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EFFECT OF INORGANIC SALTS ON ADSORPTION PROCESS

by

Pai-Yuan Horng

Dissertation submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of
Doctor of Engineering Science
January 1990

APPROVAL OF DISSERTATION

EFFECT OF INORGANIC SALTS ON ADSORPTION PROCESS

By

Pai-Yuan Horng

for
Department of Civil and
Environmental Engineering

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Title of Thesis : Effect of Inorganic Salts on Adsorption Process

Pai-Yuan Horng, Doctor of Engineering Science, 1990

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ABSTRACT

Small amounts (0.0 M-0.01 M) of inorganic salts (sodium chloride, calcium chloride, and aluminum chloride) added to bituminous coal fly ash and granular activated carbon in batch adsorption treatment experiments indicates the possibility of enhancing the extent and rate of adsorption process.

Experiments were conducted on aqueous solutions of highly toxic and hazardous chemicals, those include : phenol, benzene, toluene, isopropyl alcohol, and methyl-isobutyl ketone. Single and multiple solute systems were examined separately. Removal of organic pollutants was measured using a Flame Ionization Detector Gas Chromatograph.

This study investigated the role of inorganic salts during the sorption process. The results of this study show the improvement of treatment efficiency by the addition of inorganic salts depends on the characteristics of the solute, the sorbent, the salt, and the solution. The results also reveal that the adsorptive capacity of sorbents can establish a linear relationship with the concentration of inorganic salts.

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TABLE OF CONTENTS

VI CONCLUSIONS

LIST OF TABLES

LIST OF FIGURES

Adsorption Isotherms

Effect of Inorganic Salts on Adsorption Capacity

Multi-component Adsorption Equilibria

Kinetic Studies

First Order Reversible Kinetic Fit

SECTION I

INTRODUCTION

1.1 Introduction

The increasing concern over the public health aspects of trace organic contamination in drinking water focuses new interest in adsorption as a removal mechanism for such pollutants. Although many investigators have already done work in the area of adsorption, very little work has been done on the use of flyash as an adsorbent for the treatment of hazardous organics. Furthermore, a scan of the literature reveals no studies concerning the use of inorganic salts as an enhancement factor in flyash adsorptive efficiency. The literature reveals that different adsorbents display varing degrees and types of adsorption mechanisms in the presence of inorganics salts. Also, many pretreatment processes (eg. ion-exchange, lime-soda softening, coagulation) often result in significant changes in the inorganic composition in water supply. The presence of inorganic salts in groundwater and wasterwater sources suggests that the exploration of the adsorption mechanisms associated with the use of inorganic salts is worthwhile. Adsorptive capacity is the most important property of adsorbents, because it determines how much wastewater or groundwater can be treated per unit of adsorbent. Adsorptive capacity establishes both the direct operating cost for treatment and sizing of process equipment and systems.

Activated carbon has been recognized as the most efficient adsorbent in adsorption processes. Parallel adsorption experiments using activated carbon and flyash are conducted in order to establish a better understanding of the adsorption mechanism associated with the presence of inorganic salts. The present study focuses on the use of sodium chloride, calcium chloride and aluminum chloride salts. Sodium chloride is the most common salt found in groundwater and wastewater. Calcium chloride, a divalent salt, is used in ion-exchange and lime-soda pretreatment process. Aluminum chloride (trivalent salt) is used in the coagulation process.

1.2 Literature Review

This review focuses on the effects of nonreactive inorganic salts on the rate and extent of anionic and neutral organic adsorption onto negatively charged adsorbents. By using the existing knowledge of the effect of inorganic salts on adsorption, the observed phenomena is explained by explored mechanisms. Various kinds of adsorbents, adsorbates, and inorganic salts possess different characteristics. It is worthwhile to explore this matter in more detail.

1.2.1 Effect of Salts on Adsorptive Capacity

Black et.al(1) [1960] found that the addition of calcium chloride in the concentration range of 25-250 mg/l could increase the adsorption of anionic polymer onto kaolinite. Coughlin et.al(2) studied the influence of chemisorbed oxygen in adsorption and reported that in the presence of calcium chloride, within the concentration range of 0 - 4.0 mM, adsorption of sodium benzene sulfonate onto activated carbon was enhanced up to 300 percent. Snoeyink et.al(3)[1969] investigated the sorption behavior of phenol and nitrophenol by activated carbon. at various pH's. They found that at pH 10, the addition of sodium chloride (0.0 - 1.0 M) increased the adsorption of p-nitrophenol onto activated carbon about 25-100 percent, At pH 2 ,no increase in adsorption was obtained. They also reported that the existence of some anions (i.e. ClO_4^-, PO_4^{-3}, $SO_4^{=}$, NO_3^-) did not affect the adsorption of the system at a pH of 2. Digiano and Weber (4)[1973] studied the sorption kinetics found that in the presence of PO_4 (K^+ salt), in the concentration range of 0.0 - 0.01 M, the adsorption of 2,4-dinitrophenol were doubled at a neutral pH. Zogorski and Faust(5)[1976] studied the effect of phosphate buffer on adsorption, they found that in the presence of PO_4^{-3} (Na^+ salt), in the concentration range of 0 - 0.05M, the adsorption of 2,4-dichlorophenol onto activated carbon only slightly increased for pH's greater than 8. they also found that when the pH was less than 6, the adsorption increased 30 percent. Kavanaugh(6)[1977] investigated the interaction of iron with adsorption. He found that the adsorption of citrate is very dependent on the ratio of citrate and Fe^{+3}(concentration range 0.0 - 0.36 mM). In the ratio range of citrate to Fe less than 1, the adsorption of citrate onto activated carbon increased, within the ratio range of 1-4, the adsorption of citrate decreased. McCreary and Snoeyink (31) studied the adsorption of humic substances. They reported that small concentrations of PO_4^{-3} (i.e. 0.0 - 5.0 mM) could increase the adsorption of soil fulvic acid onto activated carbon at a neutral pH value. Weber et.al (32) [1980] extensively studied the adsorption of humic acids. They found that in the presence of Ca^{+2}, Mg^{+2} (0.0 -10 mg/l) and NaOCl (0.0 -3.5 mg/l) in solution, there is a substantial increase in the adsorption of humic acid onto activated carbon. Using a lower concentration range of Fe^{+3} (i.e. 0.0 - 0.05 mg/l), no effect on the adsorption of humic acid was observed . Randtke and Jepsen (32) [1981] found that the presence of Fe^{+3} and Al^{+3} , below the required concentration for coagulation, showed no effect on adsorption of fulvic acids. In 1982 (32), they studied the effect of salts on adsorption of fulvic acids onto activated carbon and concluded the following :

1). calcium,magnesium, and soldium salts enchance the adsorption of fulvic acids onto activated carbon; calcium was the most effective, magnesium slighly less effective than calcium, and soldium the least effective.

