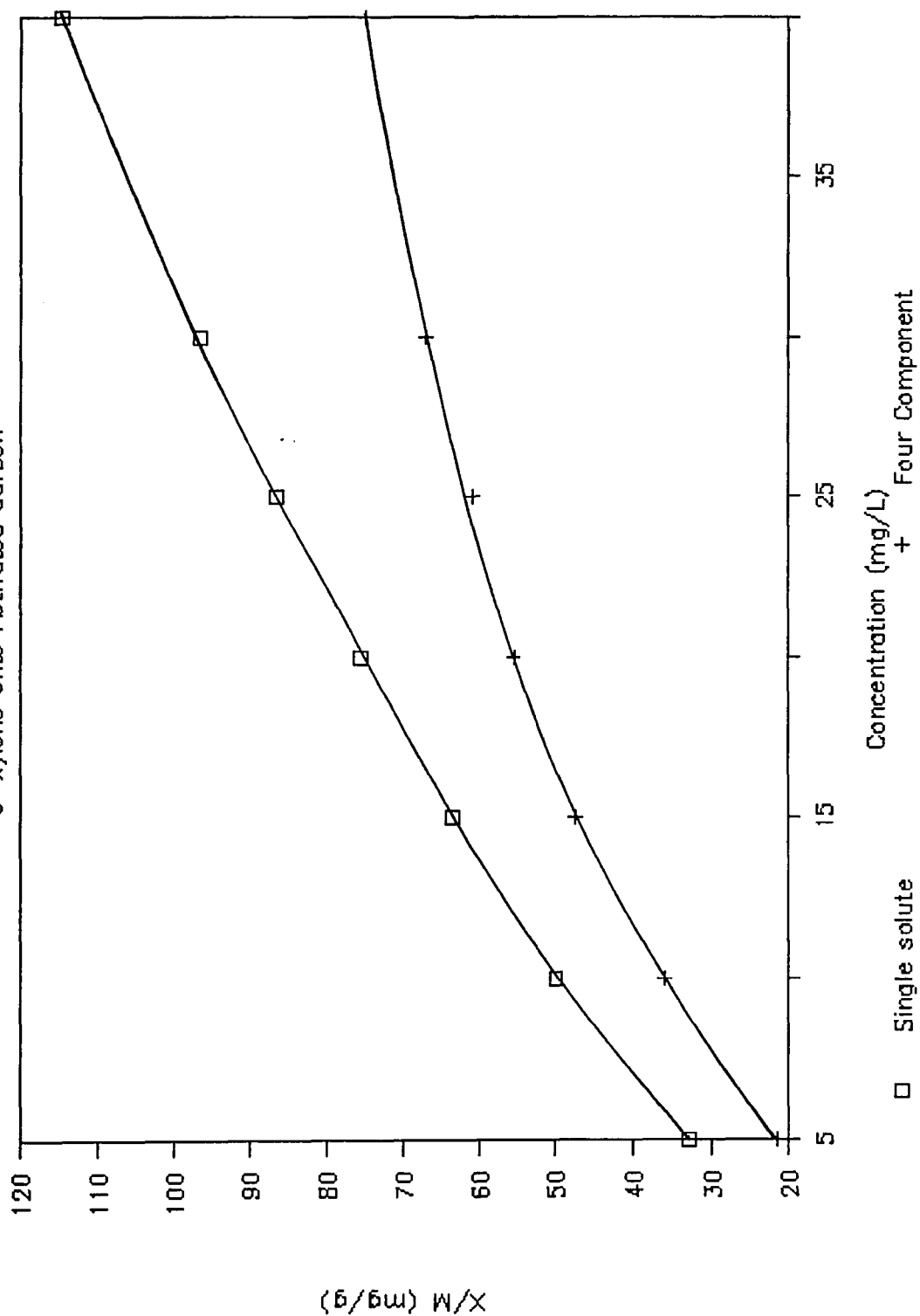
Figure D.18 Four Component Equilibria

Butyraldehyde onto Activated Carbon

X/M (mg/g)

Concentration (mg/L)

□ Single solute   + Four Component

D.18
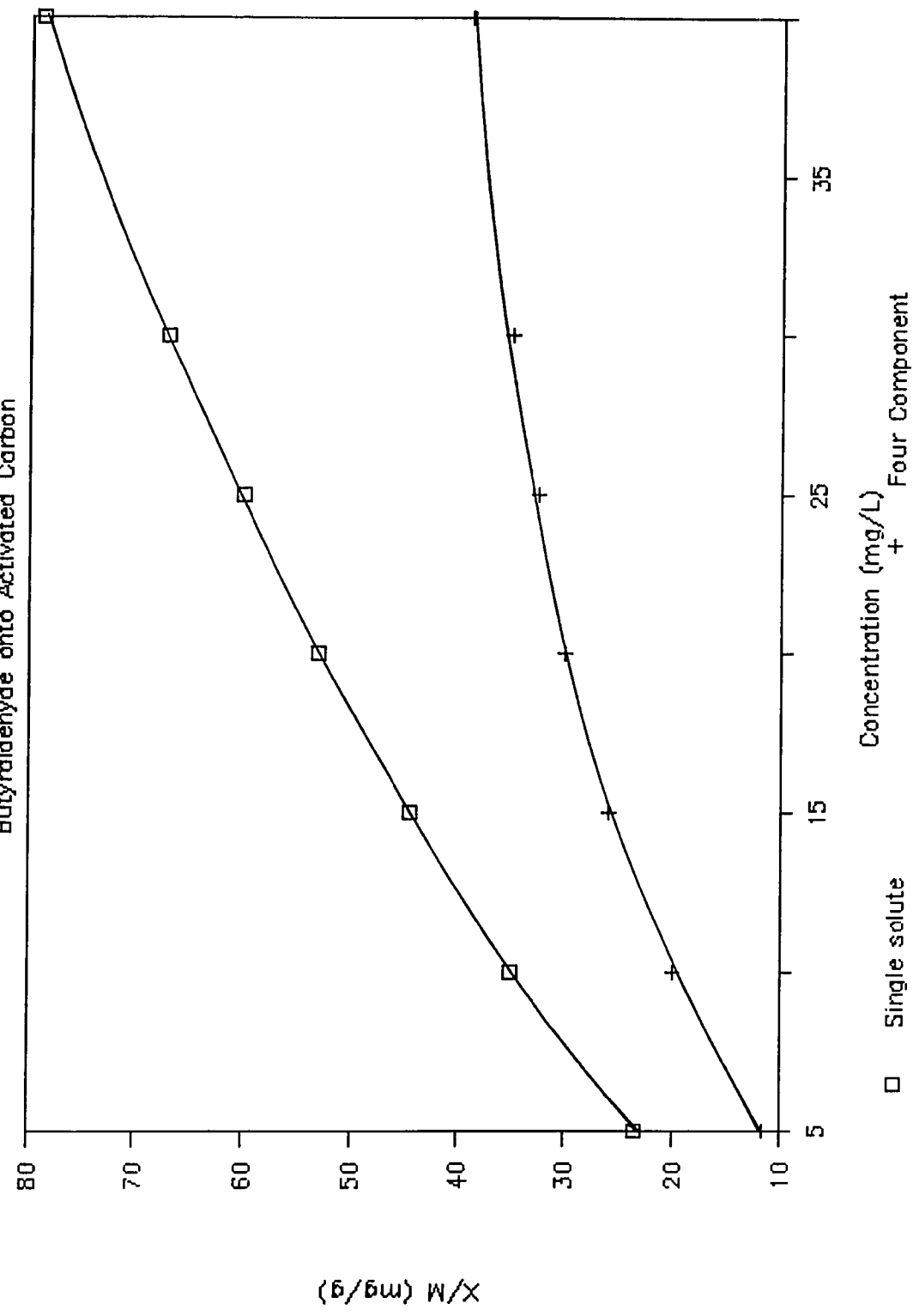
Figure D.19 Four Component Equilibria
MIBK onto Activated Carbon

X/M (mg/g)

Concentration (mg/L)

□ Single solute   + Four Component

D.19
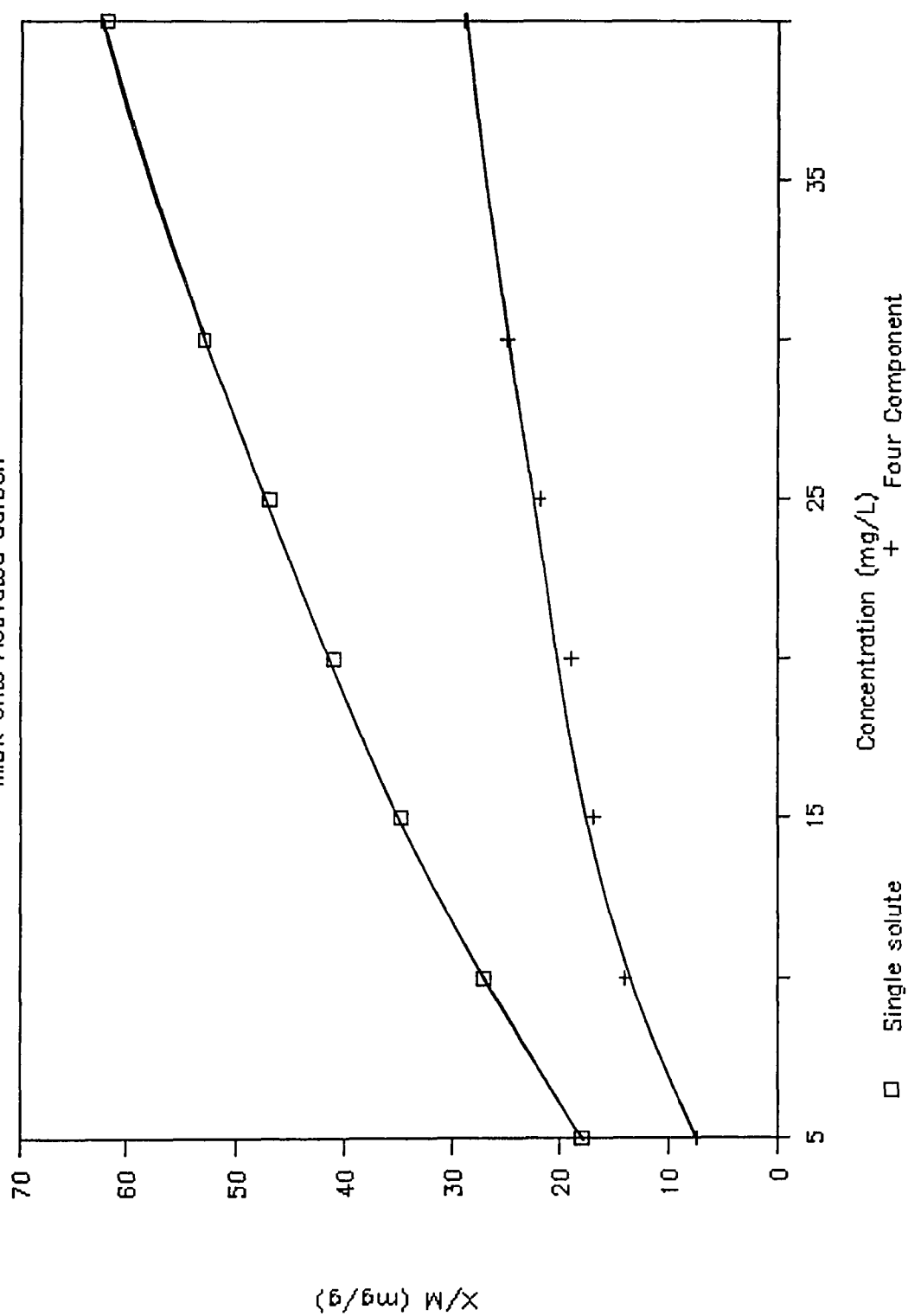
Figure D.20 Four Component Equilibria

Butanol onto Activated Carbon

X/M (mg/g)

Concentration (mg/L)

□ Single solute   + Four Component

D.20
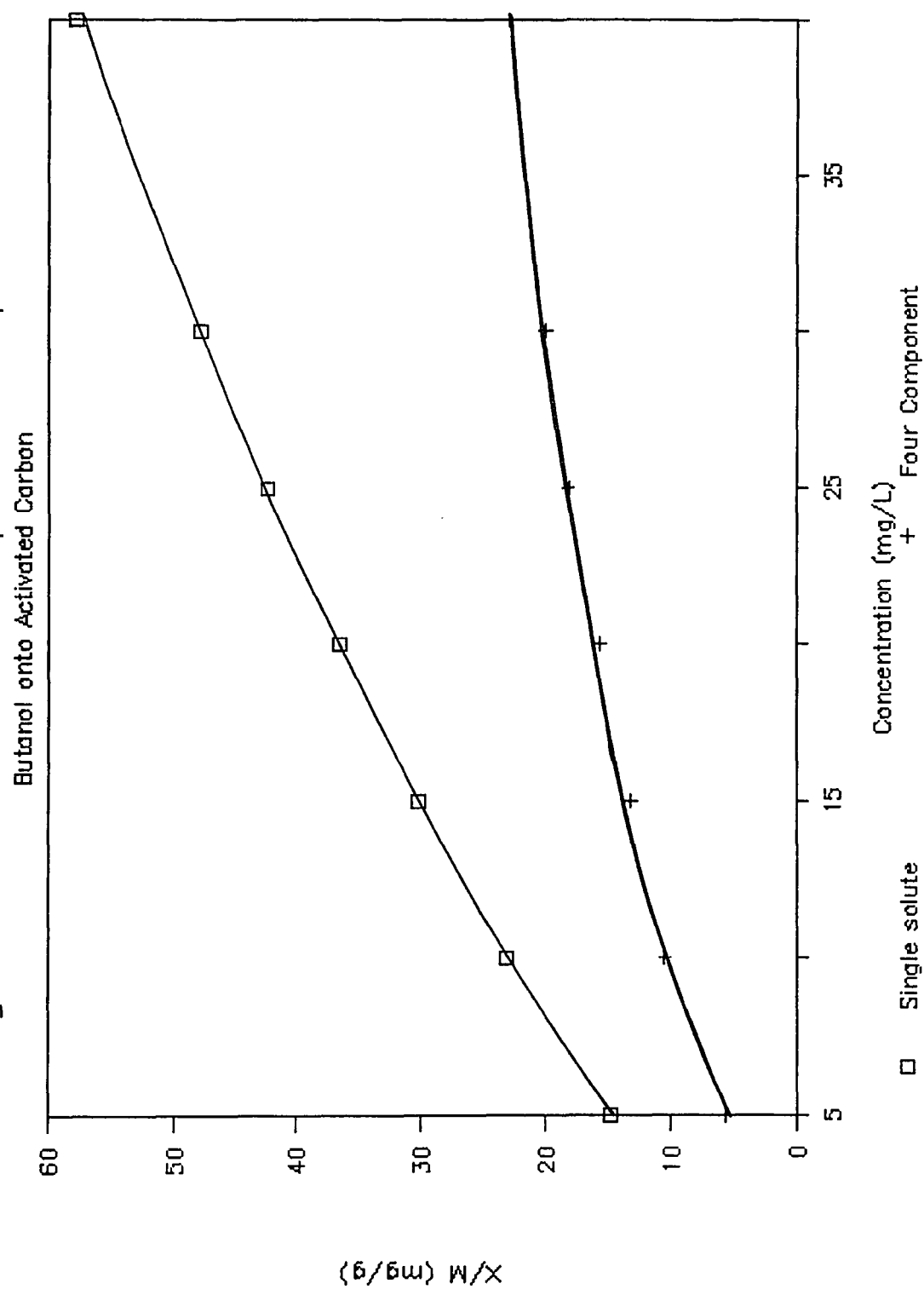
APPENDIX - 'E'

SINGLE SOLUTE ADSORPTION
DYNAMICS

Figure E.1. Single Solute Dynamics
Butanol onto Wellmore Flyash

Concentration Remaining (mg/L)

Volume (L)

□ Effluent   + Influent
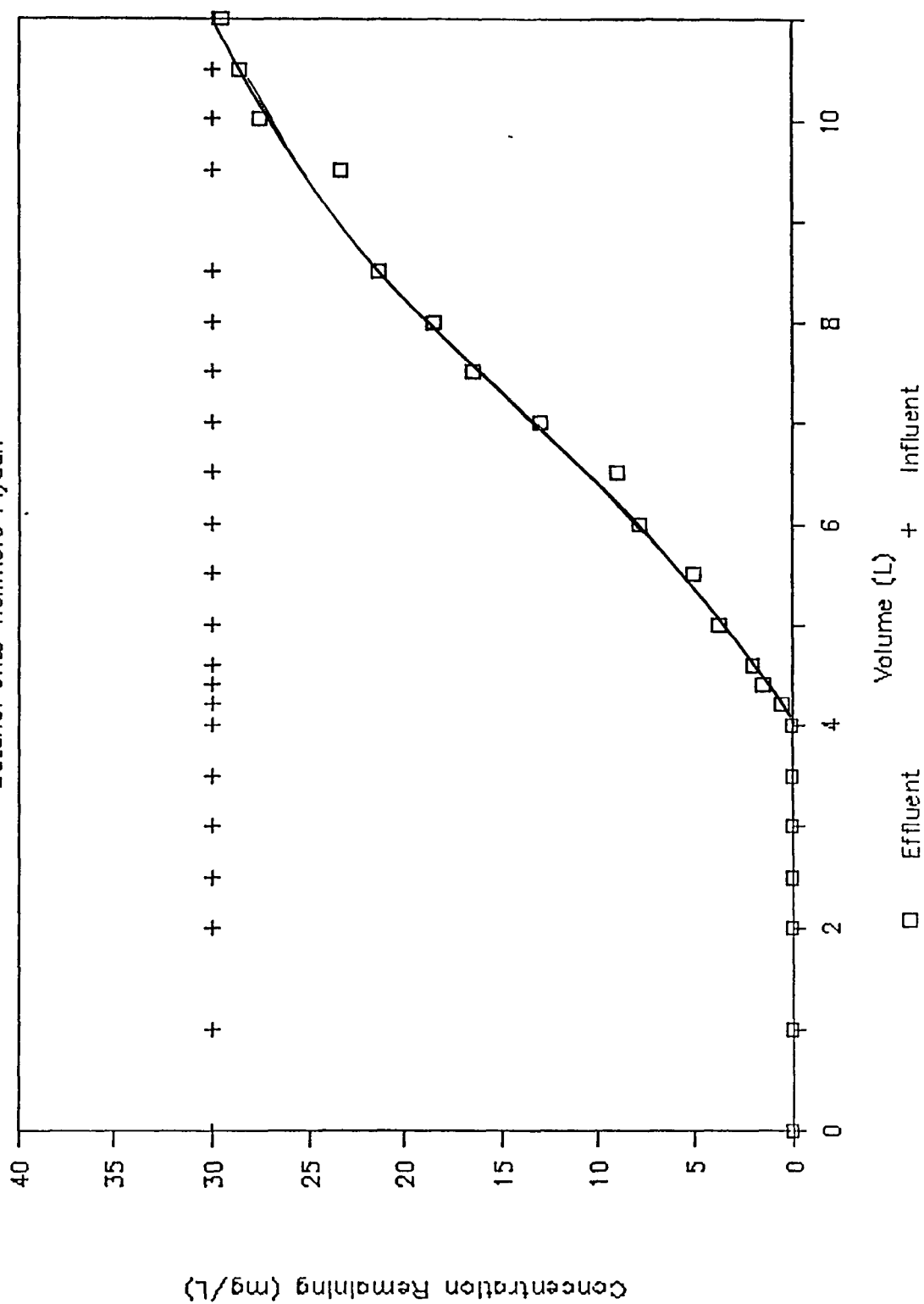
Figure E.2.Single Solute Dynamics
Butanol onto Conemough Flyash

Concentration Remaining (mg/L)

Volume (L)