2). Various inorganic anions had no observable influence on the adsorption of fulvic acids.

3). The enchancement of fulvic acid adsorption by calcium and magnesium was less pronounced at low pH.

4). Adsorptive capacity was not sensitive to change in salt concentration at low concentration of salt (< 1.0 mM) with little adsorption occurring in the absence of added salts. 5). Sodium chloride and sodium sulfate had no effect on the adsorption of fulvic acids when calcium or magnesium was present at a concentration of 0.5 mM.

Weber et. al (46) [1983] studied the ion-effect on adsorption of humic substances and reported that the adsorptive capacity of activated carbon for adsorption of humic substances can be markedly enhanced by certain cationic species. The effect of Ca^{+2} and Mg^{+2} are greater than those of Na^{+1} and K^{+1} by more than an order of magnitude; Ca^{+2} has a slightly greater effect than Mg^{+2}, and K^{+1} has a slightly greater than Na^{+1}. However, they also found that solution with increasing Al(III) and Fe(III) concentrations decreased adsorption of humic acids onto activated carbon. Weber et.al(47) stated that, pretreatment with alum or lime affected the subsequent adsorption of TOC by granular activated carbon, with alum coagulation generally improving overall adsorbability. They also found that the higher the Ca^{+2} concentration, the higher removal of TOC from humic acid solution. Semmens et. al (49) [1986] studied the influence of coagulation on removal of organics by activated carbon. They found that the effect of coagulation was dramatic with removal of TOC improving as the coagulant dose was increased.

1.2.2. Effect of Salts on the Rate of Adsorption

Very few experimental data related to the rate of adsorption as a function of inorganic salts' concentration have been reported. This is may be due to the fact that the observable rate is not only a function of interparticle diffusion, but also a function of adsorptive capacity. If inorganic salts have a significant effect on adsorptive capacity, the relationship between adsorption rate and adsorptive capacity and the relationship between concentration of inorganic salts and adsorptive capacity must be estabilished separately. Based on that, Digiano and Weber (4) found that the diffusion coefficients of dinitrophenol are 0.79 x 10^{-5} sq cm/sec and 1.1 x 10^{-5} sq cm/sec in the absence and presence of 0.01 M potassium phosphate buffer solution , respectively. The addition of phosphate buffer increases the uptake rate significantly. Weber et.al (32) [1980] reported that Ca^{+2}, Mg^{+2} and OCl^{-1} enhanced rate of adsorption of humic acids, but did not correlate the rate change to the intraparticle diffusivity. Zogorski and Faust (5) found that the rate of adsorption of dichlorophenol and dinitrophenol was not significantly affected by the presence of 0.05 M phosphate buffer solution. Weber et. al (46) [1983] studied that the effect of Ca^{+2} concentration on rates of adsorption of humic acid. They suggested that a further investigation be conducted to determine whether the rate enhancements are attributable to increased adsorptive capacities and to the resultant increased driving force for adsorption, or if the effect of enchanced rates of mass transport should also be included.

1.2.3. Mechanisms

Mechanisms proposed to elucidate the observed effects of salts on adsorption contain a considerable amount of speculation. Due to the condition of experiments, mechanisms responsible for enhancing or retarding the adsorption in the presence of salts, may have different explanations. However the effect of inorganic salts on adsorption of organic pollutants can categorized into three aspects :

1). Adsorbate-salt interactions in solution

Cations from the dissociation of salts react with organics in solution prior to adsorption. The salts alter the solubility or the degree of ionization of organic molecules (via the common ion effect, ion paring, or complexation) and as a result decrease the concentration of organic molecules in solution. Senoeyink, et.al(3) reported that ion-pair formation is the major factor responsible for the enhanced adsorption of p-nitrophenol in the presence of sodium chloride. Most investigators have found that the presence of salts do not significantly affect the adsorption of simple nonionized molecules. This may be due to the absence of electrostatic effects and complex formation. However Friant and Suffet (35) studied the adsorption of some volatile organics and reported that salts significantly affect the vapor-phase partitioning of several simple nonionized organic compounds. This finding suggestes that salts may be able to influence the adsorption of such compounds onto solid surface by a " salting-out " or " salting in " mechanism. The solubility effect on complex organic molecules by inorganic salts has also been reported by other investigators.(33,36,37,38) Except for the possibility of aggregation or change in the configuration of the complex ion,(6) increasing the concentration of inorganic salts can increase the adsorption of complex molecules.(1,6,31,32,33)

2). Adsorbate-salt interaction on surface

Another proposed mechanism is that the interaction berween the cations and organic anions take place on the surface of the adsorbent. The interactions are in true dynamic equilibrium; they continue to react with one another, before and after the adsorption takes place. If the adsorbent surface is negatively charged,the concentration of cations near the surface will be higher than in the bulk solution. If adsorption take place, the organic anions are attracted by the surface, resulting in the concentration of organic anions increasing at the surface. The cations in the solution or on the surface can alter the packing, spacing, and alignment of adsorbed organic anions. If the cations neutralize the charged functional group, the molecules may lie flatter, taking up more space and thus reducing adsorptive capacity; or they may draw close together increasing the adsorptive capacity.(2)

3). Adsorbent-salt interaction

There are two possible ways that the adsorbent-salt interaction can affect the adsorption. One is through the neutralization of electrostatic replusion between adsorbate and adsorbent ; the other is the formation of adsorbent-salt-adsorbate complexes. A number of investigators (1,3,6,31,32,39,40) have attributed this mechanism to their observed phenomena. Negatively charged surfaces of adsorbent and organic compounds are able to complex metal ions. Snoeyink and Weber (41) studied the physico-chemical nature of the surface of carbon and suggested that the salts adsorbed on the surface of active carbon might affect the adsorption not only by complex formation, but also by ion-pair formation, oxidation-reduction reactions and precipitation reactions.