□ Effluent   + Influent

E.2
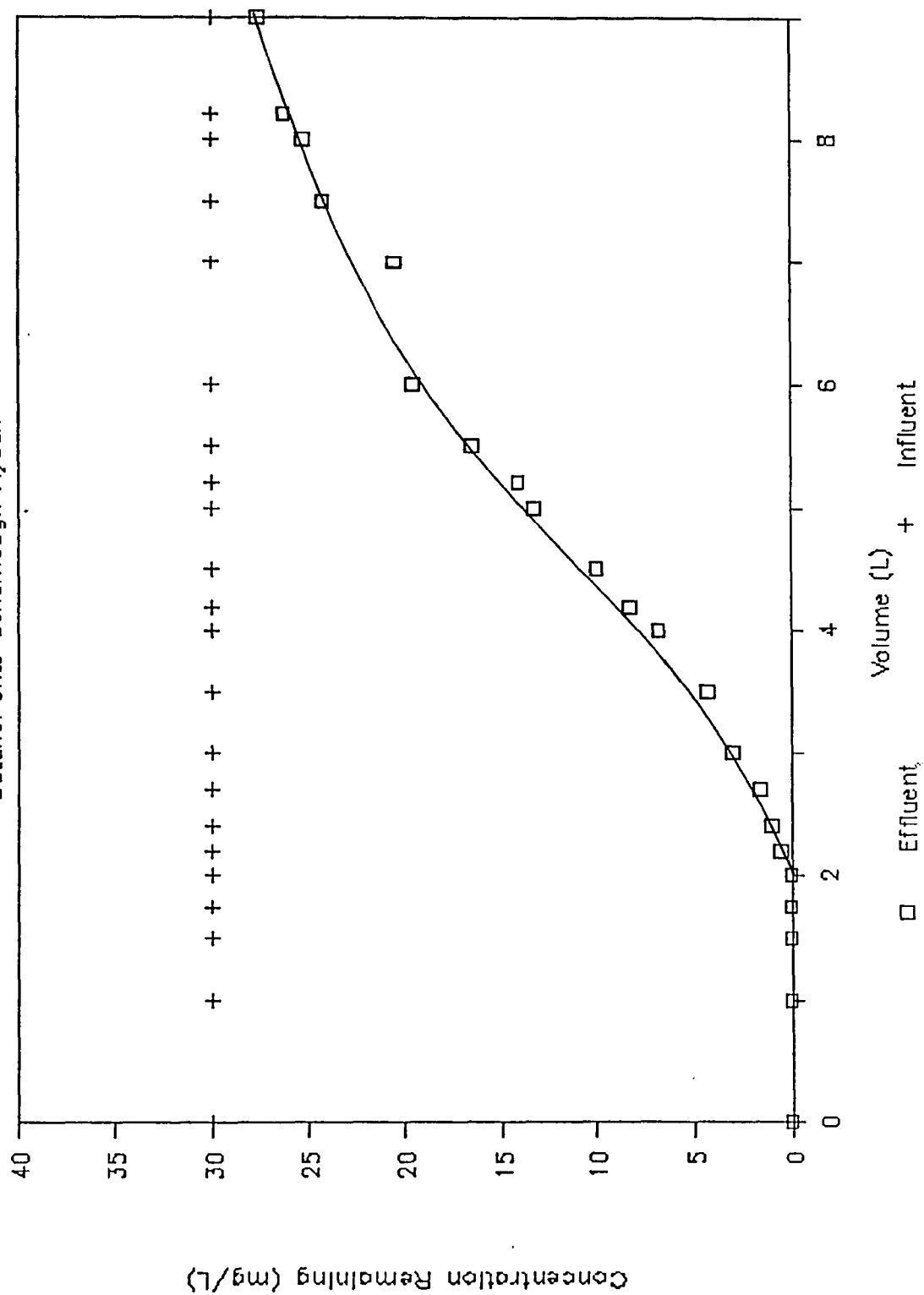
Figure E.3. Single Solute Dynamics
Butanol onto Blender Flyash

□ Effluent   + Influent

Volume (L)

Concentration Remaining (mg/L)

E.3
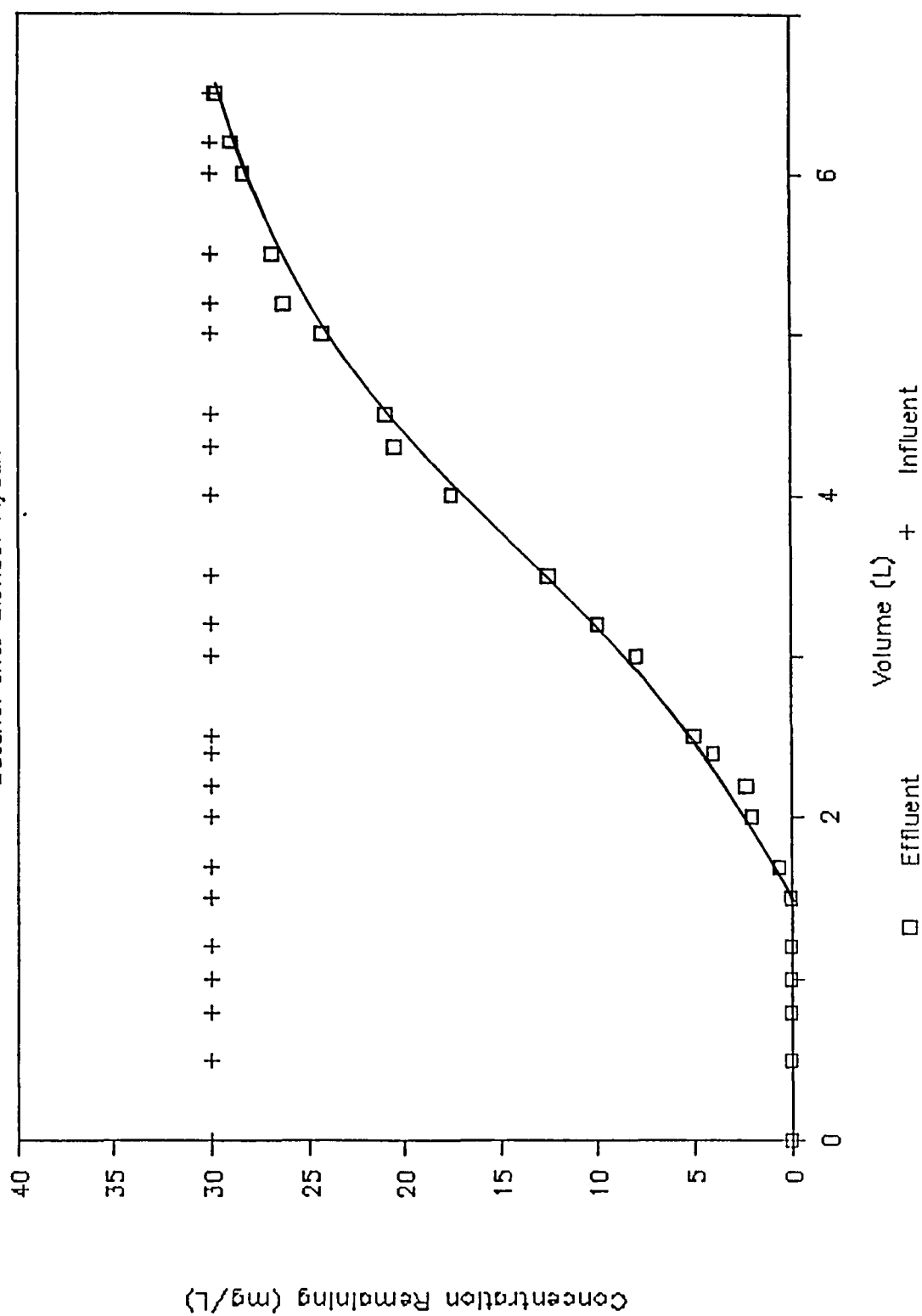
Figure E.4.Single Solute Dynamics
Butanol onto Deephollow Flyash

Concentration Remaining (mg/L)

Volume (L)   + Influent   □ Effluent

E.4
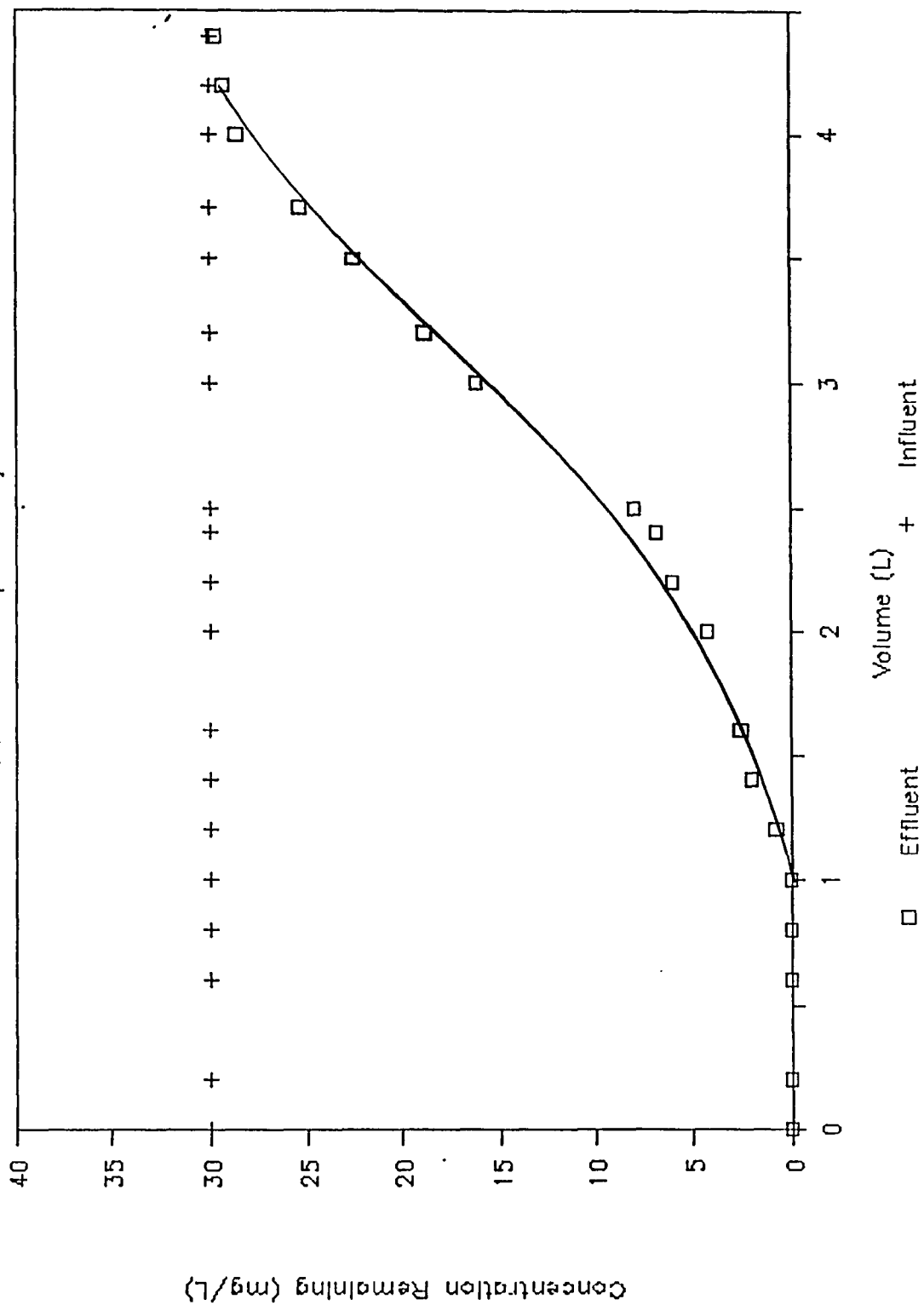
Figure E.5. Single Solute Dynamics

Butanol onto Keystone Flyash

Concentration Remaining (mg/L)

Volume (L)   □ Effluent   + Influent
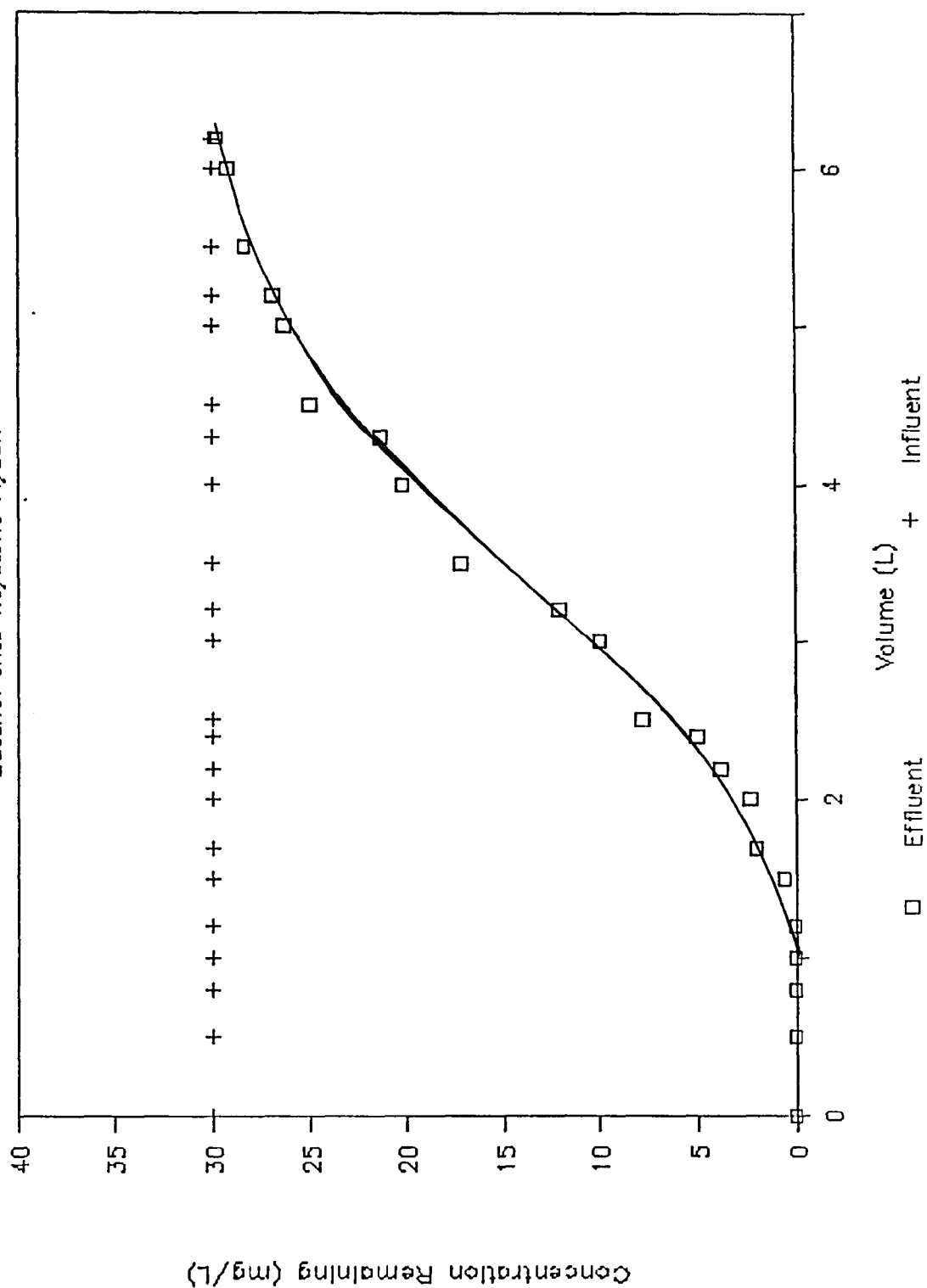
Figure E.6. Single Solute Dynamics
Butanol onto Upshore Flyash

Concentration Remaining (mg/L)

Volume (L)   +   Influent   □   Effluent
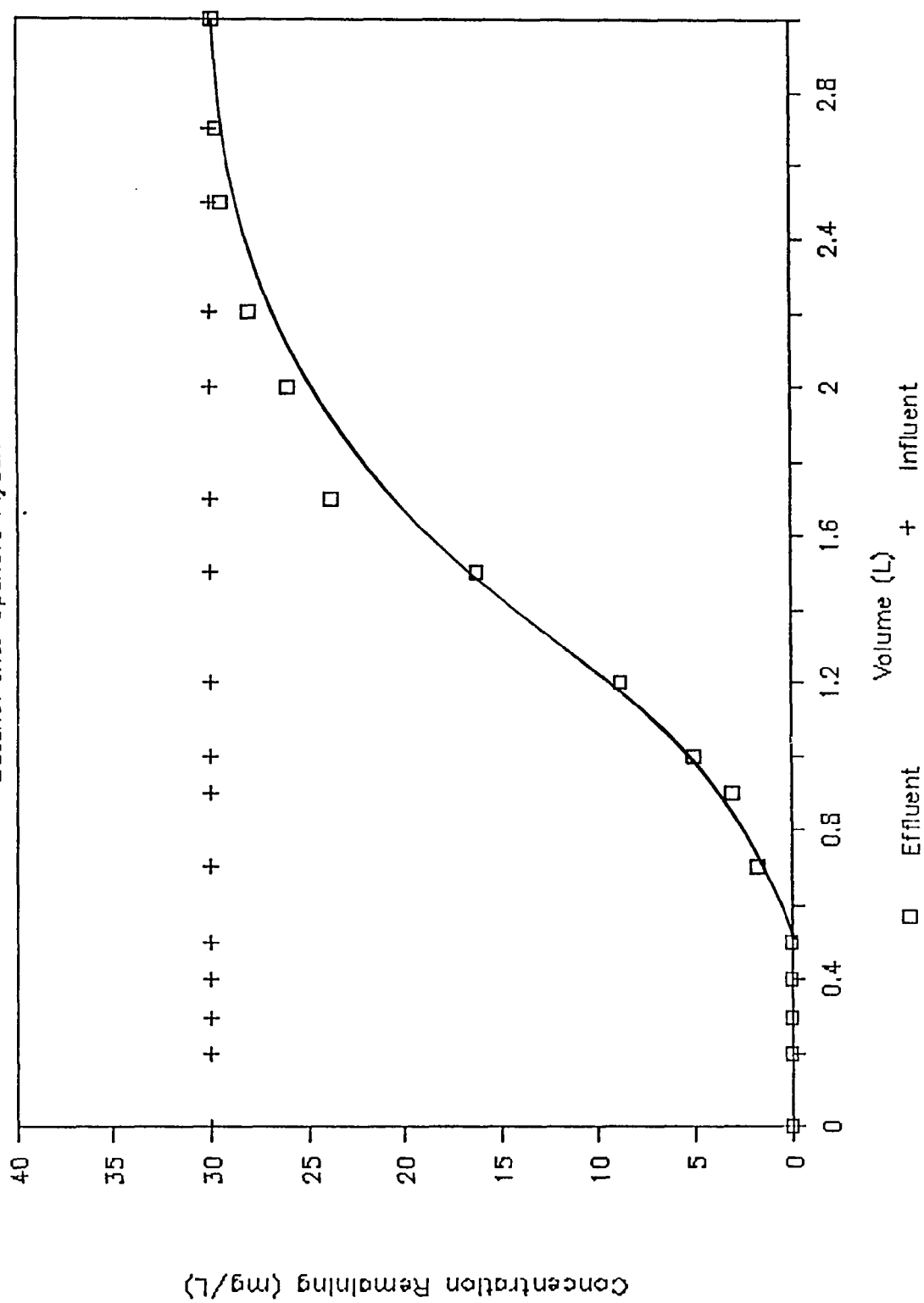
Figure E.7 Single Solute Dynamics
Butanol onto Militant Flyash

E.7
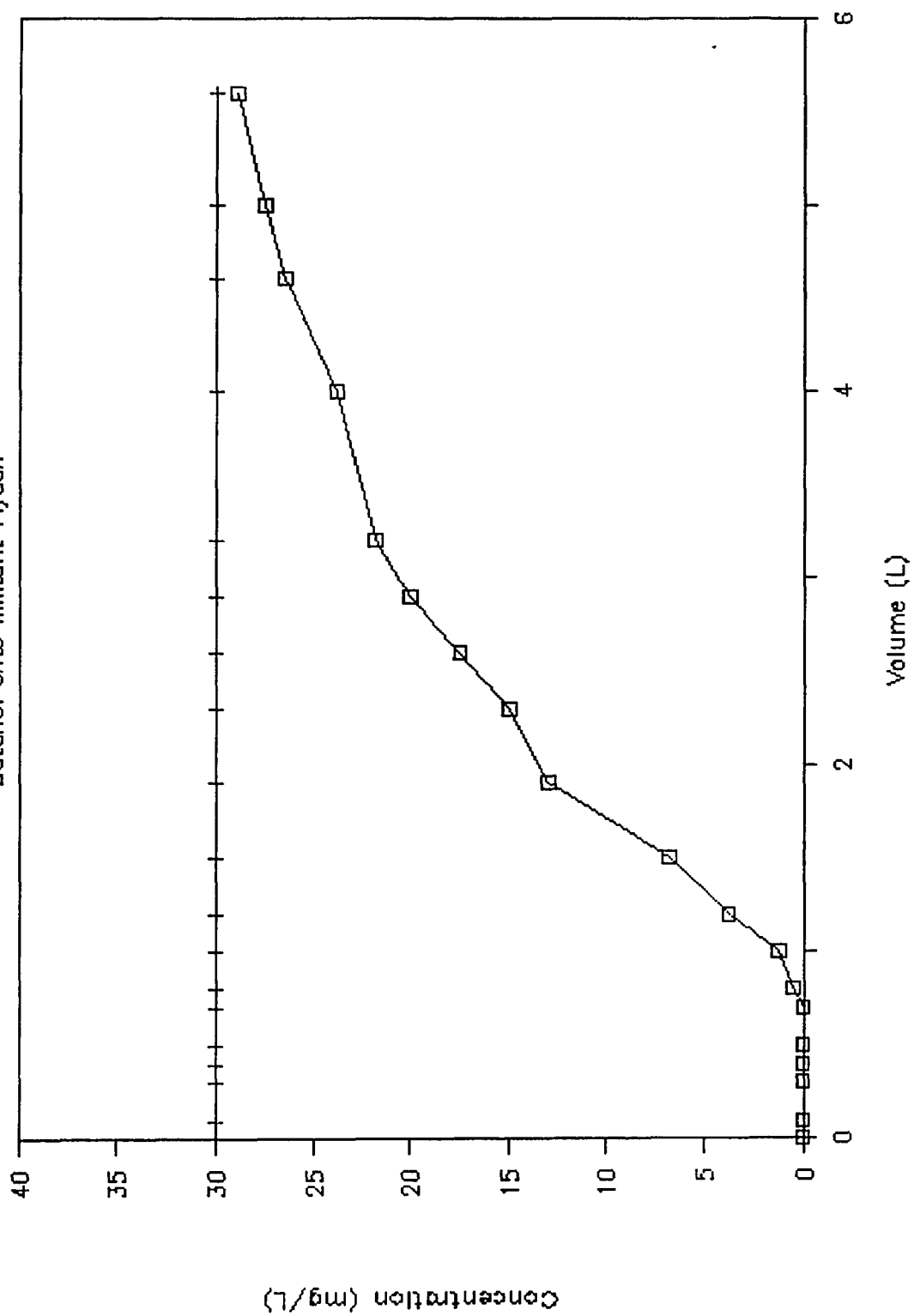
Figure E.8. Single Solute Dynamics

Butyraldehyde onto Wellmore Flyash

Concentration Remaining (mg/L)