SECTION II

THEORY

Adsorption from the liquid phase has been studied less extensively than adsorption from the vapor phase. However, in industrial processes, adsorption of liquid phases on solids, particularly activated carbon, has become a widely used operation for the purification of water and wastewaters. There is no difference in principle between adsorption from liquid and vapor phase since, thermodynamically, the adsorbed phase concentration in equilibrium with a liquid must be precisely the same as that which is in equilibrium with the saturated vapor. Unfortunately, the simple model isotherms, developed primarily to describe adsorption from the vapor phase, are at their best at low sorbate concentrations and become highly unreliable as saturation is approached. Therefore, such models have their limitations of applicability for the correlation of liquid phase adsorption data.

2.1. Single Solute Equilibrium Models

The most frequently used theoretical model for describing adsorption equilibrium is due to Langmuir (13). The Langmuir Model was originally developed to represent chemisorption on a set of distinct localized adsorption sites. The kinetic derivation is based on the following assumptions.

1). Molecules are adsorbed at a fixed number of well-defined localized sites.

2). Each site can hold one adsorbate molecule.

3). All sites are energetically equivalent.

4). There is no interaction between molecules adsorbed on neighboring sites.

For the kinetics of condensation and evaporation of gas molecules at a solid surface, the following considerations apply :

At equilibrium the rate of condensation must be equal to the rate of evaporation. Therefore,

$$\text{Rate of condensation} = K_a p(1-\theta)$$

$$\text{Rate of evaporation} = K_d\,\theta$$

If q_s is the symbol of the total number of sites per unit weight or volume of adsorbent, q is the number of sites occupied by molecules, and $\theta = q/q_s$ is the fractional coverage, then

$$K_a\, p\,(1-\theta) = K_d\,\theta \qquad (2\text{-}1)$$

$$\theta/1-\theta = K_a / K_d\, p = bp \qquad (2\text{-}2)$$

where $b = K_a / K_d$ is the adsorption equilibrium constant.

Equation (2-2) may be rearranged to the commonly quoted form.

$$\theta = q/q_s = bp / 1 + bp \qquad (2\text{-}3)$$

This expression shows the correct asymptotic behavior for monolayer since at stauration $p \longrightarrow \infty$, $q \longrightarrow q_s$, and $\theta \longrightarrow 1.0$ while at low sorbate concentrations, Henery's law is approached.

$$\lim_{p \to 0} (\, q/p \,) = bq_s = K_H \qquad (2\text{-}4)$$

where K_H = Henry's constant.

q_s is supposed to represent a fixed number of surface sites and it should therefore be a temperature-independent constant while the temperature dependence of the equilibrium constant should follow a Vant Hoff equation :

$$b = b_o \exp (- \Delta H_o / RT) \qquad (2-5)$$

Since adsorption is exothermic (ΔH negative) , b should decrease with increasing temperature. Here, b_o is a constant containing the entropy term, H is the energy of adsorption, R is the universal gas constant, and T the absolute temperature(14). In the aqueous solution, $\theta = q/Q$, equation (2-3) can be rearranged into :

$$q = QbC / 1+ bC \qquad (2-6)$$

Where q is the amount of adsorbate per unit weight of adsorbent in equilibrium with a solution concentration C, Q is the amount of adsorbate per unit weight adsorbent forming a complete monolayer on the surface.

The Langmuir Equation is applicable only to the low-pressure (low concentation) portion of the isotherm at which the adsorbed film is monomolecular. The theory was extended in 1938 by Brunauer, Emmet, and Teller(10), whose model of multimolecular adsorption known as the B.E.T. theory, postulated a number of simultaneous Langumir-type adsorption between each two successive molecular layers. The theory derived by the following assumptions :

1). the energy of adsorption of the bare solid surface is uniform and characteristic of the solid.

2). the energy of adsorption in the second and succeeding layers of adsorbate are uniform, and are all equal to the heat of liquefaction of the adsorbate.

The final expression of B.E.T. theory in gas phase is :

$$V = V_m B p / \{ (p_o - p) [1 + (B - 1) (p / p_o)] \} \qquad (2\text{-}7)$$

where p_o is the saturation vapor pressure of adsorbate and V is the amount of gas adsorbed at an equilibrium p amd V_m is the amount adsorbed at surface saturation , $B = b/b_o = \exp (- \quad H/RT)$, B is a constant expressive of the energy of interaction with the surface. In aqueous solution, $V_m = Q$, $p = C$, $p_o = C_s$ the B.E.T. isotherm can be written as :

$$q = \frac{QBC}{(C_s - C)[1 + (B-1)C/C_s]} \qquad (2\text{-}8)$$

The B.E.T. equation has not been used as frequently as Lamgmuir Equation mainly because of the following drawbacks:

1). The model assumes that the surface is energetically uniform, i.e. that all adsorption sites are exactly equivalent; but there is much evidence that the surface of most solids is heterogeneous in an energetic sense(15).

2). The model neglects " horizontal" interactions between the molecules within the adsorbed layer, and takes into account only the " vertical" interactions, i.e. those acting in a direction normal to the surface. Thus according to the model on which the B.E.T. treatment is based, the heat of adsorption should never exceed half the latant heat.