Volume (L)

□ Effluent   + Influent

E.8
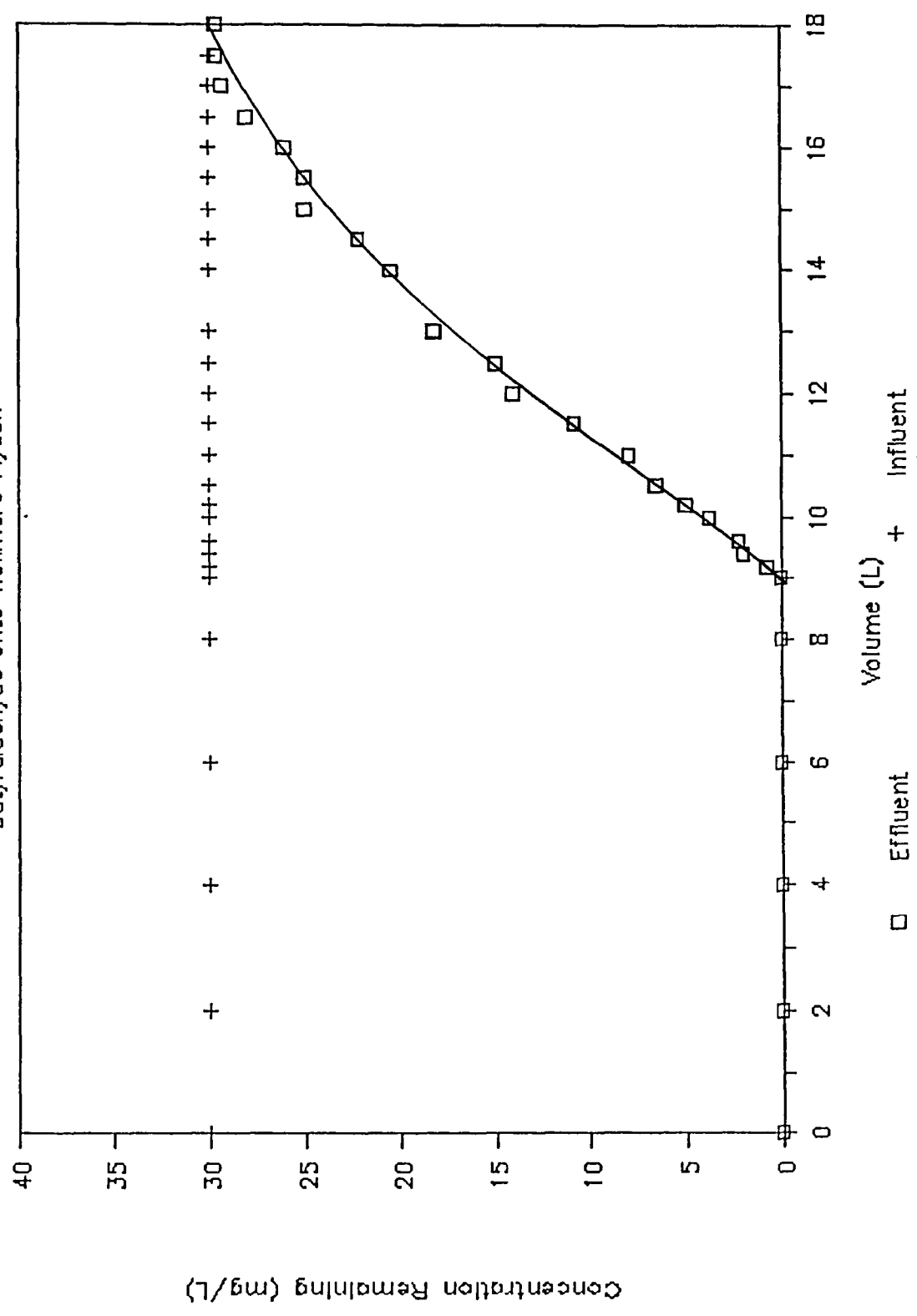
Figure E.9.Single Solute Dynamics

Butyraldehyde onto Conemough Flyash

Volume (L)

□ Effluent   + Influent

Concentration Remaining (mg/L)

E.9
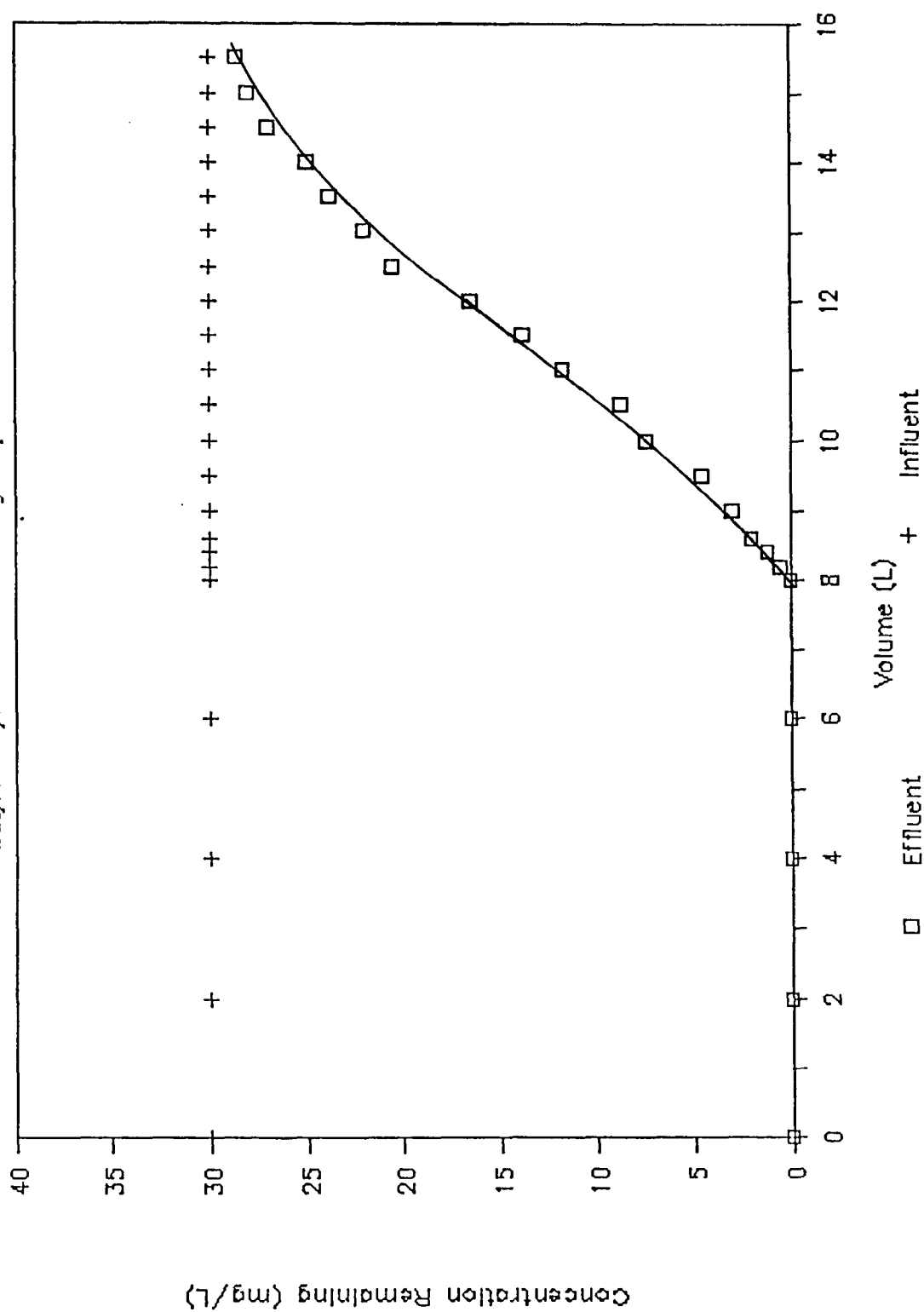
Figure E.10 Single Solute Dynamics
Butyraldehyde onto Blender Flyash

Volume (L)   + Influent   □ Effluent

Concentration Remaining (mg/L)

E.10
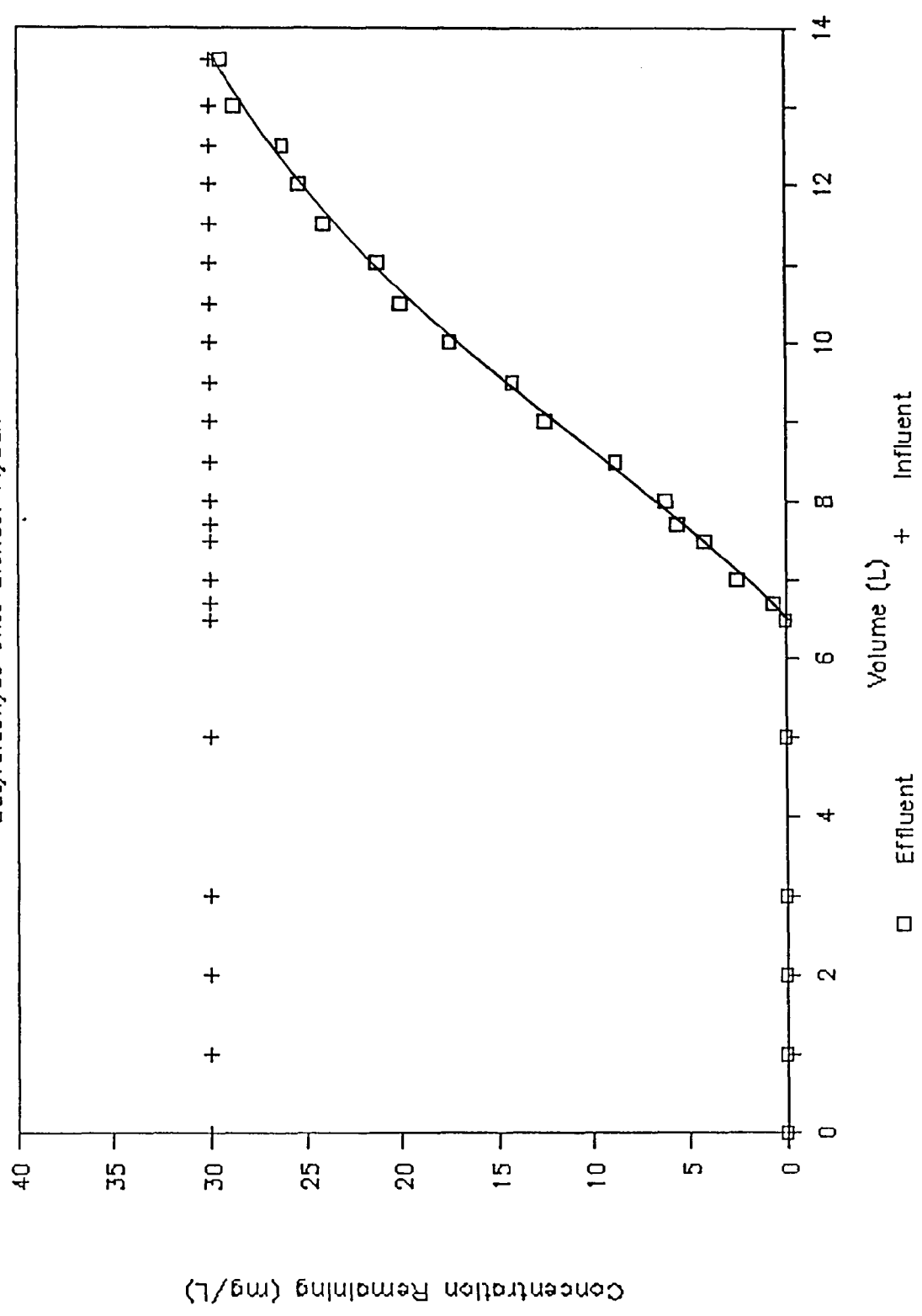
Figure E.11 Single Solute Dynamics
Butyraldehyde onto Deephollow Flyash

Concentration Remaining (mg/L)

Volume (L)

□ Effluent   + Influent

E.11
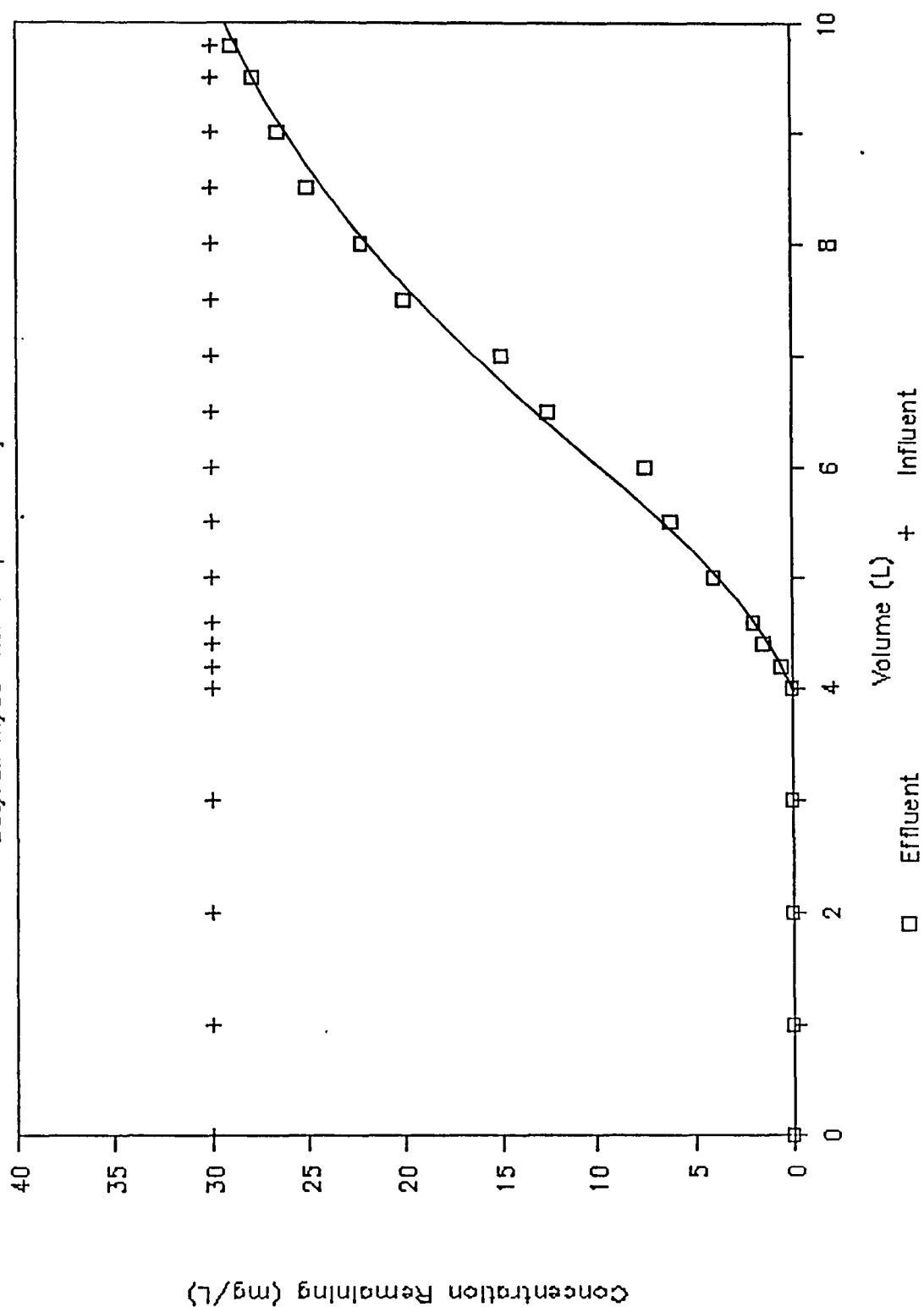
Figure E.12 Single Solute Dynamics

Butyraldehyde onto Keystone Flyash

E.12
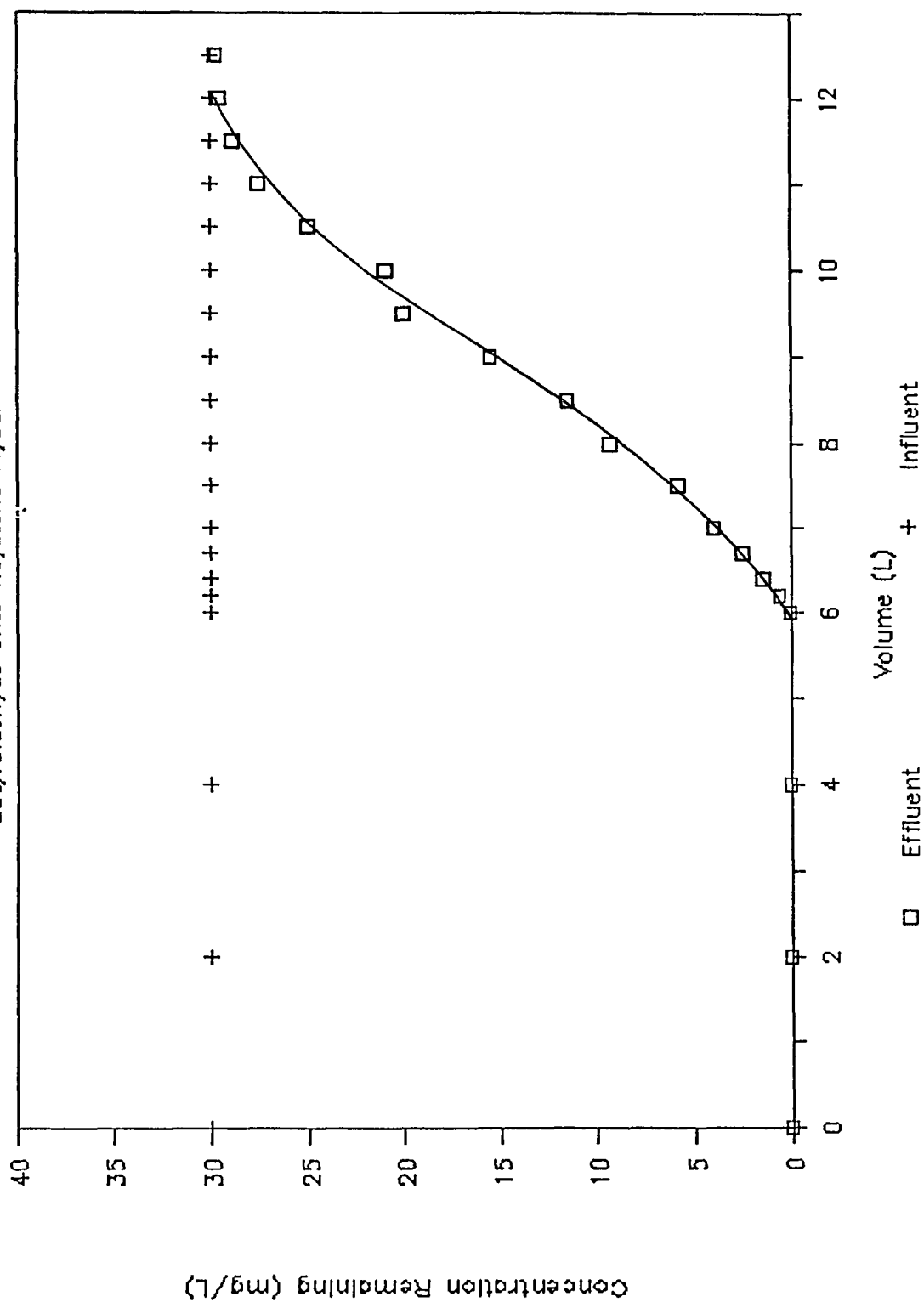
Figure E.13 Single Solute Dynamics

Butyraldehyde onto Upshore Flyash

Volume (L)

+ Influent

□ Effluent

Concentration Remaining (mg/L)