3). The B.E.T. Equation make the assumption that the number of adsorbed molecular layers become infinite when the saturated vapor pressure is reached. In fact there are numerous cases in which the number of molecular layers in finite even when the solid is exposed to the saturated vapor.(16)

Another equation, the Freundlich Equation for isotherm adsorption, derived from the adsorption energy theory has been widely used for many years (Freundlich, 1926). The equation has the general form (in aqueous solution):

$$q = K_F \; C^{1/n} \qquad (2\text{-}9)$$

where K_F and n are statistically-determined best fit constants. The equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of the equation:

$$\log q = \log K_F + 1/n \log C \qquad (2\text{-}10)$$

This is the equation of a straight line with a slop of 1/n and intercept K_F at C =1. If q is plotted on the ordinate of logarithmic paper and c is plotted on the abscissa, a straight line is obtained. The constants "n" and "K_F" can be used to define both the nature of the adsorbent and the adsorbate. A high "K_F" and "n" value, for example, indicate good adsorption throughout the concentration range studies. A low "K_F" and "n" value would infer low adsorption at dilute concentrations with high adsorption at more concentrated levels(17).

The major problem with this model is that it does not reduce to a linear adsorption expression at very low concentrations(18). However, over a practical range of concentrations encountered in sorbent adsorption, this equation is successsfully employed for correlating experimental data, and due to its simplicity, it has been used in this study.

2.2 Adsorption Forces and Energies

The forces involved in adsorption are of two kinds, physical and chemical. Physical adsorption involves only relatively weak intermolecular forces; chemisorption involves the formation of a chemical bond between the sorbate molecules and the surface of the adsorbent. The forces acting in physical adsorption are identical with the intermolecular forces of cohesion, the van der Waals forces, which operate in the solid, liquid and gaseous state. These forces are electrostatic, and three effects are known which lead to van der Waals attraction : Keesom's orientation effect, Debye's induction (polarization) effects, and London's dispersion effect. The orientation effect is of significance for the mutual interaction of molecules which have permanent dipoles, and the magnitude of the effect is inversely proportional to the temperature. The induction effect is caused by an induced polarization of molecules which results from the action of a permanent dipole when the molecule is situated in its proximity; it is independent of the temperature. The attractive adsorbate-adsorbent interactions (adsorption forces) can be distinguished as the following :

1). dispersion or London forces
2). induction forces
3). electrostatic forces
4). hydrogen bonding
5). charge transfer
6). covalent bonding or ion exchange (chemisorption)

(1). dispersion forces

Dispersion forces exist between energy nonbonded, adjacent pair of atoms, and these forces completely account for the van der Waals attraction between nonpolar molecules in the liquid or solid state.

The energy of dispersion interaction E_{11} between two adjacent atoms of the same kind is given as :

$$E_{11} = \frac{-3\alpha_1^2 I_1}{4 r_{11}^6} \qquad (2\text{-}11)$$

Here α_1 is the polarizability of an atom of type 1 and I_1 is its ionization potential. r_{11} refer to the distance separating the two adjacent atoms. Similarly, the dispersion interaction between two dissimilar atom 1 and 2, E_{12}, is given as :

$$E_{12} = \frac{-3\alpha_1\alpha_2}{2 r_{12}^6}\left[\frac{I_1 I_2}{I_1 + I_2}\right] \qquad (2\text{-}12)$$

Where r_{12} is the distance separating atoms 1 and 2, and $_2$ and I_2 refer to the polarizability and ionization potential of atom 2. Values of the ionization potential [I_1 amd I_2) normally do not vary over wide limits, and as a result equation (2-12) can be reduced to an approximate, but more useful equation$^{(19)}$.

$$E_{12} = \frac{-3 \alpha_1 \alpha_2 I_1 I_2}{4 r_{11} r_{22} \quad I_1 I_2} = - \sqrt{\frac{3 \ {}_1 I_1}{4 r_{11}}} \sqrt{\frac{3 \ {}_2 I_2}{4 r_{22}}} = \sqrt{E_{11}} \sqrt{E_{22}} \tag{2-13}$$

That is, the dispersion energy of interaction between two dissimilar atoms 1 and 2 is given as the geometric mean of corresponding interaction energies between like atoms (1-1 and 2-2). The contribution of dispersion interactions to the adsorption energy of an atom of type 1 on a surface composed of atom 2 may be obtained from equation (2-12) or (2-13) by summing the various atom-atom interactions between atom 1 and all the atoms of the adsorbent :

$$\begin{aligned} E_1 &= \sqrt{E_{11}} \sum \sqrt{E_{22}} \\ &= C \alpha_1 \end{aligned} \tag{2-14}$$

For a given adsorbent the contribution of dispersion interactions to the adsorption energy of atom 1 is proportional to the polarizability of atom 1 since molecular polarizability is equal to the sum of atomic polarizabilities of the constitutent atoms, equation (2-14) may also be applied to the adsorption of molecules . For the adsorption of nonpolar molecules onto nonpolar adsorbent surface it is widely accepted that dispersion force contribute essentially all the adsorption energy $^{(20)}$.

(2). induction forces

Inductive forces exist when one of two adjacent atoms or molecules has a permanent electrical field associate with it, e.g., a charged ion or a molecule with a permanent dipole moment. Under the influence of this field, the electrons of an adjacent atom or molecule are polarized so as to give an induced dipole moment which interacts with the field. The energy of this inductive interaction is given as

$$E_i = \frac{1}{2} \alpha_1 F^2 \qquad (2\text{-}15)$$

where α_1 refers to the polarizability of the polarized atom or molecule and F is the field strength in the vincinity of the polarized molecule. Inductive interations are relatively unimportant in determining the van der Waals attraction between molecules in the liquid or solid phase.

(3). Electrostatic forces

Electrostatic forces can contribute to the adsorption of polar molecules on polar adsorbents. THe energy of interaction E_e of an adsorbate dipole of moment u in a surface field of intensity F is given as

$$E_e = - u F \cos \theta \qquad (2\text{-}16)$$

where θ is the angle between the vectors of the dipole and the surface field.

(4). Hydrogen bonding

The hydrogen bonding and related weak interaction between Lewis acids and bases make important contribution to adsorption energy in a number of adsorption systems. Polar adsorbents are normally covered with hydroxyl groups, and in some cases these hydrogen bond to basic or weakly basic adsorbate. Similarly, adsorbates with hydrogen donor properties should be capable of hydrogen bonding with proton acceptor groups on the adsorbent surface.