E.13
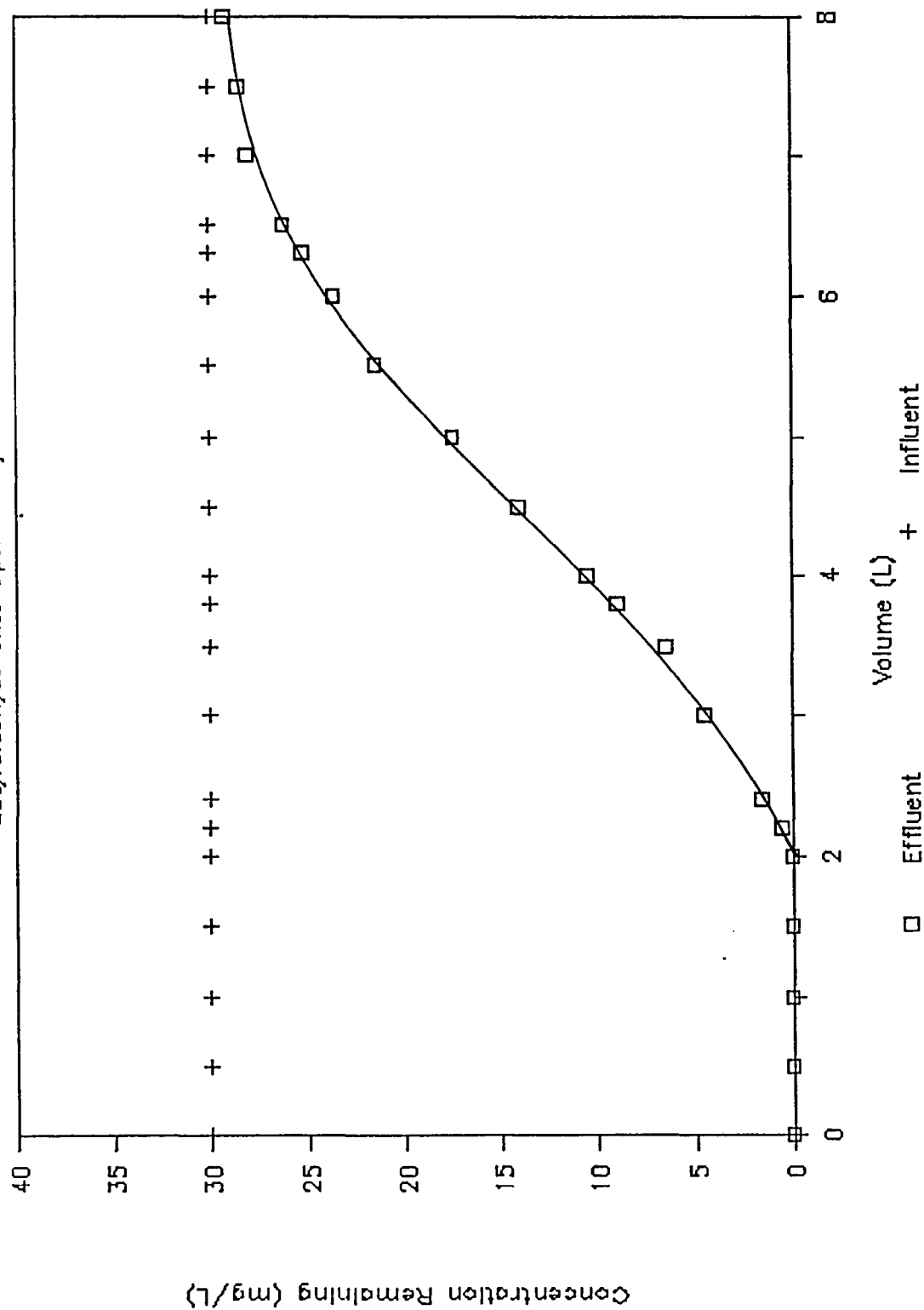
Figure E.14 Single Solute Dynamics

Butyraldehyde onto Militant Flyash

E.14
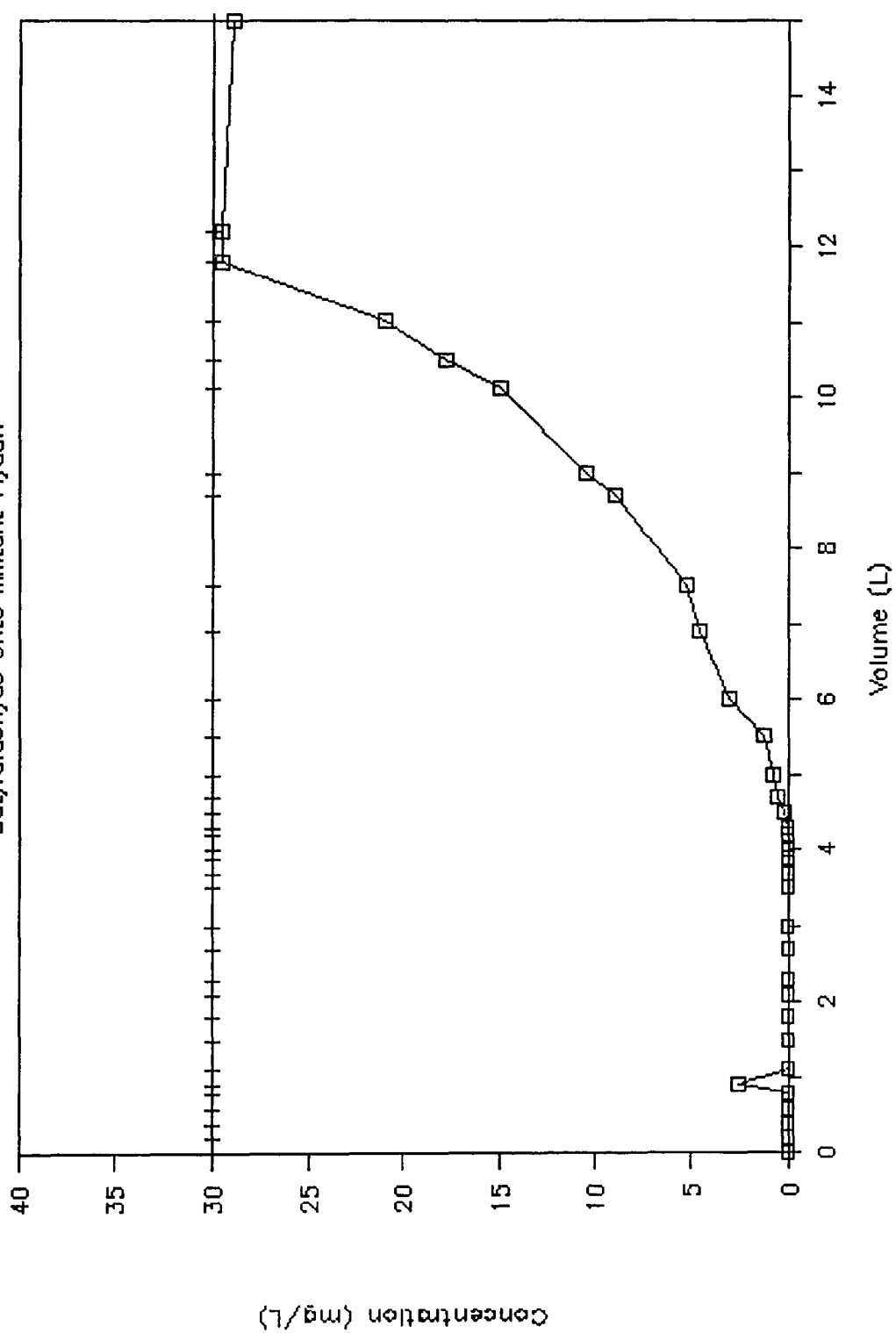
Figure E. 15   Single Solute Dynamics

o-Xylene onto Wellmore Cactus

E.15
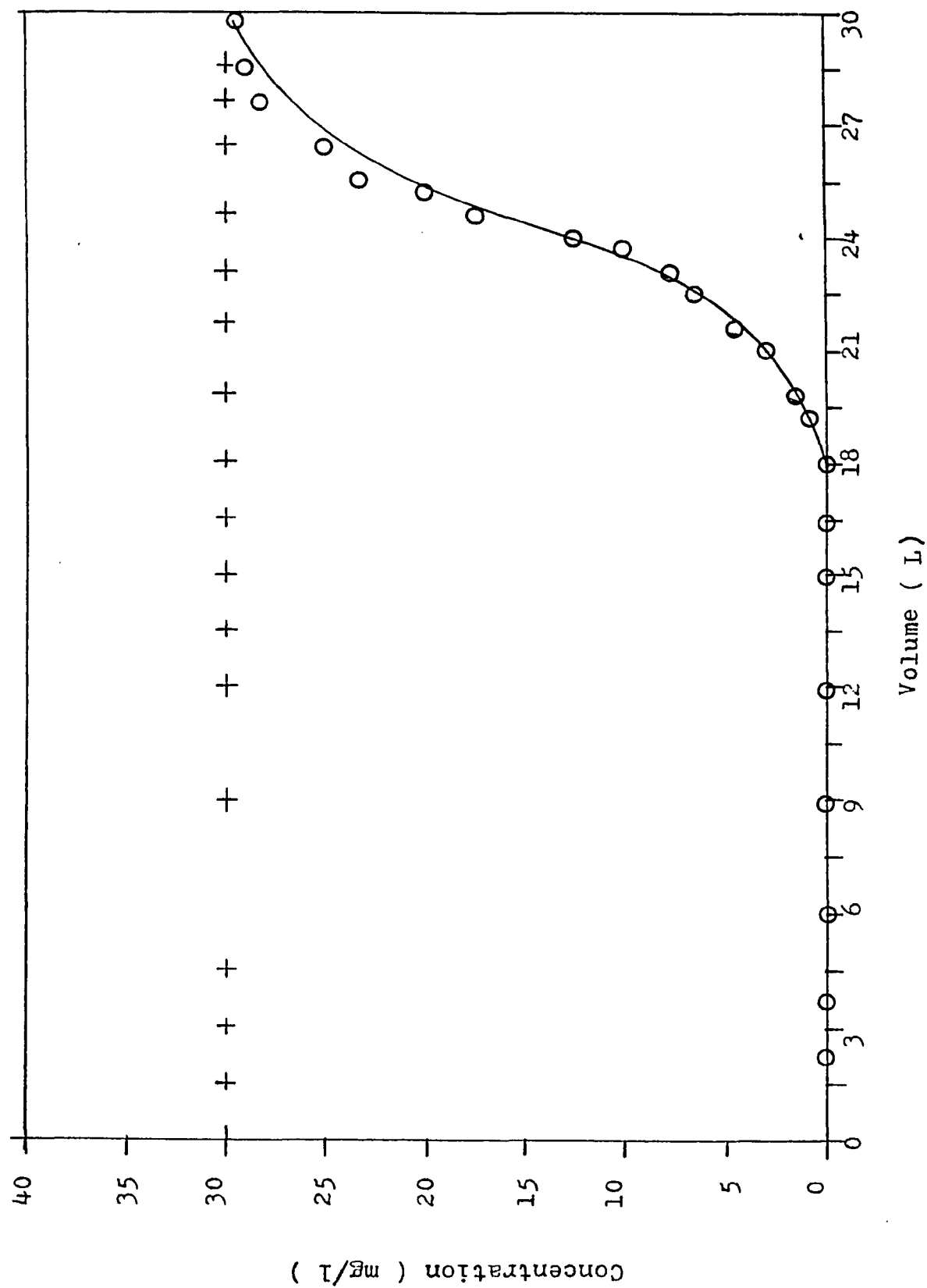
Figure E.16 Single Solute Adsorption
o-Xylene onto Conemough Flyash

Volume (L)

Concentration (mg/L)

□   Effluent   +   Influent

E.16
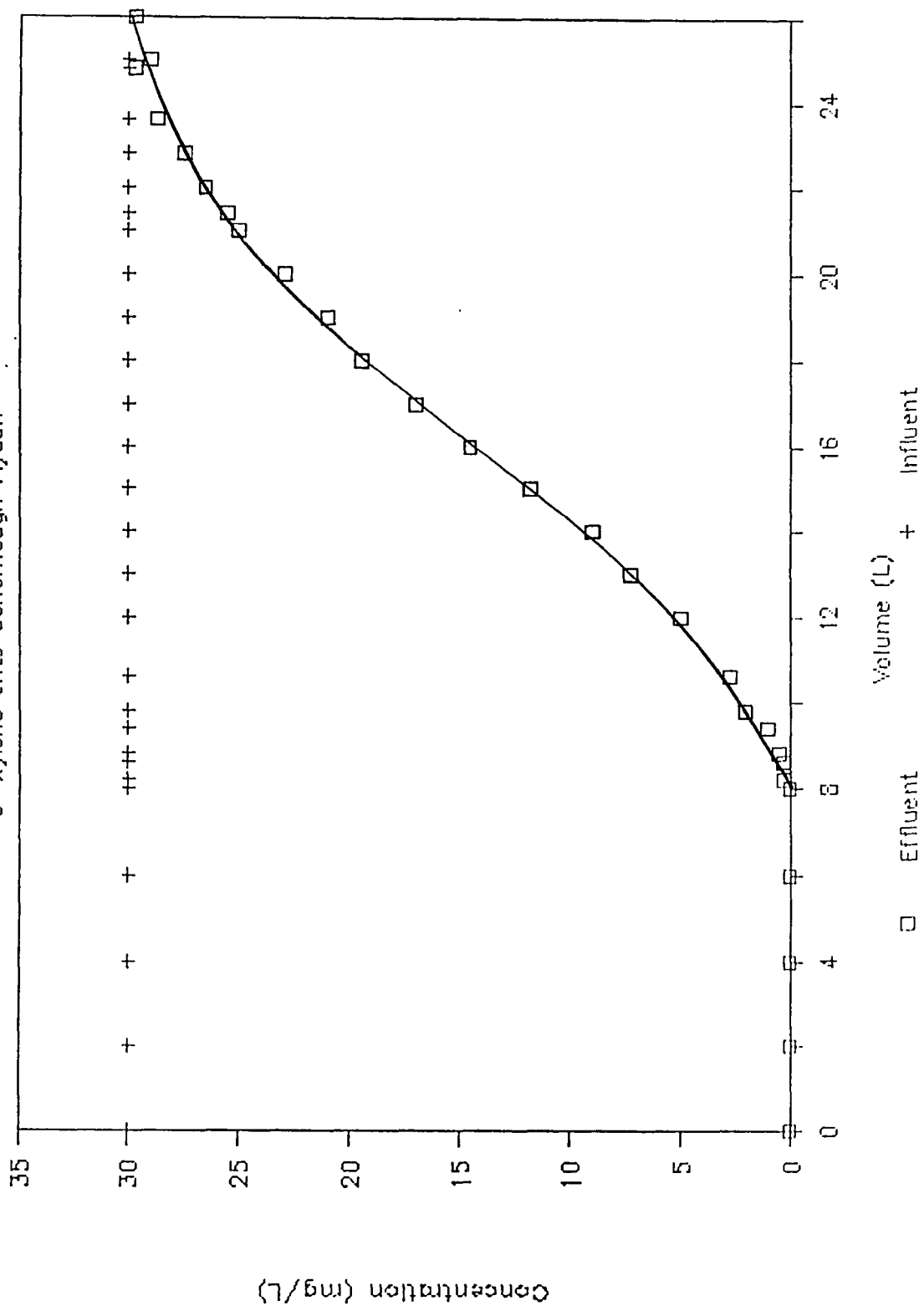
Figure E.17 Single Solute Adsorption

o–Xylene onto Blender Flyash

Concentration (mg/L)

Volume (L)

+   Influent

□   Effluent

E.17
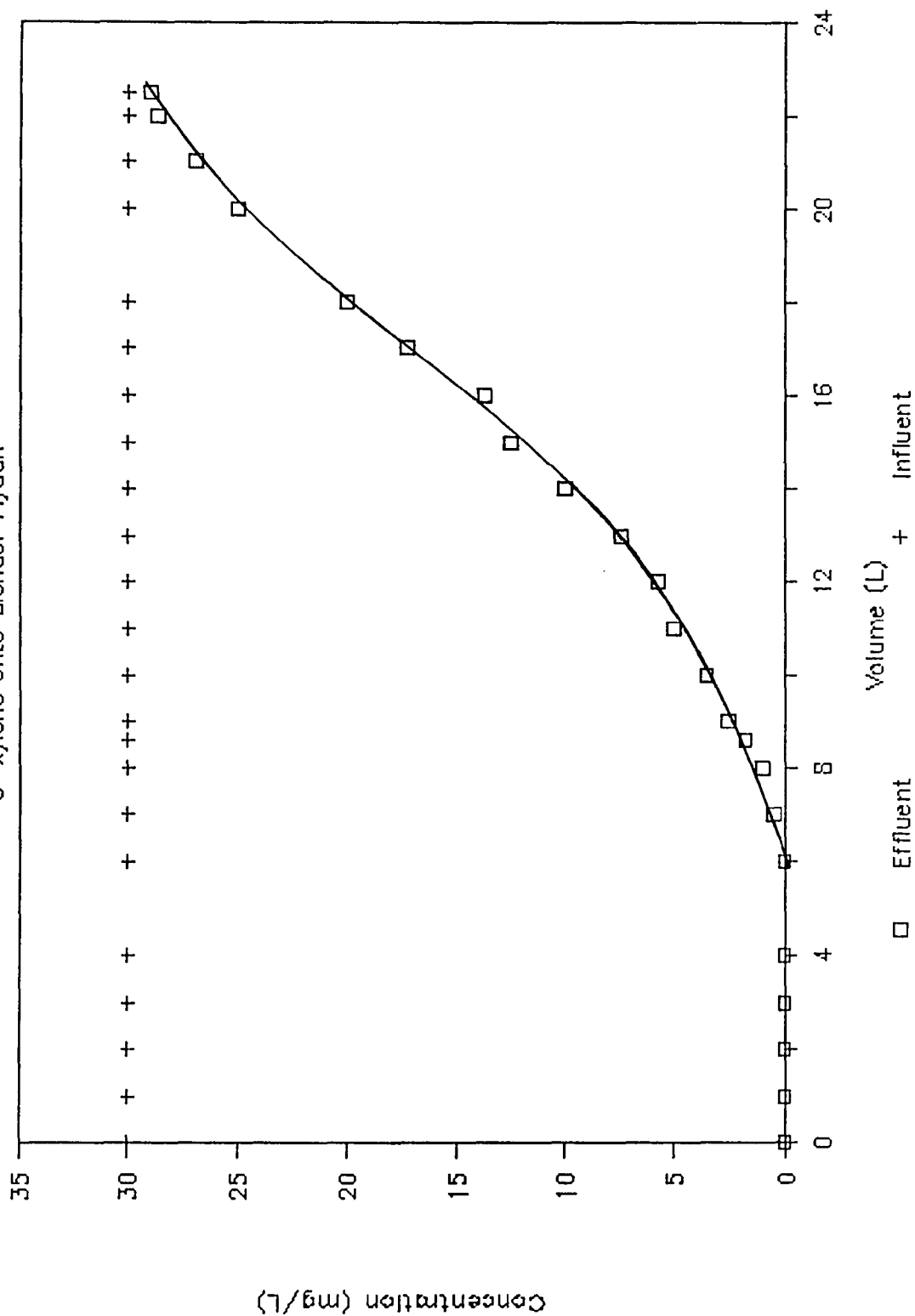
Figure E.18 Single Solute Adsorption
o-Xylene onto Deephollow Flyash

Volume (L)   +   Influent

□   Effluent

Concentration (mg/L)

E.18
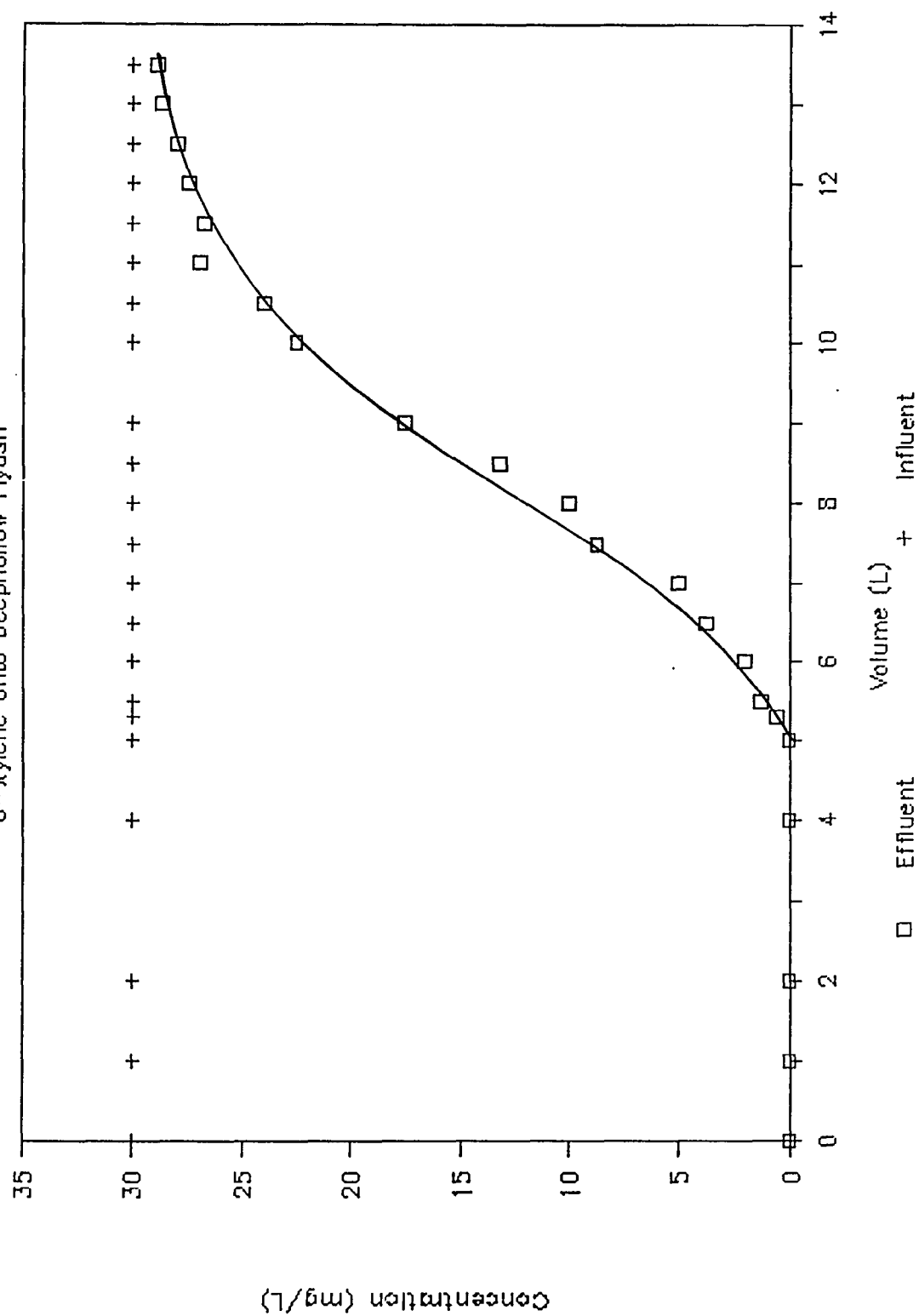
Figure E.19 Single Solute Adsorption
o-Xylene onto Keystone Flyash