(5) Charge transfer

Charge transfer between two interacting molecules X and Y, to give a complex of the form $X^{+}Y^{-}$, plays a role in the bonding of many milecular complexes(21,22). Generally, it is proposed that electron transfer occurs from adsorbate X to a surface site A to give a charge transfer complex of the form $X^{+}A^{-}$, or an adsorbed complex in which the latter structure is an important resonance form. THe more easily an electron is given up by the adsorbate, the more stable is the structure $X^{+}A^{-}$ and the greater is the adsorption energy of X. Consequently, the principal test for the importance of charge transfer interactions in adsorption has been the correlation of adsorbate ionization energy with adsorption energy; the lower the ionization energy of X, the greater its adsorption energy.

(6). Covalent bonding or ion exchange (chemisorption)

Covalent bonding or ion exchange is generally unimportant in the adsorption of neutral organic compound. Chemisorption sometimes requires for its operation a certain energy to be supplied and is then called activated adsorption. In chemisorption the adsorbent is bound to the surface by forces originating from the exchange or sharing of valence electrons, as occurs in chemical bonds.

2.3.Kinetics of Adsorption in Batch Systems

When a solid adsorbent comes into contact with a liquid sorbate, the number of molecules in the liquid phase decreases. During their motion, the molecules strike the surface and remain trapped on the surface for a certain time, i.e. they become adsorbed. The rate in which the number of molecules in the liquid phase decreases depends on the velocity with which they reach the sites on the surface at which they are adsorbed. For many applications of adsorption and ion exchange, the rate of interparticle transfer in turn governs the overall rate of removal of solute from solution. The overall rate of adsorption is usually the rate of transport of the adsorbate to the sites on the surface at which they become bound. The molecules reach the adsorbing surface, eapecially with an adsorbent of such a highly developed and complex porous structures as that of active carbon, in diverse and rather complicated ways. First the solute molecule must reach the external surface of the particle of adsorbent. Under static condition, in which there is concentration in the same throughout the system, this takes place by normal diffusion (so called external diffusion), because a concentration gradient is formed through the fall in concentration of the solute near the surface. When the molecules have reached the external surface of a particle of adsorbent they can produced to the internal surface in two different ways: by diffusion in the pores or by surface diffusion.

Considering a single microporous adsorbent particle, exposed to a step change in sorbate concentration at the external surface of the particle at time zero. For most particle shapes, representation as an equivalent sphere is an acceptable approximation and transport may therefore be described by a diffusion equation, written in spherical coordinates$^{(44)}$:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 D_c \frac{\partial C}{\partial r} \right) \tag{2-17}$$

If the diffusivity is constant this equation simplifies to

$$\frac{\partial C}{\partial t} = D_c \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \tag{2-18}$$

Where D_c is the intracrystalline diffusivity and $C(r,t)$ is the adsorbed phase concentration. Even if the diffusivity is concentration dependent, the assumption of a constant diffusivity is still an acceptable approximation provide that the uptake curve is measure over a small differential chande in adsorbed phase concentration. If the uptake of sorbate by the adsorbent is small relative to the total quantity of sorbate introduced into the system, the ambient sorbate concentration will remain essentially constant following the initial step change, and the appropriate initial and boundary conditions are

$C(r,0) = C_o'$, $C(r_c,t) = C_o$, $(\partial C/ \partial r)_{r=0} = 0$

The solution for the uptake curve is then given by the expression :

$$\frac{\bar{C} - C_o'}{C_o - C_o'} = \frac{XA}{XAe} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(- \frac{n^2 \pi^2 D_c t}{r_c}\right) \tag{2-19}$$

Where C (t) is the average concentration through the particle, defined by:

$$\bar{C} = \frac{3}{r_C^3} \int_0^{r_C} C\, r^2\, dr \qquad (2\text{-}20)$$

and XA/XAe is the fractional approach to equilibrium.

For fractional uptakes greater than 70 % we may retain only the first term to obtain:

$$1 - \frac{XA}{XAe} = \frac{6}{\pi^2} \exp\left(- \frac{\pi^2 D_C\, t}{r_C} \right) \qquad (2\text{-}21)$$

In the long time region a plot of ln(1- XA/XAe) versus t should be linear with slop $- \pi^2 D_C/r_C$ and intercept $\ln(6/\pi^2)$.

At short times equation (2-19), the form of the solution is given by :

$$\frac{XA}{XAe} = 6 \left(\frac{D_C t}{r_C} \right)^{1/2} \left[\frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty} \text{ierfc} \left(\frac{n r_C}{D_C\, t} \right) \right] - 3\, \frac{D_C t}{r_C} \qquad (2\text{-}22)$$

which for XA/XAe < 0.3 reduces to

$$\frac{XA}{XAe} = \frac{6}{\sqrt{\pi}} \left(\frac{D_C\, t}{r_C^2} \right)^{1/2} \qquad (2\text{-}23)$$

In the initial region diffusion occurs as if in a semi-infinite medium and the expression for the uptake curve for any particle shape may be written:

$$\frac{XA}{XAe} = \frac{2A}{V} \left(\frac{D_c\, t}{\pi} \right)^{1/2} \qquad (2\text{-}24)$$

Where A/V is the ratio of exteranl area-to particle volume which for a spherical particles is simple $3/r_c$. A plot of fractional uptake versus $\sqrt{t}$ should therefore yield a straight line through the origin with slop $2(A/V)\sqrt{D_c/\pi}$.

2.4.Ideal Adsorbed Solution Theory

The adsorption equilibrium model for multi-component systems in this research is the Ideal Adsorbed Solution Theory, which originally developed by Myers and Prausnitz(25) to describe competitive adsorption of gases, was extended to Radke and Prausnitz(26) to aqueous mixtures of solutes. Some investigators(27,28) have used this model and report a good agreement between the predicted and experimental results. The IAST model has several adventage over other descriptive model(29). First, the generality of the model can be examined in terms of its assumptions. Subsequently, modification and improvement of these assumptions colud lead to general model applicable to wide range of solute concentrations.

The theory derived from concepts of thermodynamics with the assumption of adsorbed phase in thermodynamically ideal. That is, solute species adsorb simultaneously from dilute solution at constant temperature and spreading pressure. The spreading pressure, π , is defined as the difference between the interfacial tension of the pure solvent-solid interface and that of the solution-solid interface at the same temperature.

$$= \sigma_{\text{pure solvent-solid}} - \sigma_{\text{solution-solid}} \qquad (2\text{-}25)$$

where, σ is the surface tension

substituting Gibbs-Duhem equation

$$C_i d\, u_i^{\alpha} + C_1\, du_1^{\alpha} = 0 \qquad \text{(constant T)} \qquad (2\text{-}26)$$

into Gibbs isothermal adsorption equation :

$$- A\, d\sigma = \sum_i n_i^{\alpha}\, d\, u_i^{\alpha} + n_i^{\alpha}\, d\, u_i^{\alpha} \qquad \text{(constant T)} \qquad (2\text{-}27)$$

yield the equation :

$$- A\, d\sigma = A\, d\pi = \sum_i n_i^{m}\, d\, u_i \qquad (2\text{-}28)$$

where u = the chemical potential

n = the mole adsorbed on the solid surface

A = the area of the solid-solution interface

subscript "i" represents solute ,subscript"1" represents solvent, and subscript "α" represent the adsorbed phase.

The spreading pressure can be evaluate from equation (2-28) by :

$$(C_i^{*}) = RT/A \int_0^{C_i^{*}} \frac{n_i^{m}}{C_i}\, dC_i \qquad \text{(constant T)} \qquad (2\text{-}29)$$

Where n_i^m = the invariant adsorption of solute i

R = ideal gas constant

T = absolute temperature

C_i = the concentration of solute

The subscript"*" represents single-solute adsorption. Difference between the adsorptive capacity q_i and n_i in dilute solution is that $n_i = V\ (C_{io}-C_i)$ and $q^* = V/M \times (C_{io}-C_i)$, that is , n_i is for an unspecified amount of adsorbent, while q_i is for a specified weight of adsorbent. (where C_{oi} is the influent concentration of solute i, M is the weight of adsorbent). Therefore :

$$q_i^* = f(C_i^*) \text{ and } q_i^* = f(n_i^m) \qquad (2\text{-}30)$$

from equation (2-29) and (2-30) proposed by Kidnary and Myers$^{(30)}$, by changing variables, gives:

$$\pi_i\ (q_i) = RT / A \int_0^{q_i^*} \frac{d\log C_i}{d\log q_i}\, dq_i \qquad (2\text{-}31)$$

The ideal adsorbed phase with constant spreading pressure gives:

$$\pi\ (q_1) = \pi\ (q_2) \qquad (2\text{-}32)$$

From equation (2-31) and (2-32) cancel RT/A constant term and consider binary adsorption system yields:

$$\int_0^{q_1^*} \frac{d\log C_i}{d\log q_i}\, dq_1 = \int_0^{q_2^*} \frac{d\ \log C_2}{d\log q_2}\, dq_2 \qquad (2\text{-}33)$$

When single-solute equilibrium are described by Freundlich model :

$$q_i = K_{Fi}\ C_i^{1/ni} \qquad (2\text{-}34)$$

or

$$C_i = (\ q_i\ /\ K_{Fi}\ )^{ni} \qquad (2\text{-}35)$$

taking logarithm on both side

$$\log C_i = n_i \log(q_i\ /\ K_{Fi}) = n_i(\log q_i - \log K_{Fi}) \qquad (2\text{-}36)$$

take differential from equation (2-36)

$$d \log C_i = n_i \, d\log q_i - n_i \, d \log K_{Fi}$$

or

$$\frac{d\log C_i}{d\log q_i} = n_i \qquad (2\text{-}37)$$

substituting equation (2-37) into (2-33) n_1, n_2 are constants and gives:

$$n_1 \, q_1^* = n_2 \, q_2^* \qquad (2\text{-}38)$$

other equations required for the IAST calculation are :

$$C_i = Z_i \, C_i \qquad (2\text{-}39)$$

$$\sum_{i=1}^{N} Z_i = 1 \qquad (2\text{-}40)$$

$$q_i = Z_i \, q_T \qquad (2\text{-}41)$$

where Z_i = the mole fraction of solute "i" in the adsorbed

phase ,q_T = the total quantity of material adsorbed.

applying the initial concentration C_{oi}, Freundlich coefficients K_{Fi} and n_i and sorbent dose M/V to the above equaltions and a great deal of algebric manipulation, the following equation for each solute was derived :

$$C_i = \frac{q_i}{\sum_{j=1}^{N} q_j} \left[\frac{\sum_{j=1}^{N} q_i n_i}{n_i K_{Fi}} \right]^{n_i} \qquad (2\text{-}42)$$

where N = number of species

i,j = solute specieces i and j

from equation $q_i = V/M \, (C_{oi} - C_i)$, rearranged gives :

$$C_i = C_{oi} - q_i (M/V) \qquad (2\text{-}43)$$

substituting (2-43) into (2-42), yields:

$$c_{oi} - q_i \ (M/V) = \frac{q_i}{\sum_{j=i}^{N} q_j} \left[\frac{\sum_{j=1}^{N} q_i n_j}{n_i \ K_{Fi}} \right]^{ni} \qquad (2\text{-}44)$$

equation (2-40) is valid for all components, N nonlinear simultaneous equations with N unknown must be solved to estimate the final equilibrium state , at equilibrium

$$F_i \ (q_1, q_2, - - - q_i, q_n) = o$$

2.5.Factors Influcing Adsorption

In the presence of inorganic salts, the possible factors that can affect the adsorption system can be categorized as follows(43) :

1). the nature of the adsorbate, such as molecular weight, water solubility, diploe moment, and surface tension.