Volume (L)

Concentration (mg/L)

□   Effluent   +   Influent

E.19
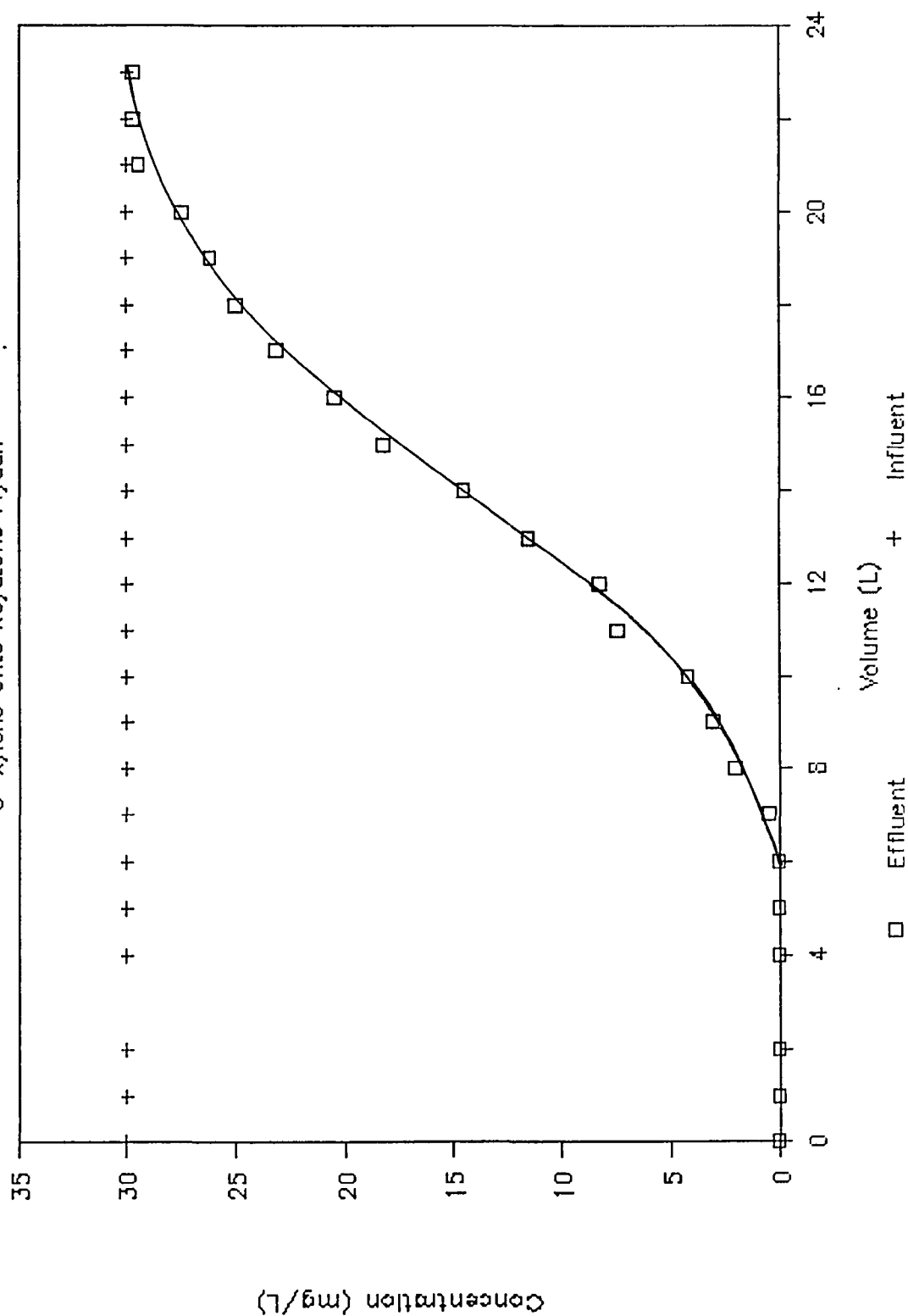
Figure E.20 Single Solute Adsorption
o-Xylene onto Upshore Flyash

E.20
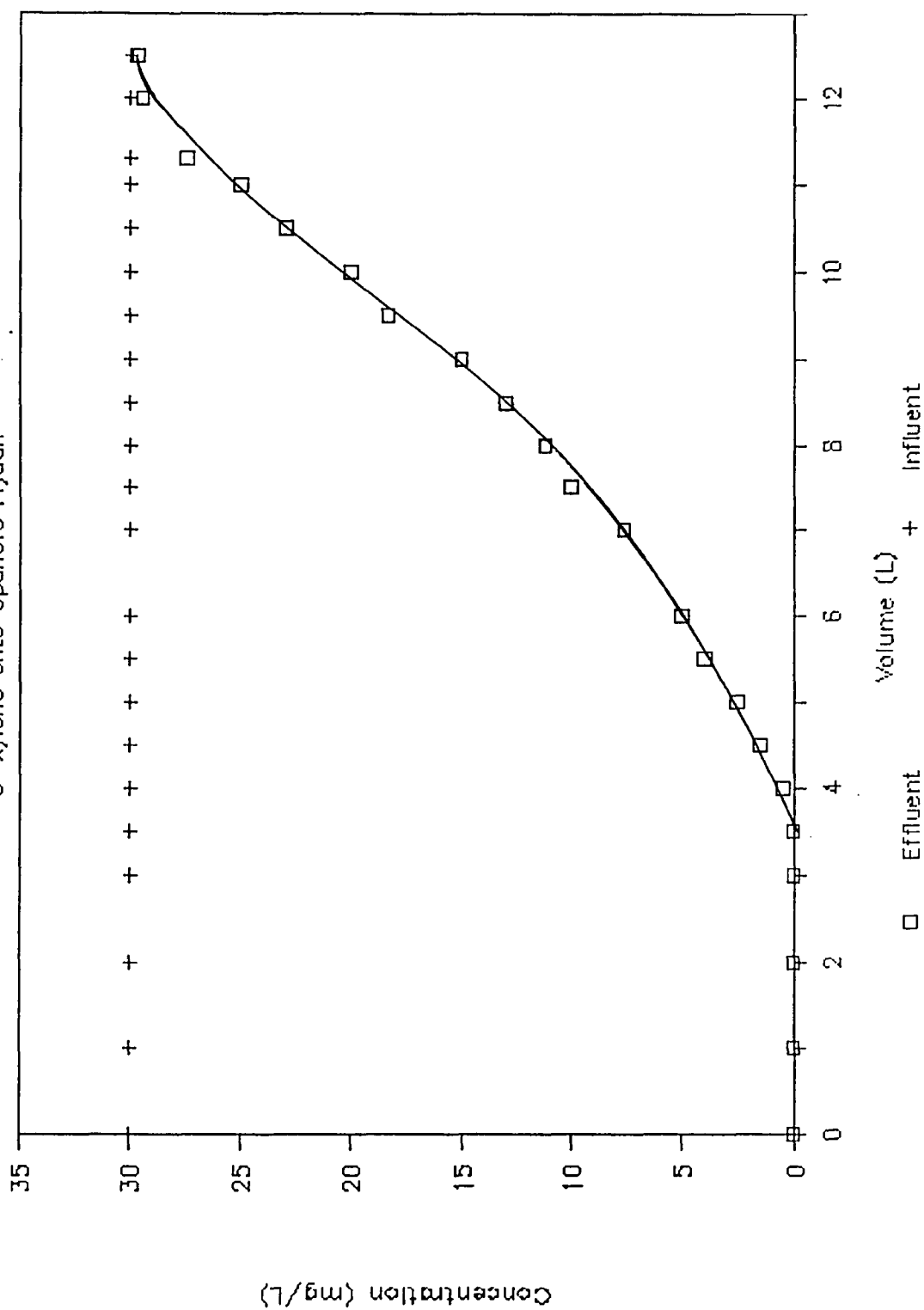
Figure E.21 Single Solute Dynamics

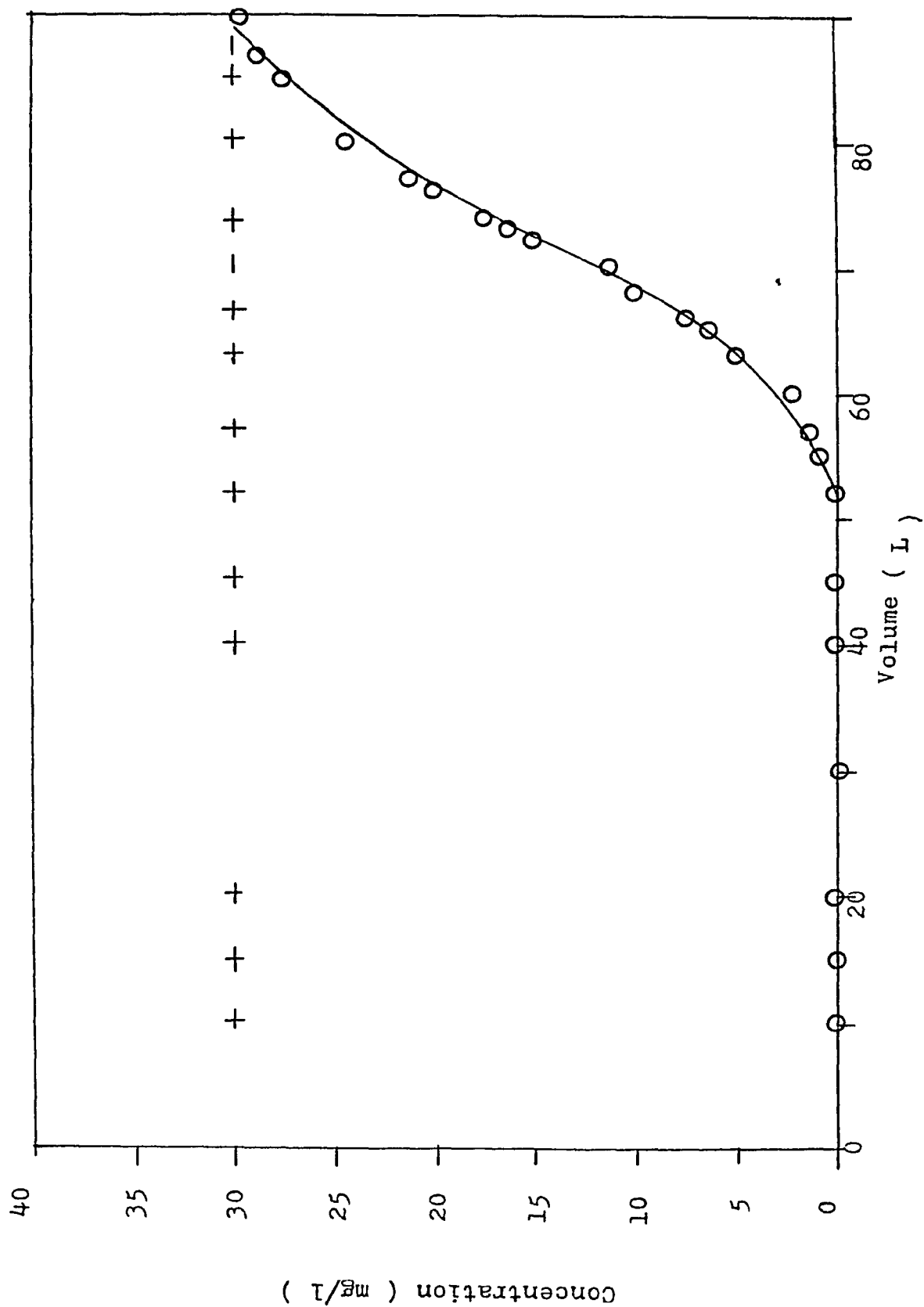O-Xylene onto Militant Flyash

Volume (L)

Concentration (mg/L)

E.21
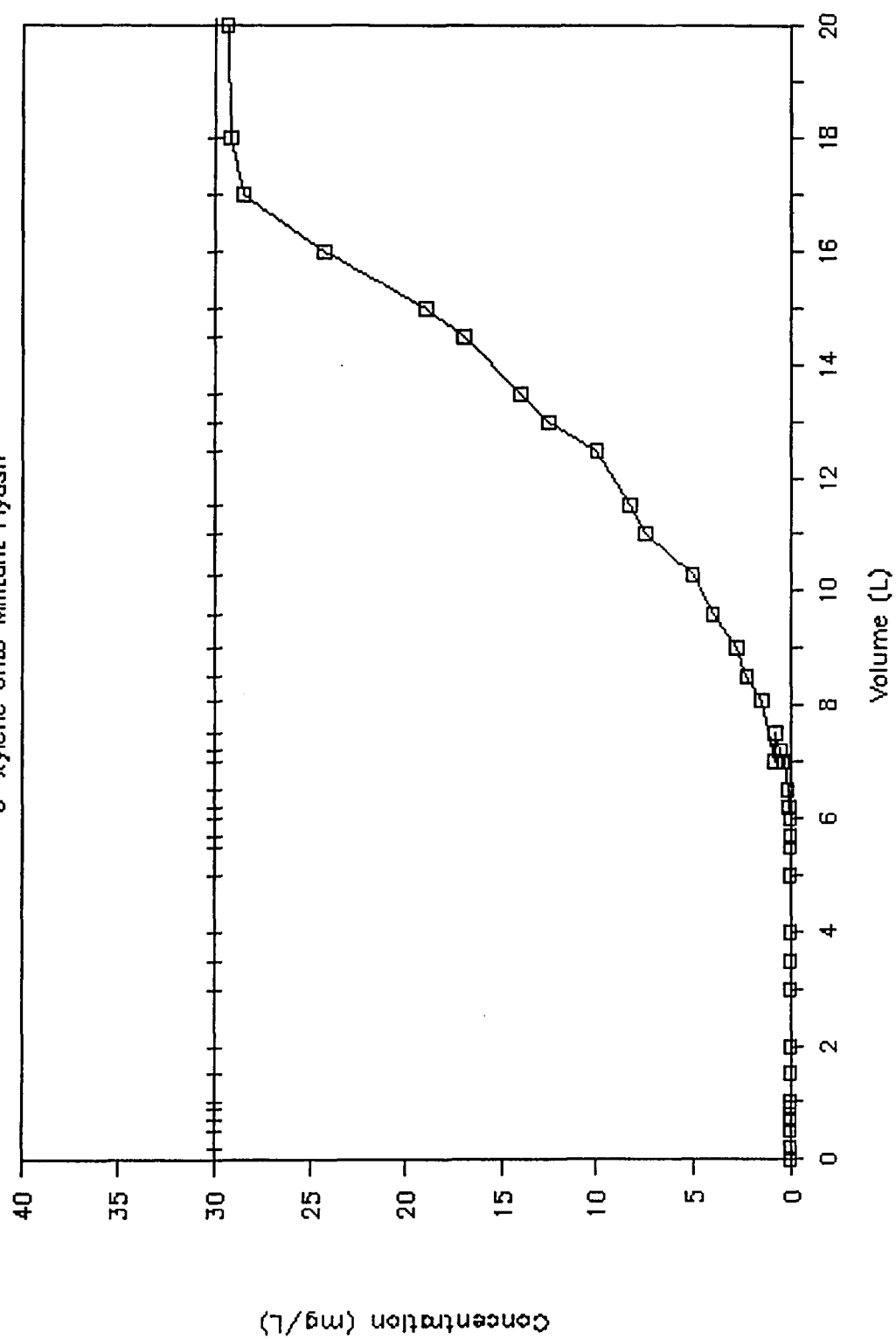
Figure E.22 Single Solute Dynamics

MIBK onto Wellmore Flyash

E.22
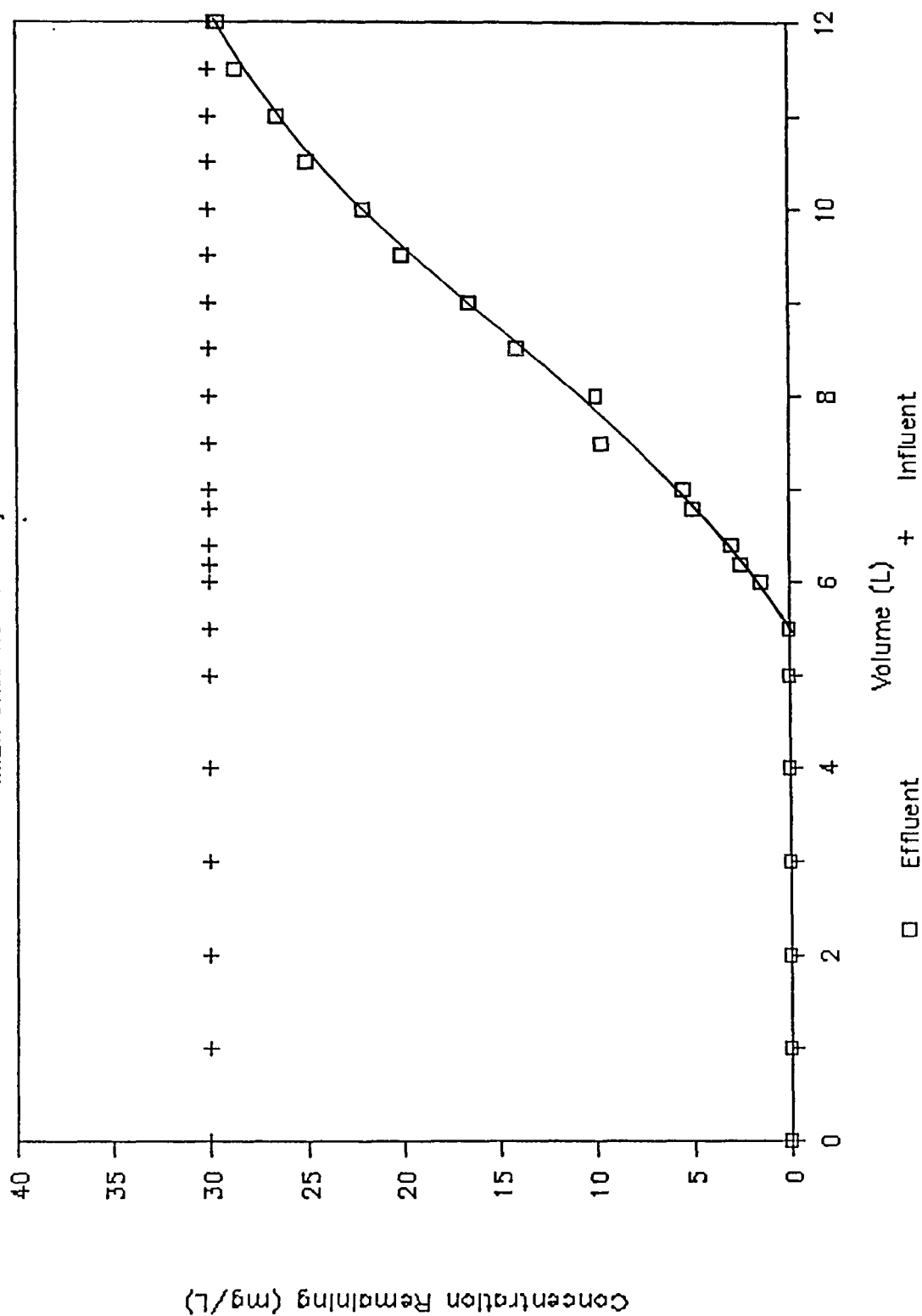
Figure E.23 Single Solute Dynamics
MIBK onto Conemough Flyash

E.23
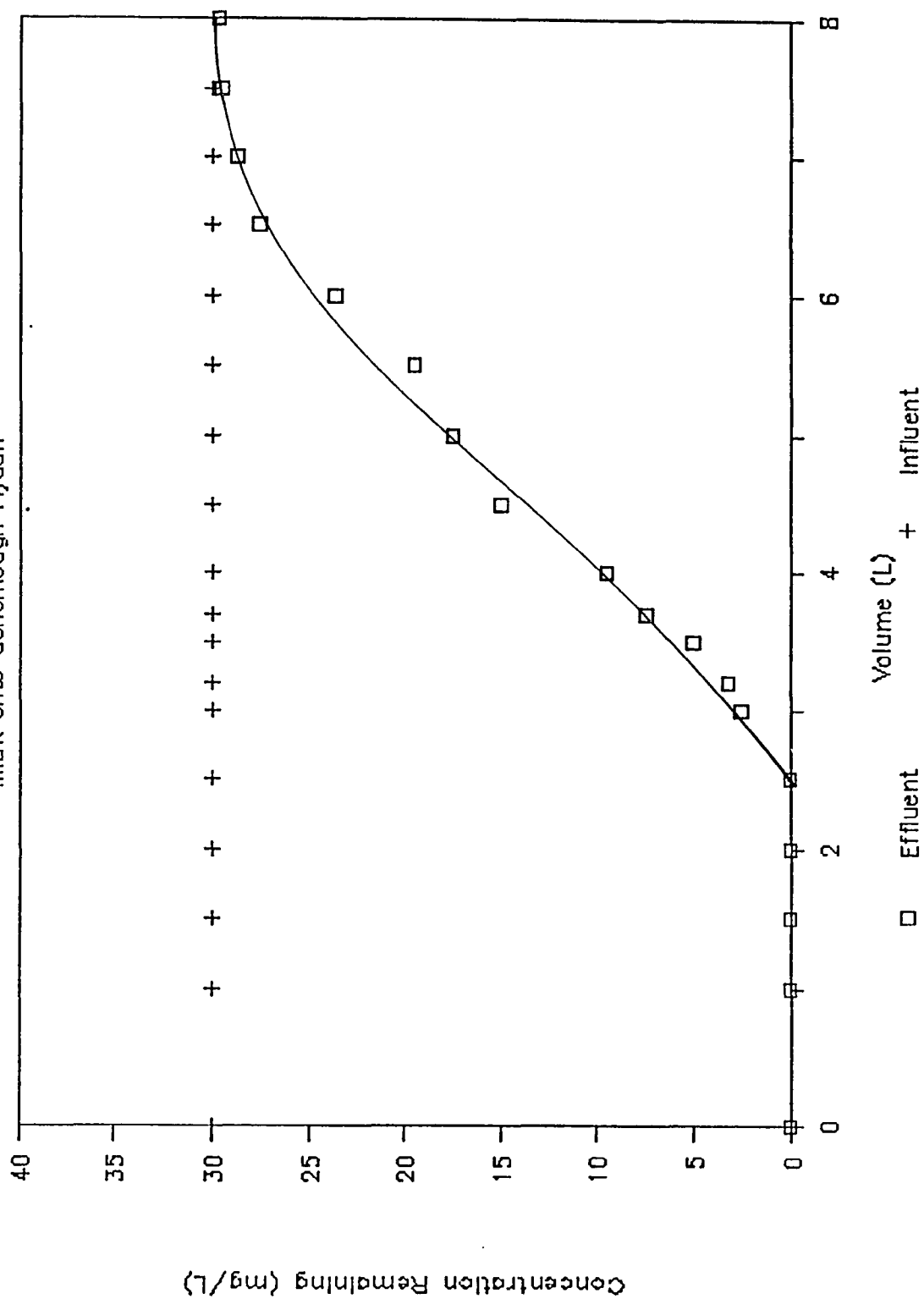
Figure E.24 Single Solute Dynamics

MIBK onto Blender Flyash

Effluent □   + Influent

Volume (L)

Concentration Remaining (mg/L)

E.24
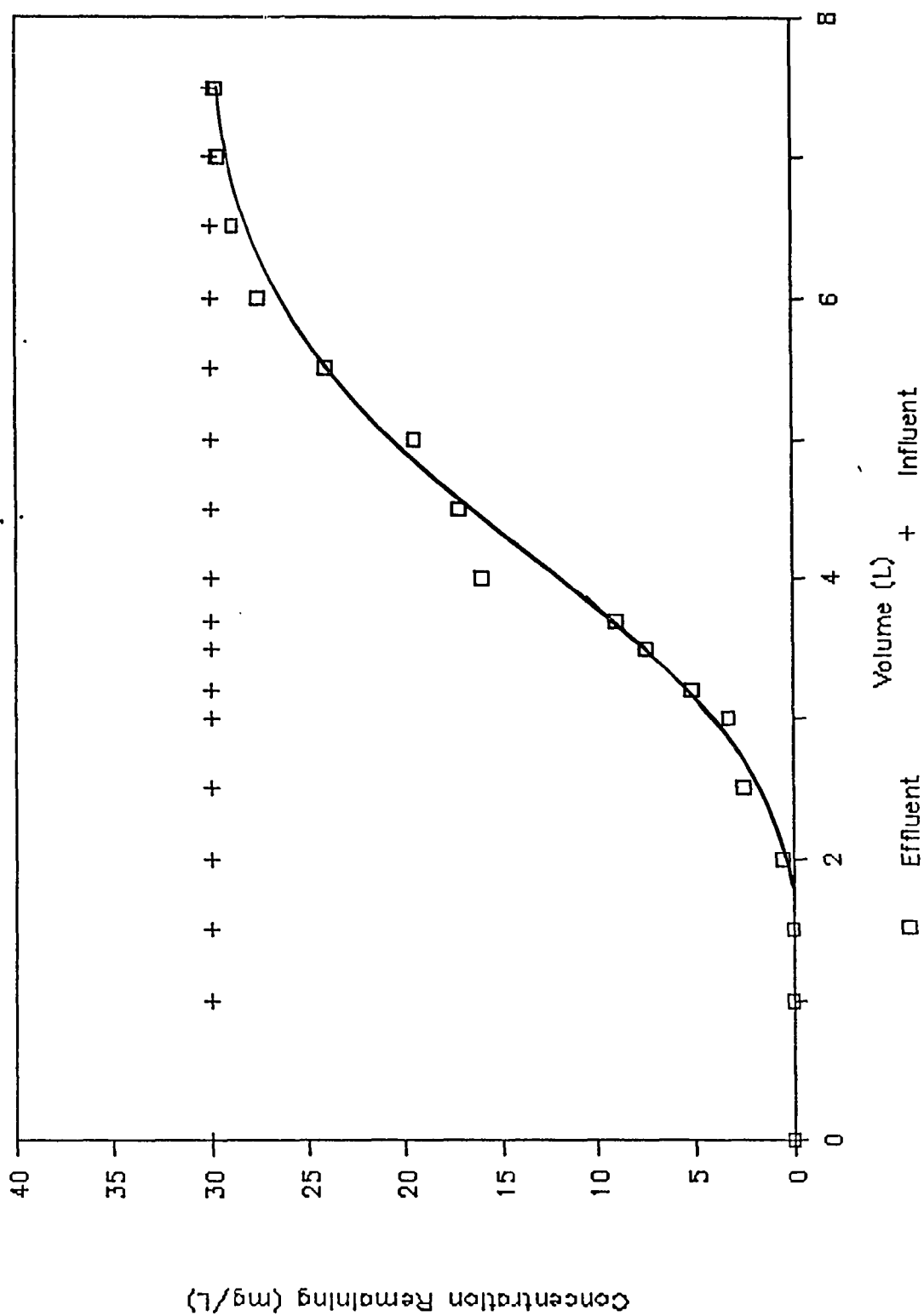
Figure E. 25   Single   Solute   Dynamics

Aniline onto Activated Carbon
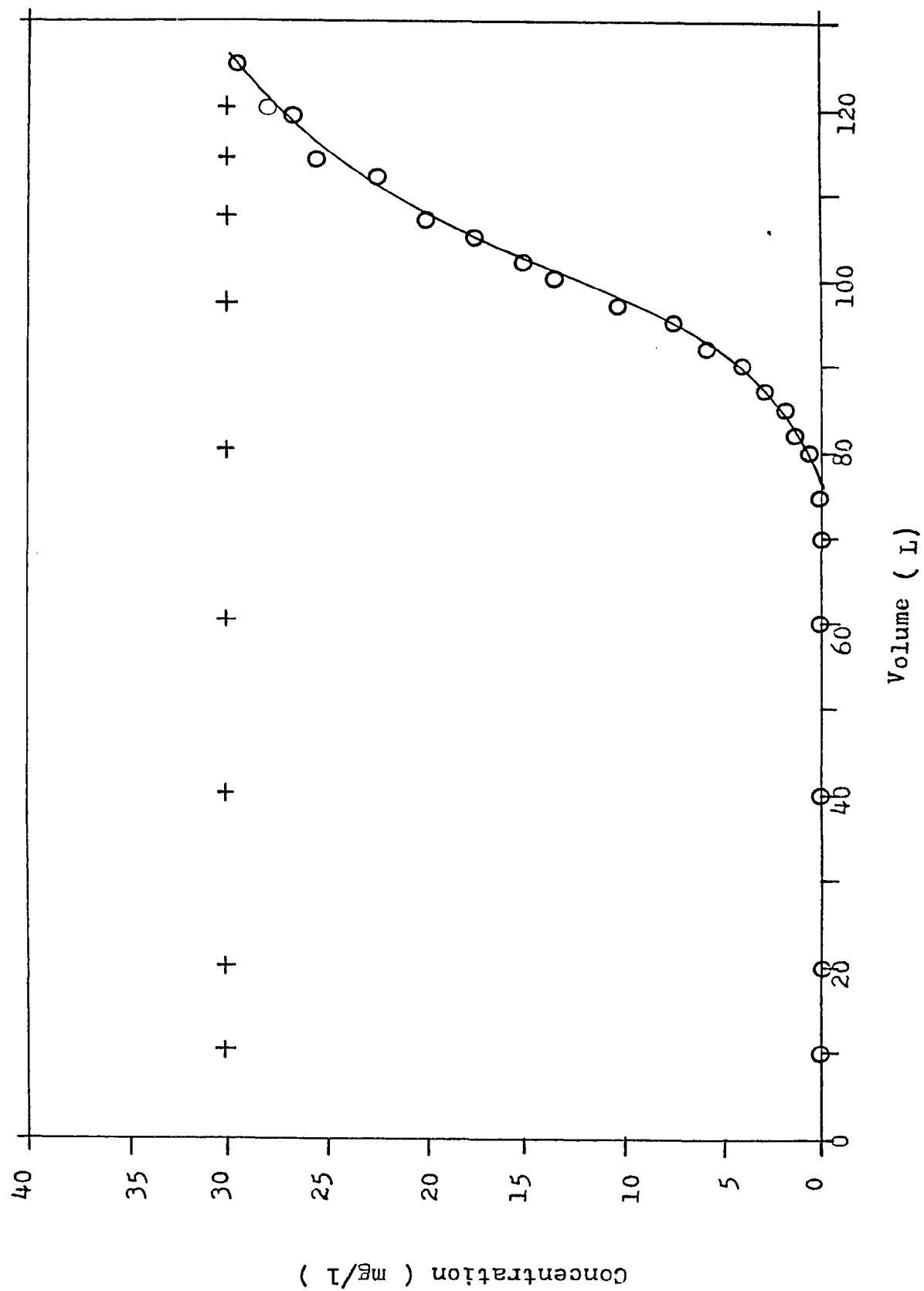
Figure E. 26   Single   Solute   Dynamics

o-Xylene onto Activated Carbon

E.26
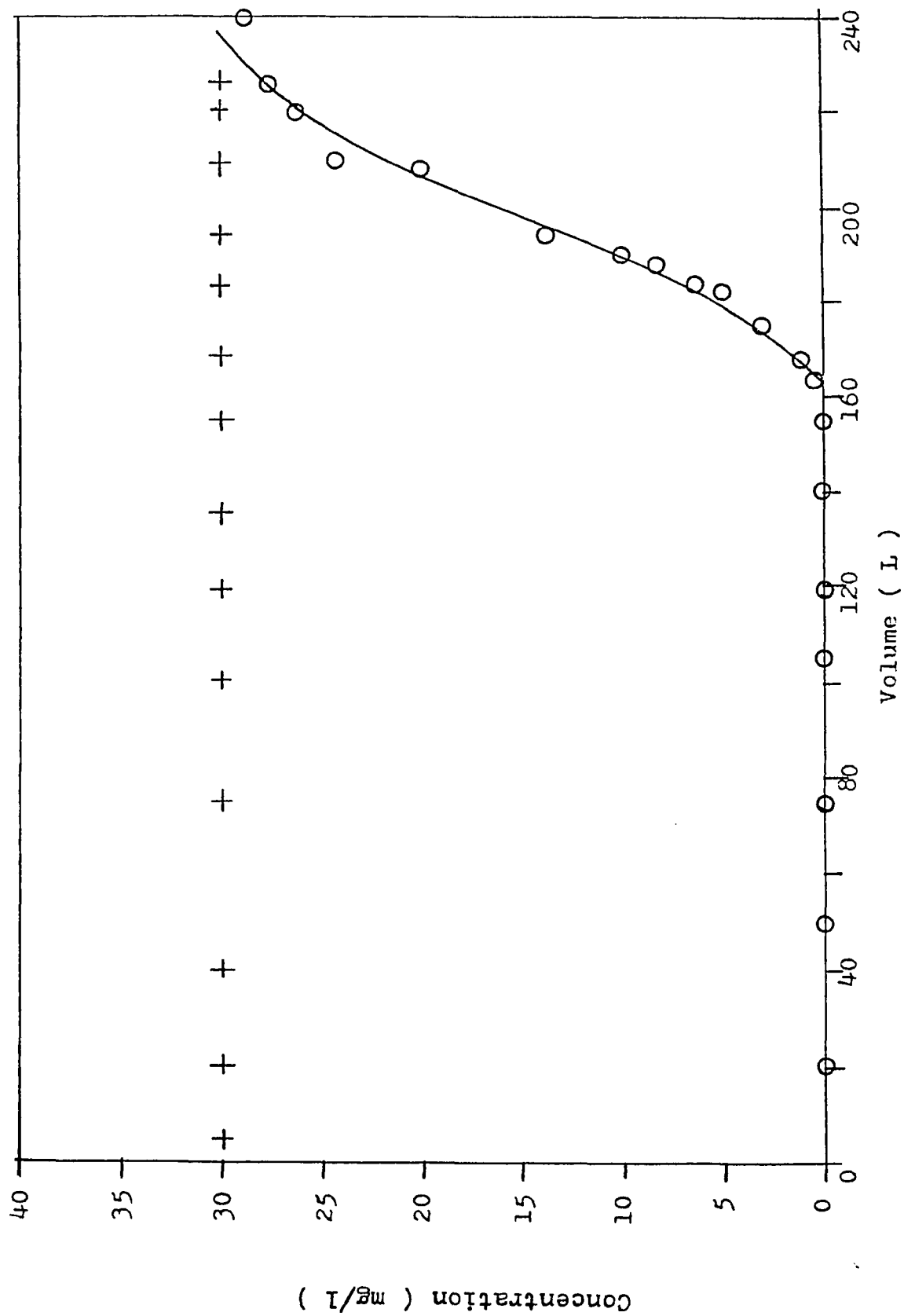
Figure E. 27   Single Solute Dynamics

Phenol onto Activated Carbon

Volume (L

Concentration (mg/L)

E.27
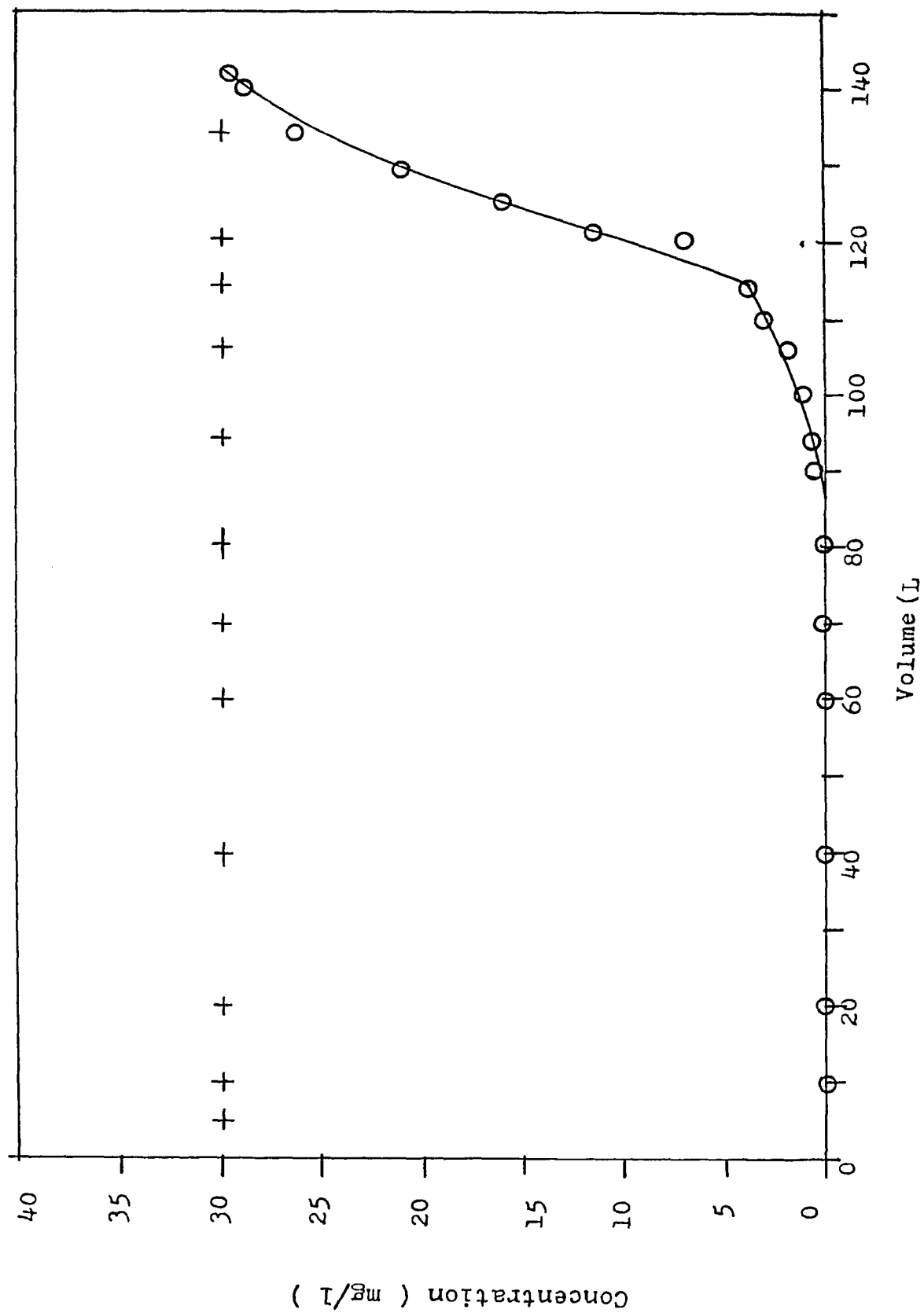
Figure E. 28   Single Solute Dynamics

MIBK onto Activated Carbon

E.28

Figure E.29 Single Solute Dynamics
MIBK onto Upshore Flyash

Concentration (mg/L)