2). the nature of inorganic salts, such as molecular weight, aqueous solubility, and index of refraction.

3). the nature of the solution, such as pH, temperature, concentration of inorganic salt, adsorbate concentration, and competitive solutes.

4). the nature of the adsorbent(activated carbon and flyash) , the important physical characteristics of the sorbent include surface area, pore size and distribution.

The study of this research is focusing on the nature of the solution, by fixing some of the parameters in (3), change a few of the remaining ones, the adsorption behavior has been studied systematically to some degree.

SECTION III

OBJECTIVES AND SCHEME OF WORK

3.1. Objectives

This research is intended to determine the effect of inorganic salts on the adsorption process and adsorbents, such as, activated carbon and flyash. Adsorbates studied are representative of naturally occurring organic substances present in most water supplies or priority pollutants.

This study focuses on the presence and use of salts and their effects on adsorptive capacity of adsorbents. The objectives of the research are :

1. To identify the adsorption mechanism of activated carbon and flyash in the presence of inorganic salts.
2. To compare the effects of inorganic salts on adsorption between activated carbon and flyash.
3. To find out the optimum condition for adsorption in presence of inorganic salts. There are various parameters that can affect the adsorptive capacity, such as, the nature of the adsorbent, the nature of the solution, and the nature of adsorbate. By fixing some of these parameters and changing the remaining ones, the effect of inorganic salts on sorption process can be studied systematically.
4. To examine the effect of interactions between inorganic salts and compounds during the multi-solute sorption process.
5. To establish a relationship in finding the effect of inorganic salts on the extent and rate of adsorption process.

3.2. Scheme of Work

In order to reach the above objectives, the scheme of this study is scheduled as follows.

1. Single dosage tests (i.e. batch) of pollutants and inorganic salts is providing basic quantitative information on whether or not inorganic salts enchance the adsorption process for flyash.

2. In order to identify the adsorption mechanism of various adsorbents, the concentration of inorganic salt is measured before and after adsorption via conductivity measurements and standard titration. In this technique, the pH value of the diluent is measured both before and after each adsorption experiment. This determines whether the inorganic salts exert either a catalytic effect or in fact participate in the adsorption process by some chemico-physical mechanism. Inorganic compounds studied were monovalent, divalent and trivalent salts. Organic compounds selected in this study are those of current pollution concern in wastewater streams and/or at hazardous waste sites. At present, three kinds of aormatic compounds -- phenol, toluene, and benzene , two kinds of alphatic compound -- Methyl isobutyl ketone (MIBK) and Isopropyl alcohol (IPA) have been selected for this investigation.

3. For single solute adsorption, the optimum pH value, dosage of adsorbent and kinetics for each compound are under sutdy. Based on the data obtained, adsorption isotherms are being quantified for various concentrations of inorganic

salts.

4. Batch isotherm studies are also being conducted using multicomponent solution and inorganic salts to examine how inorganic salts affect the multicomponent adsorption system and to examine the interaction of compounds and salts during the sorption process.

5. Kinetic studies are being executed using single solute with and without inorganic salt added separatively. The kinetic investigation is helpful in establishing the inorganic salt effect reaction rate in single compound systems .

SECTION IV

MATERIALS AND METHODS

The nature of the adsorbents and the experimental and analytical techniques that were used to determine the solute concentration are described in this section.

4.1.Adsorbent Characteristics

The adsorbents used in this research were flyash and activated carbon. Flyash taken from the Hudson generating station was named Hudson flyash. It is a waste product of electric power plants and produced in large quantities during the burning of coal. It is generally collected from the flue gases by means of electrostatic precipitation before it escapes from the stacks. The individual particle size of this material ranges from 0.3 to 100 microns. The principal chemical constituents are silica, alumina, iron, sulfur trioxide, alkali and alkaline earth metals(7). The effectiveness of flyash as an adsorbent for organic has been found to be greatly dependent on the carbon content.(8) The important properties of Hudson flyash were provided by the research and testing laboratory of PSE&G Research Corporation are listed in Table 4.1. Methods used for analyze flyash were A.S.T.M. C-188, C-204, C-311, and C-430. The flyash was washed throughly for three hours using 1000 miniliter of deionized water per 100 grams of flyash, and dried overnight in an oven at 105°C prior to use.

Activated carbon used in this research was "Witco Grade 718", petroleum hydrocarbon base (surface area = 1050

Table 4.1 FLY ASH ANALYSIS

CONSTITUENT			PERCENT BY WEIGHT (DRY BASIS)	
			RESULTS	ASTM C. 618
SILICA		SiO_2	36.28	
IRON OXIDE		Fe_2O_3		
ALUMINUM OXIDE		Al_2O_3	48.34	
SUM OF SILICA, IRON OXIDE, AND ALUMINUM OXIDE			84.62	MIN 70
TITANIUM OXIDE		TiO_2		
CALCIUM OXIDE		CaO	2.96	
MAGNESIUM OXIDE		MgO	1.73	MAX 5.0
SULFURIC ANHYDRIDE		SO_3	0.86	MAX 5.0
PHOSPHORIC ANHYDRIDE		P_2O_5		
SODIUM OXIDE		Na_2O		
POTASSIUM OXIDE		K_2O		
CARBON		C	1.90	
LOSS ON IGNITION			1.61	MAX 12.0
TOTAL				
AVAILABLE ALKALIES		Na_2O	0.82	MAX 1.5
MOISTURE			0.052	MAX 3.0
WET SIEVE TEST				
% RETAINED	% PASSED			
60				
100	60			
200	100			
325	~~200~~		27.09	MAX 34
400	325			
	400			
SURFACE AREA (A) CM^2/CM^3			6793	
DENSITY GM/CC			2.41	
PACKING DENSITY LB/CU. FT			71.61	

m^2/g approximately, 12x30 mesh)[manufacture information]. The material was soaked overnight in distilled water and dried at 105 °C for 12 hours, and allowed to cool in a dessicator prior to use.(8)

4.2. Adsorbate Properties

Benzene, toluene and phenol were selected as aromatic target compounds during the experiment. The selection was based on physical properties, toxicity and water solubility. Isopropyl alcohol (IPA) and methyl isobutyl keton (MIBK) have been shown to have a relatively higher adsorbability among alcohols and ketone groups respectively.(8) In addition to the consideration of their physical properties, the the above two alphatic compounds were selected as target compounds in this study. Table 4.2 lists some selected physical properities of target compounds. All above compounds used were laboratory reagent grade (99.99 % pure), ordered from Fischer Scientific Compony, Springfield, N.J.