Volume (L)   +   Influent

□   Effluent

E.29
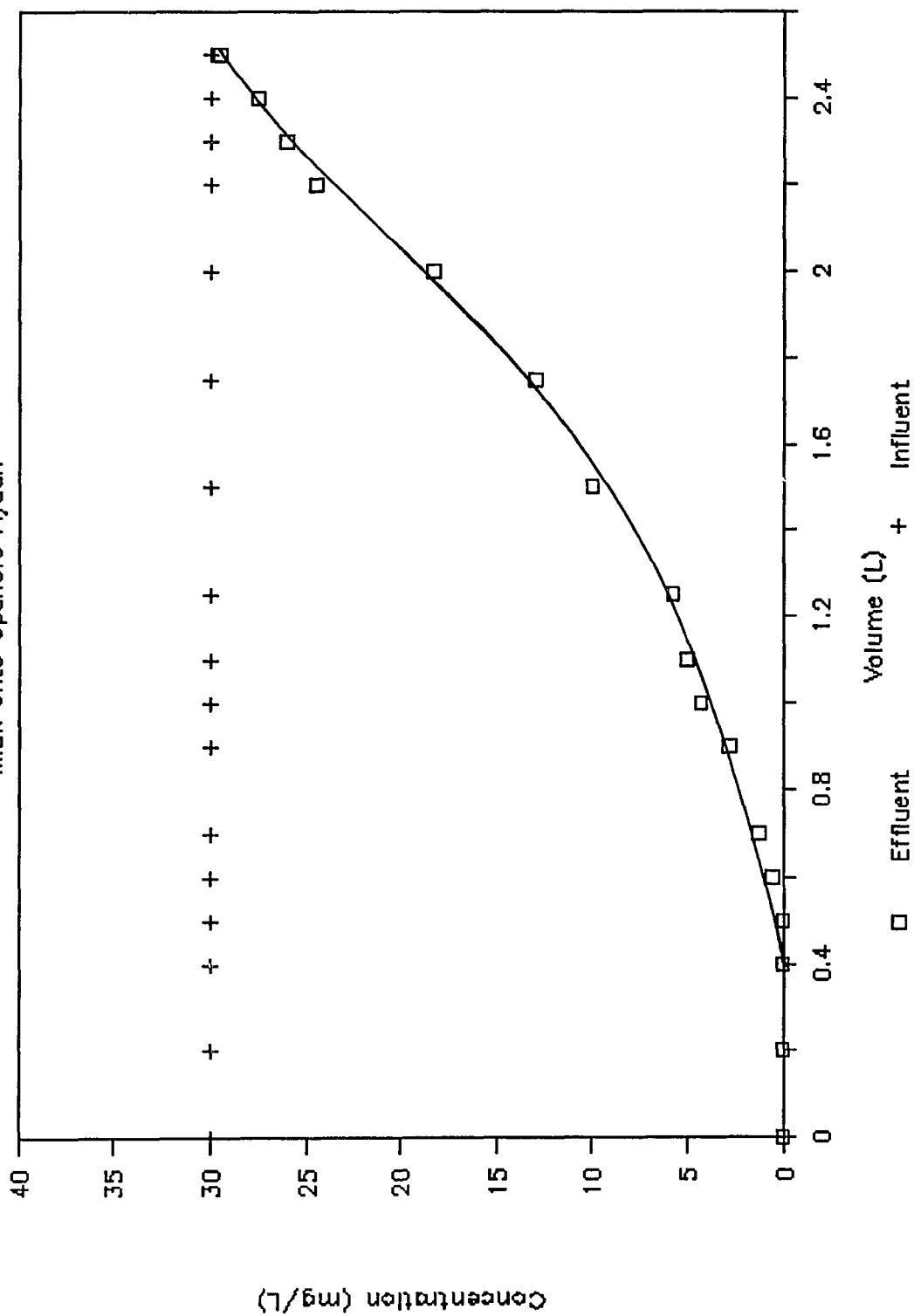
Figure E.30 Single Solute Dynamics

MIBK onto Keystone Flyash
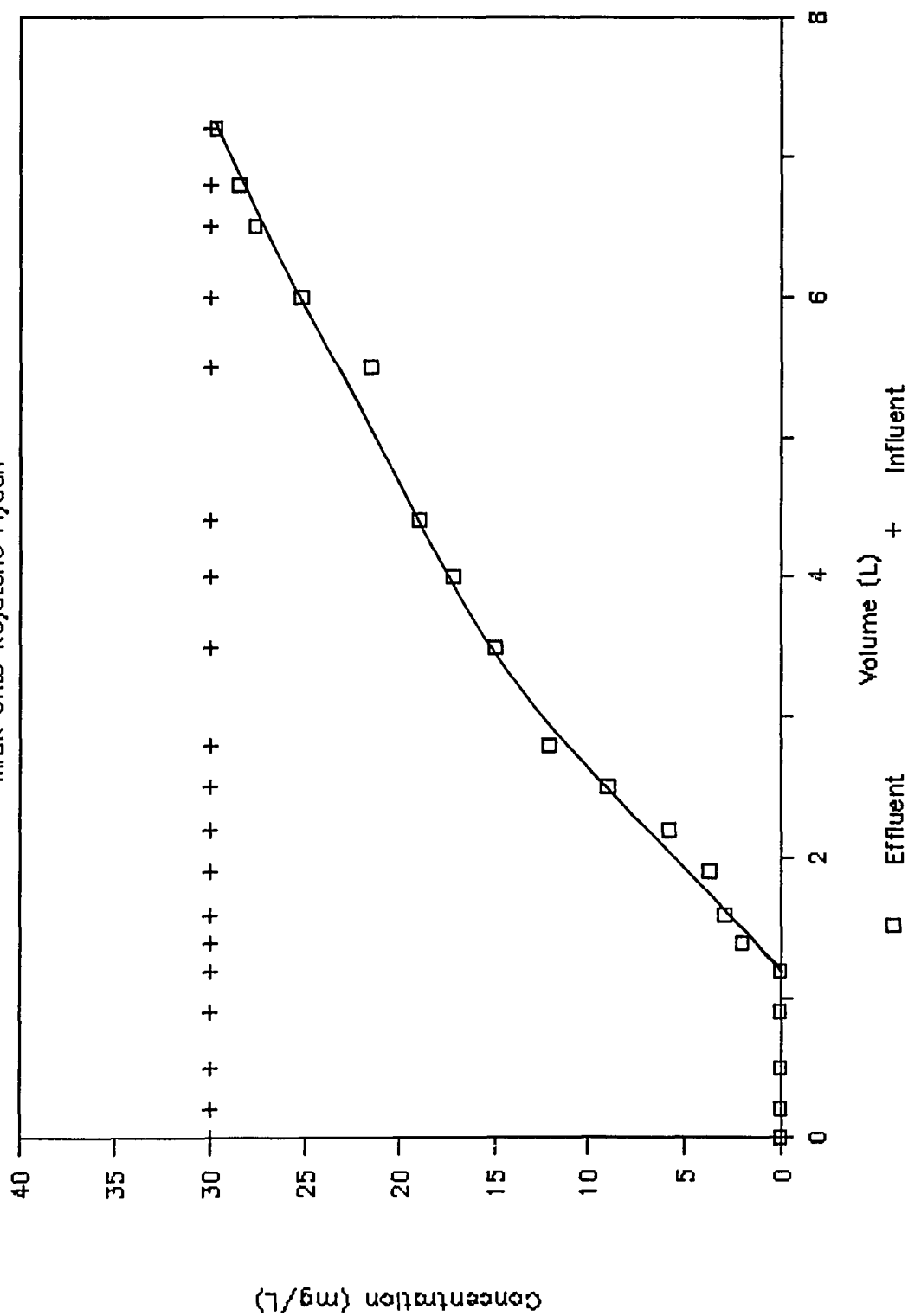
Figure E. 31   Single Solute Dynamics
MIBK onto Militant Flyash

Concentration (mg/l)

Volume (L)

E.31
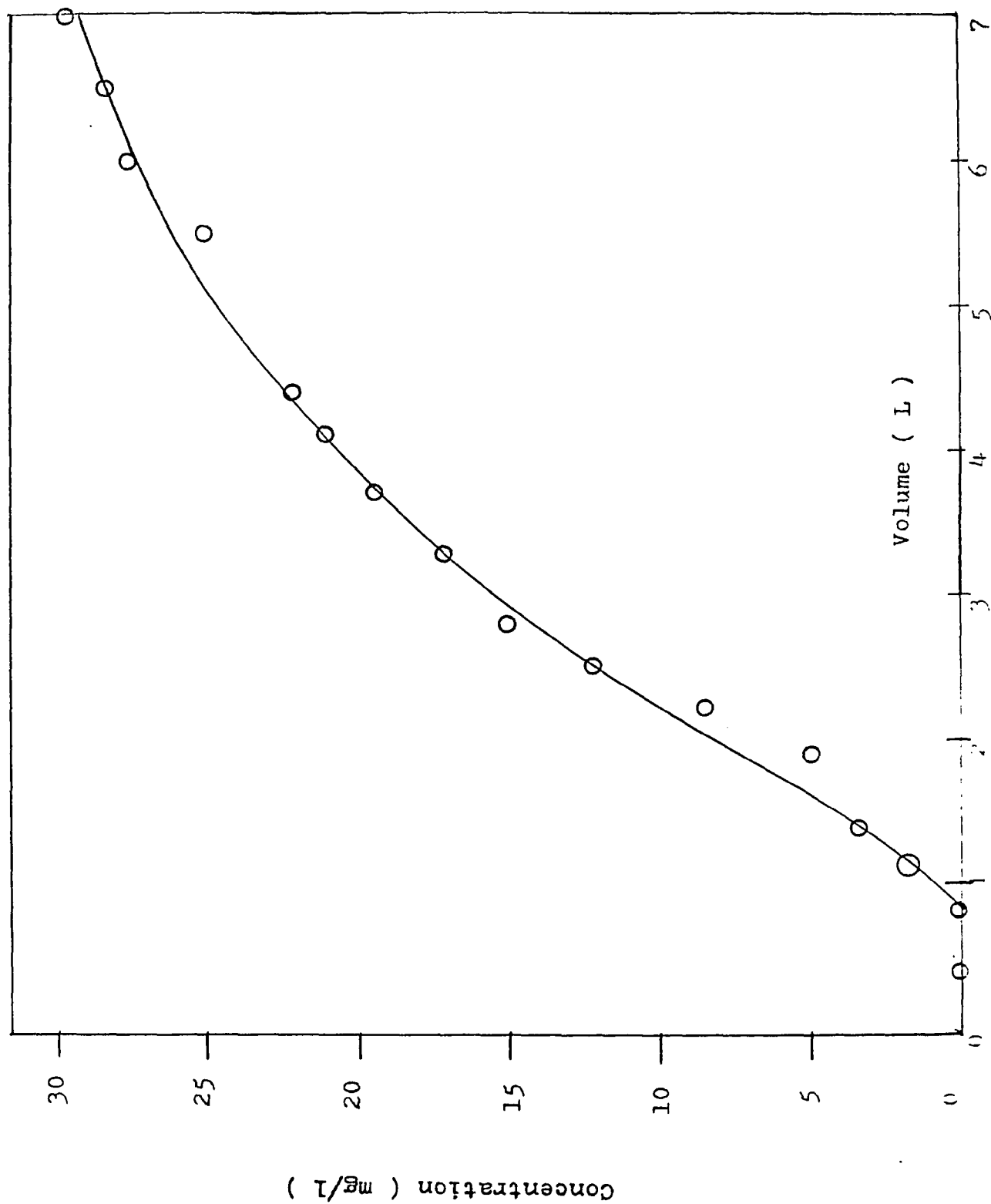
APPENDIX - 'F'

MULTI SOLUTE ADSORPTION
DYNAMICS

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Figure F.1. Two Component Dynamics

Sorbent : Militant Flyash

Volume (L)

Concentration (mg/L)

□ Butyraldehyde   + o-Xylene

F.1
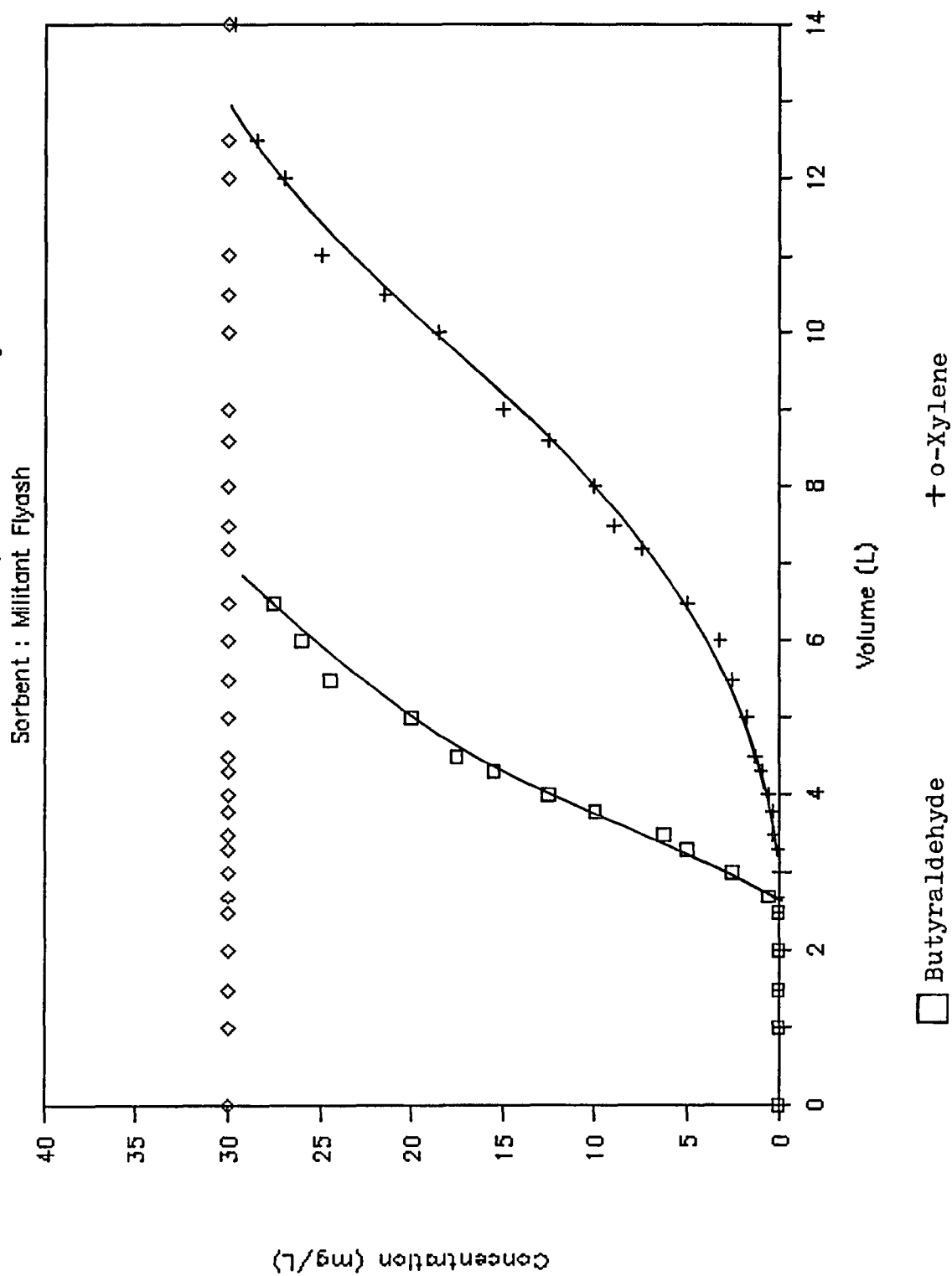
Figure F.2. Two Component Dynamics

Sorbent : Militant Flyash

Concentration (mg/l)

Volume (L)

□ Butanol   + o-Xylene

F.2
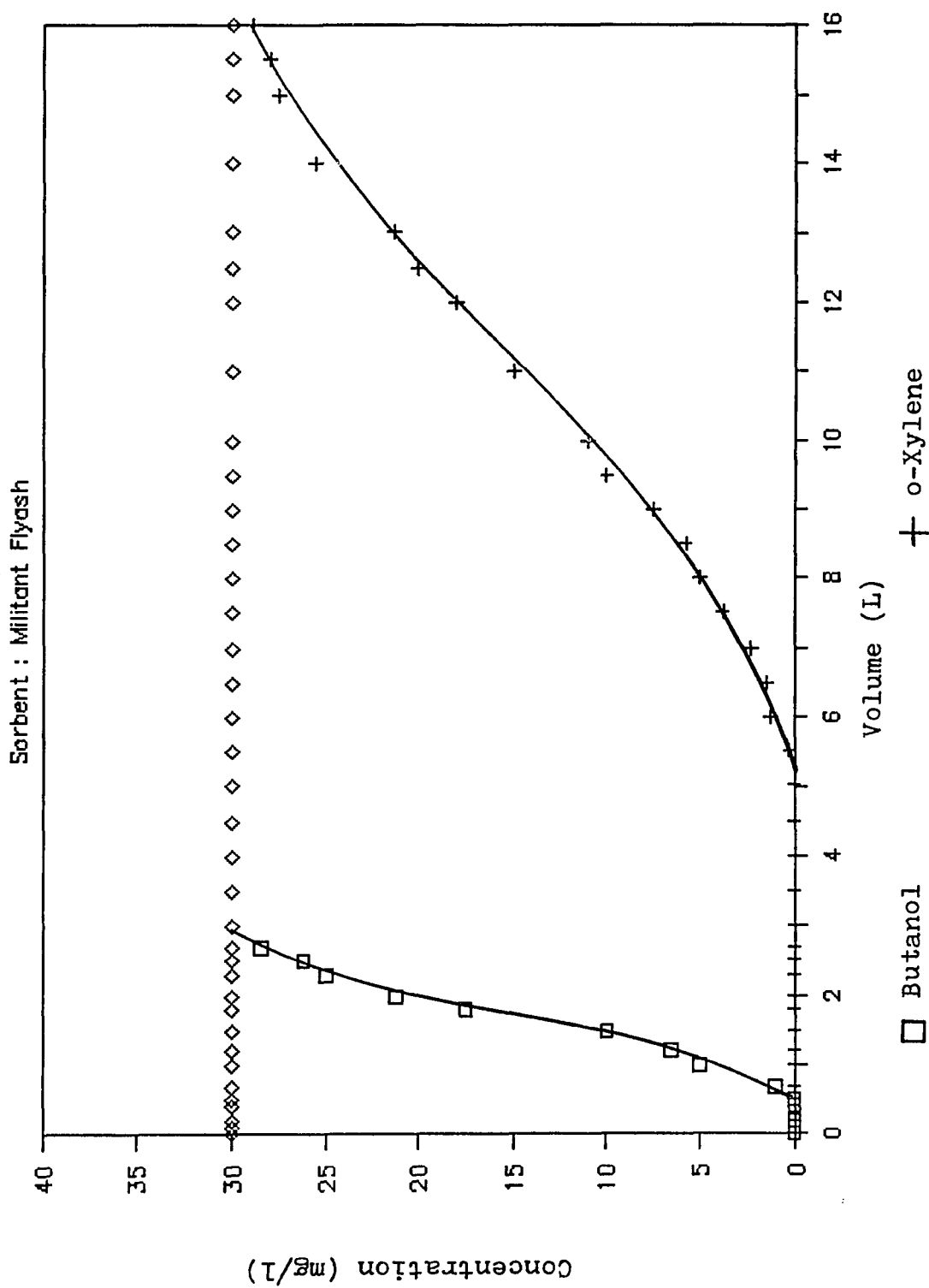
Figure F.3. Four Component Dynamics

Sorbent : Militant Flyash

+ Butanol,   ◇MIBK,   △ Butyraldehyde,   ▢o-Xylene

F.3
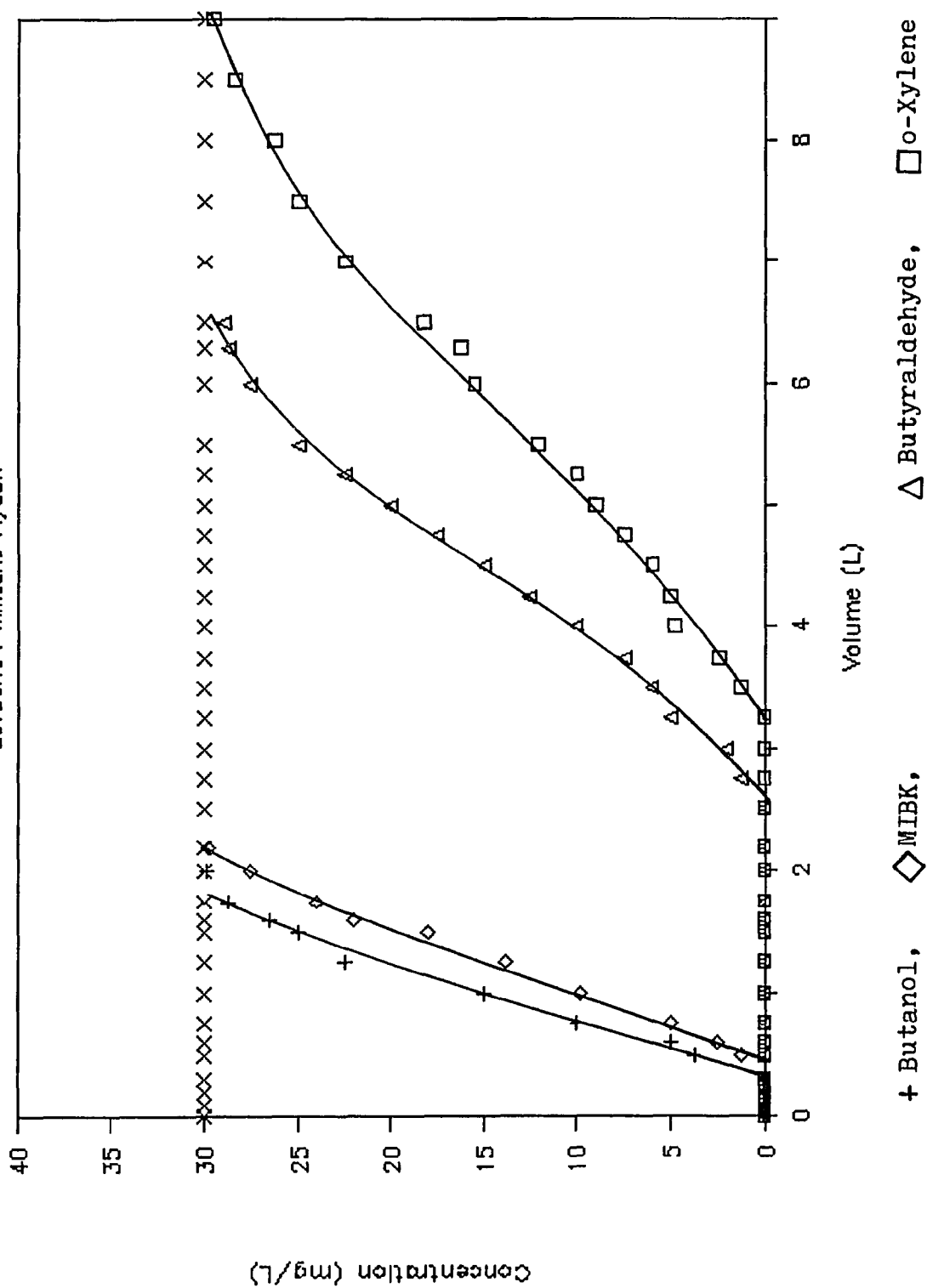
Figure F.4. Four Component Dynamics

Sorbent : Activated Carbon

Legend: □ Butanol, ✦ MIBK, ◇ Butyraldehyde, △ o-Xylene

Axes: Concentration (mg/L) vs Volume (L)

F.4
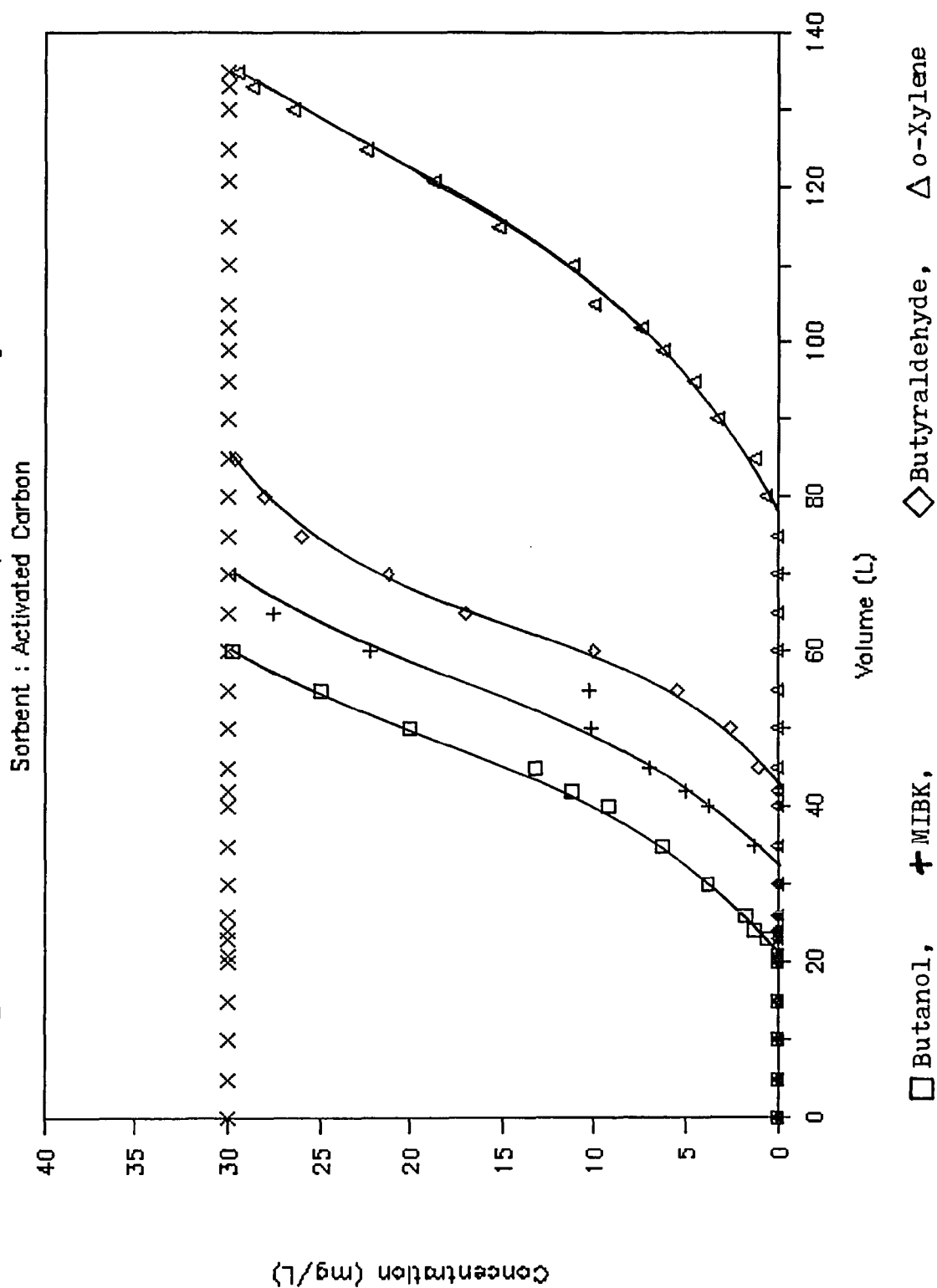
Figure F.5. Two Component Dynamics

Sorbent : Activated Carbon

Concentration (mg/L)

Volume (L)

□ Butyraldehyde   + o-Xylene

F.5
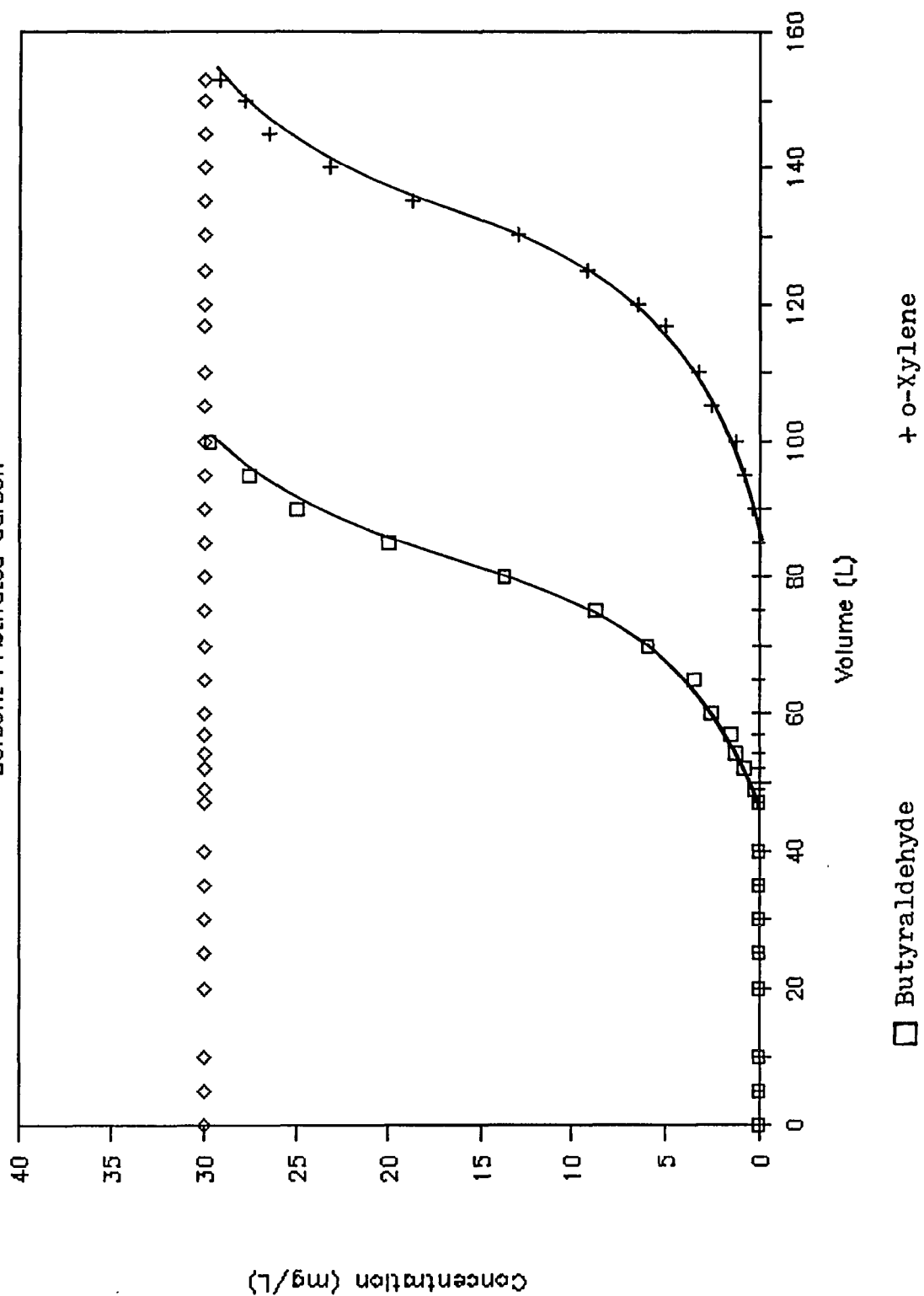
<u>APPENDIX - 'G'</u>

DESORPTION STUDY

Fig G.1 Desorption Study
Sorbent:MilitantFlyash,Sorbate:O-Xylene

G.1
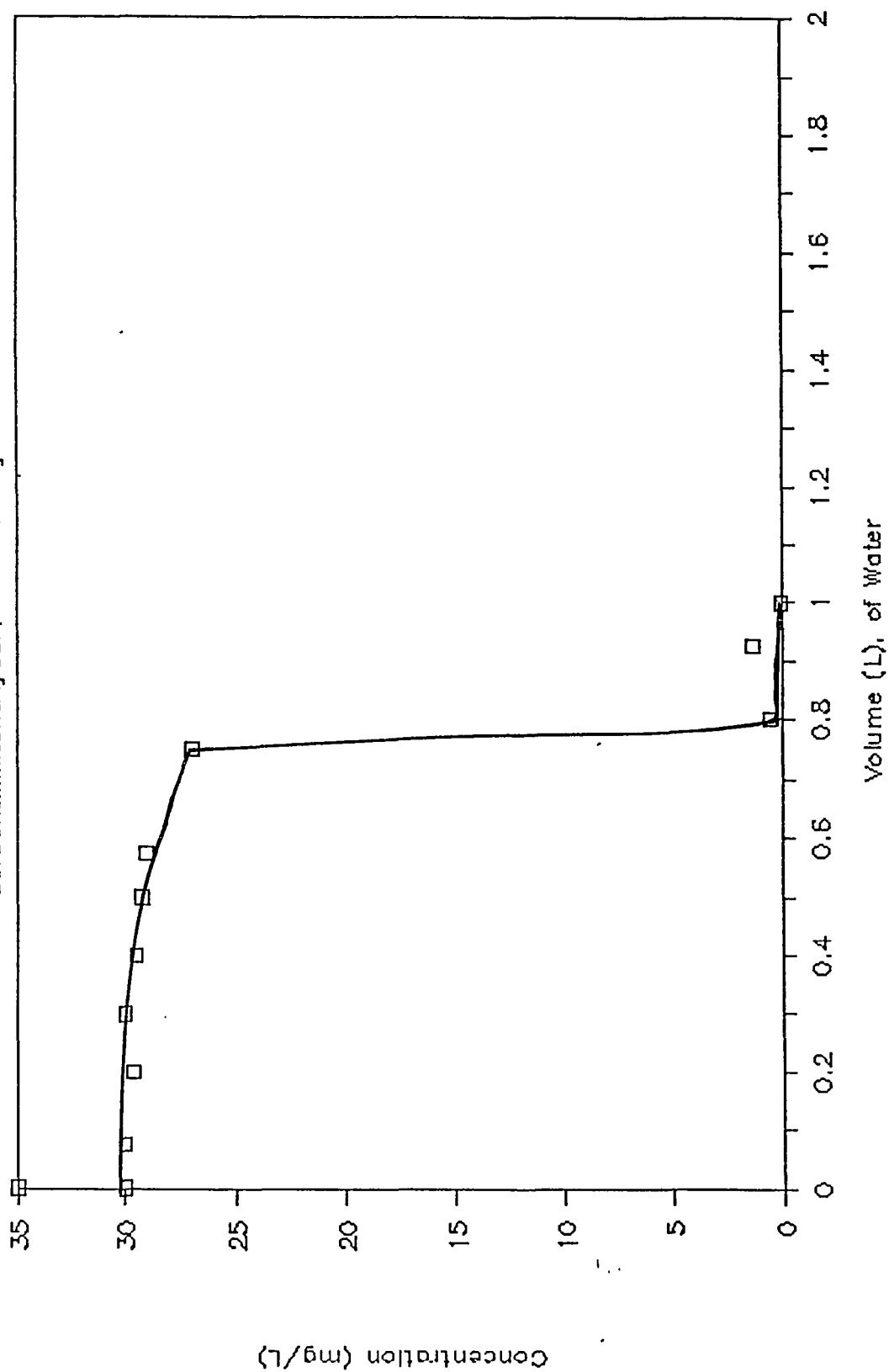
Fig G.2 Desorption Study
Sorbent:Militant Flyash,Sorbate:Aniline
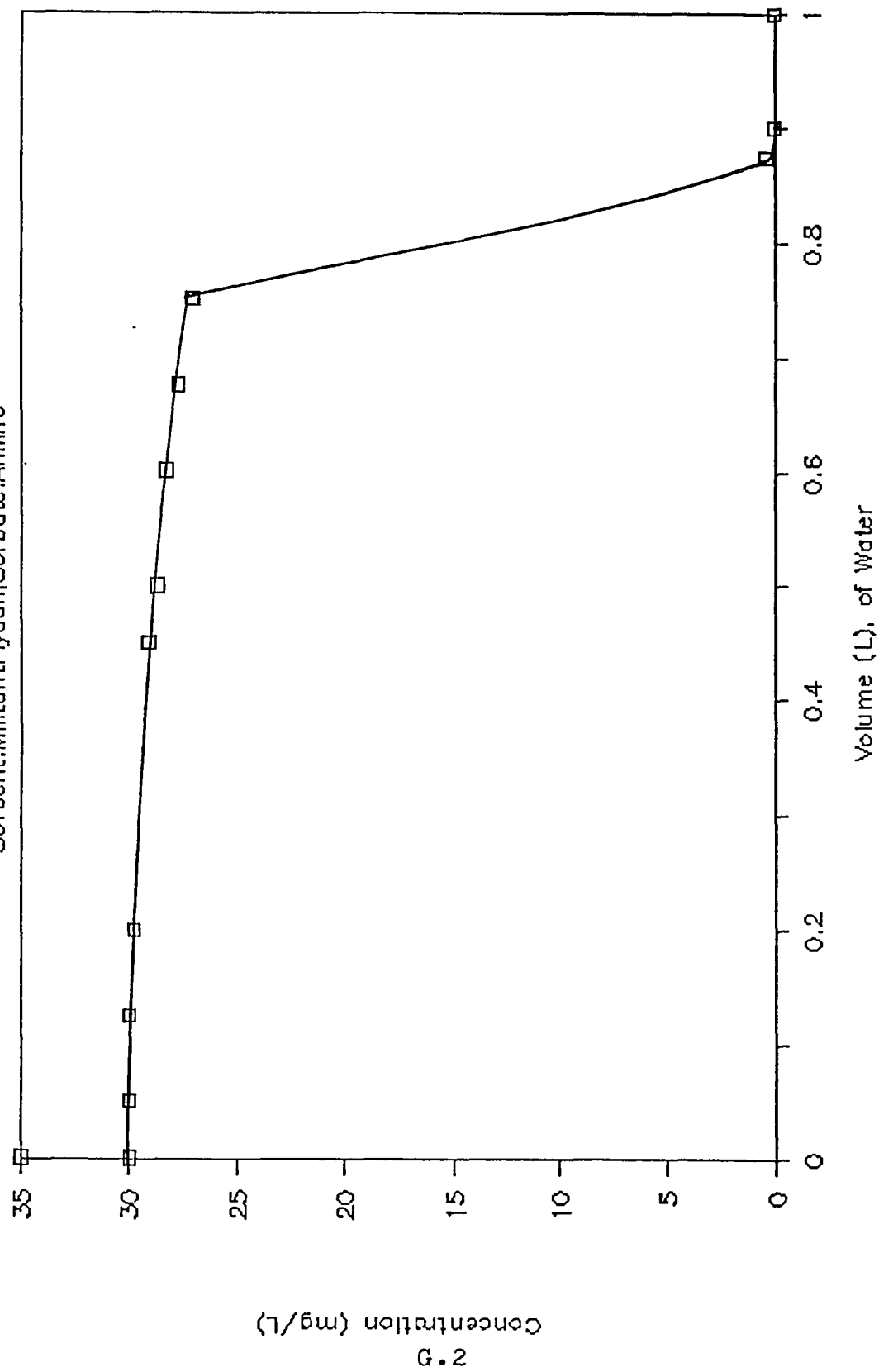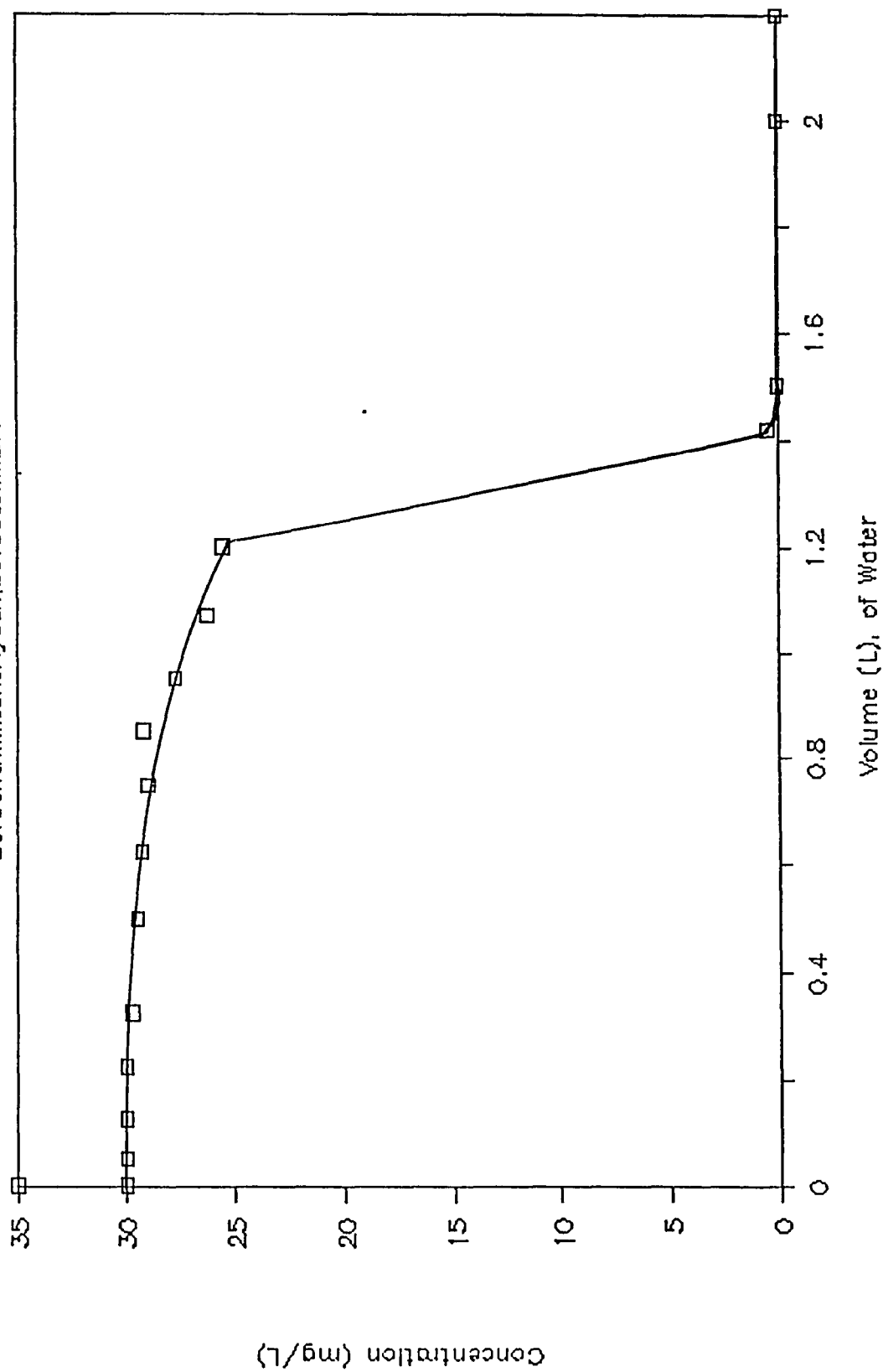
Concentration (mg/L)

Volume (L), of Water

G.2

Fig G.3 Desorption Study

Sorbent:MilitantFlyash;Sorbate:MIBK

Concentration (mg/L)

Volume (L), of Water

G.3

Fig G.4 Desorption Study
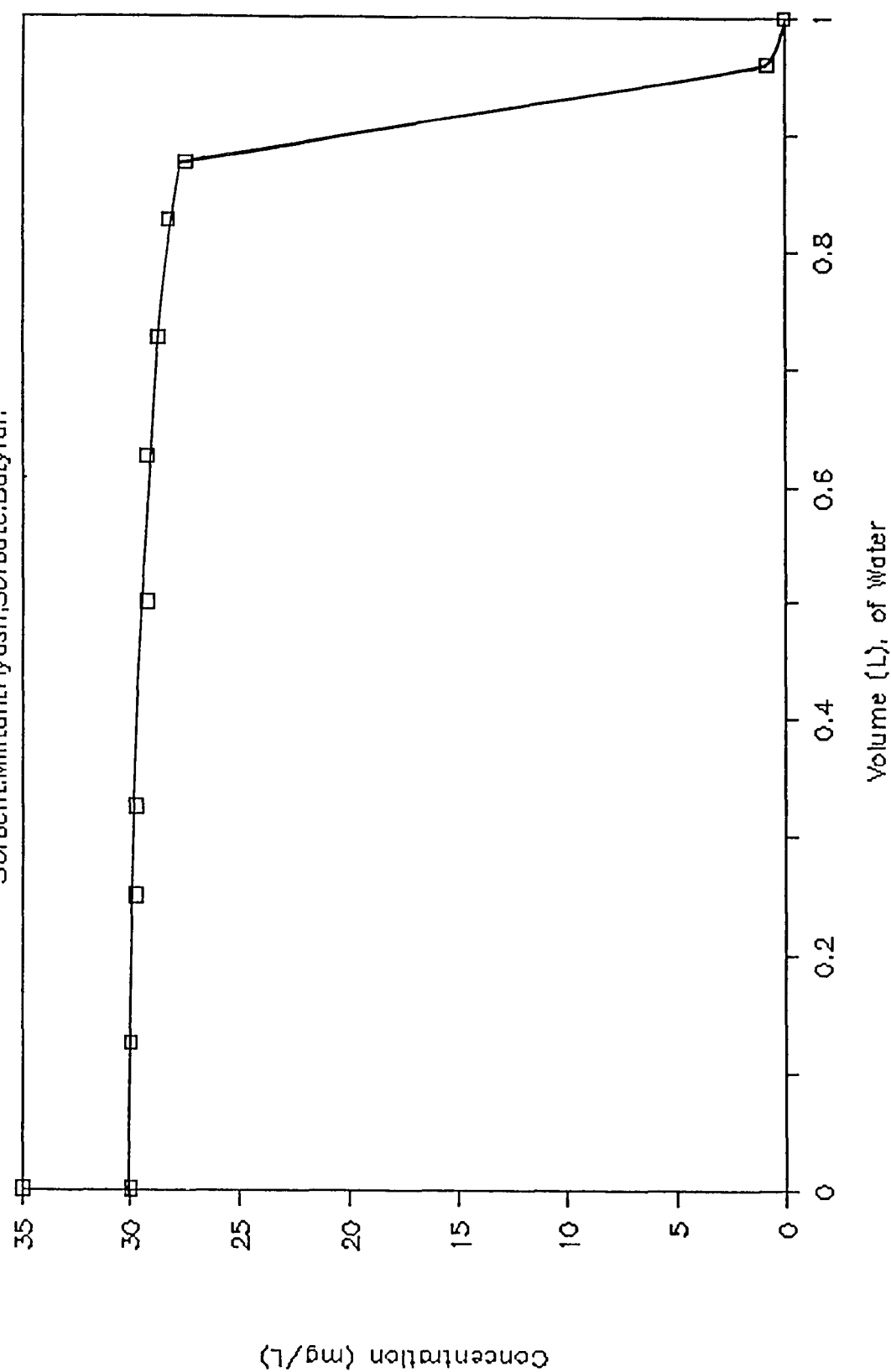Sorbent:Militant Flyash,Sorbate:Butyral.

Volume (L), of Water

Concentration (mg/L)

G.4

Fig G.5 Desorption Study
Sorbent:Militant Flyash,Sorbate:Butanol

Volume (L), of Water

Concentration (mg/L)

G.5