4.3. Properties of Inorganic Salts

The selection of inorganic salts was based on their valence and their possible presence in wasterwater treatment plant. The inorganic salts used were monovalent (NaCl), divalent ($CaCl_2$) and trivalent ($AlCl_3$). Some selected physical properties of these salts are listed in Table 4.3.(10)

4.4. Experimental Procedure

Table 4.2 Selected Physical Properties of Target Compounds(10)

Property	Toluene $C_6H_5CH_3$	Benzene C_6H_6	Phenol C_6H_5OH	MIBK $CH_3COC_4H_{10}$	IPA C_2H_6CHOH
Toxicity	100ppm skin 8-hrTWA	10 ppm skin 8-hrTWA	5 ppm skin 8-hrTWA	50 ppm 8-hrTWA	400 ppm 8-hrTWA
Molecular Weight (g/mole)	92.15	78.12	94.11	72.10	60.09
Solubility in Water(%)	0.05	0.06	6	1.9	∞
Kow(9)	328.38	88.44	28.86	29.20	0.70
Dipole Moment (Debyes)	0.36	0	1.45	3.08	1.67
Density Water =1 @ 20°C	0.866	0.879	1.07	0.801	0.785
Surface Tension dynes/cm @20°C	28.50	28.85	40.90	26.00	21.70

* TWA (Time Weighted Average)

* K_{ow} : Partition Coefficient (Octane-Water system)

Table 4.3 Selected Physical Properties of Inorganic Salts

Property	Sodium Chloride NaCl	Calcium Chloride $CaCl_2.2H_2O$	Aluminum Chloride $AlCl_3$
Molecular Weight	58.44	110.99	133.34
Index of Refraction	1.5442	1.52	N.A.
Density	2.165	2.15	2.44
Melting Point ^0C	801	772	190
Solubility in water (g/100c.c)	35.7	74.5	69.9

N.A.= NOT AVAILABLE

4.4.1. Selection of Optimum Sorbent Dosage

Various quantities (i.e. 5g,10g,15g,20g, 30g and 40g) of Hudson flyash and activated carbon (0.1g,0.2g,0.3g,0.4g,0.5g 0.8g and 1.0g) were placed in 700 ml glass bottles provided with a rubber-lined septum and plastic screw cap. The appropriate aqueous solution of organic pollutant was added to the 700 ml glass bottle followed by an accurately weighed amount of inorganic salt (amoumt equal to 5 mM in solution). The bottles were completely filled to the top with the solution. The solution allowed to reach equilibrium by shaking for 12 hours, and then leaving it stand overnight. The clear supernatant was then analyzing by injecting an aliquot into a Perkin-Elmer Model 8500 Gas Chromatograph equipped with a flame ionization dector.

4.4.2. Effect of Inorganic Salts on Single Solute Isotherm Adsorption Equilibria

Experiments were carried out at constant room temperature (about 22°C). Accurately weighed 20 grams of Hudson flyash or 0.4 grams of activated carbon were placed in 700 ml glass bottles equipped with a rubber-lined septum and plastic screw cap. The glass bottles were then filled with test solution at a various range of concentration (10 mg/l to 100 mg/l). With a specific concentration of organic pollutant, an accurately weighed of various concentration of inorganic salts were conducted to the bottles. The experiments were performed in paralle with and without the addition of inorganic salts. The pH was adjusted. The appropriate pH for each sorbent and sorbate was determined empirically. The sealed bottles were shaken for 12 hours. and allowed to stand overnight. Aliquots of clear supernatant were then injected into the gas chromatograph for analysis. The amount of adsorbate adsorbed (X) is obtained by substracting the value of the equilibrium concentration from that of the influent concentration. On logarithmic paper, values of C were plotted on the abcissa against those of X/M on the ordinate, and the best straight line determined by linear regression. The pH values of the solution before and after sorption were measured by pH meter. The concentrations of inorganic salts were determined by the titration with standarized silver nitrate solution (about 0.01 N). The conductivity of solution was measured by Conductivity Bridge Model 31, Yellow Spring Instrument Co., Inc. Yellow Spring, Ohio.

4.4.3. Effect of Inorganic Salts on Multi-solute Adsorption Equilibria

To carry out the multi-component adsorption experiment under the influence of inorganic salts, the experiment were performed with and without the addition of inorganic salts simultaneously. The weights of the sorbent (same as used in single solute study) and the concentrations of inorganic salt were maintained constant. An accurately weighed amount (amount equal to 0.01 M) of NaCl and $AlCl_3$ were added to the solution when activated carbon and

Hudson flyash were used as sorbent respectively. Equal concentrations of each target organic compound was mixed thoroughly at various concentration range of 10 mg/l to 80 mg/l . The experimental procedure was followed as that used for the single solute study. Five binary system (toluene/benzene, toluene/phenol, MIBK/toluene,MIBK/IPA and IPA/toluene), three 3-component systems (phenol/benzene/ toluene,benzene/toluene/MIBK and toluene/MIBK/IPA), two 4-component (toluene/benzene/phenol/MIBK and toluene/benzene/ IPA/MIBK) and one 5-component system (toluene/benzene/MIBK /IPA/phenol) were investigated.

4.4.4. Effect of Concentration of Ionrganic Salts on Multi-component Adsorption Equilibria

The experiment was carried out by maintaining the constant of dose of adsorbent and influent concentration of individual target organic pollutant. Various concentrations of inorganic salts in the range of 0.0 mM to 10 mM were introduced . Various concentration of NaCl and $AlCl_3$ were added to the case of activated carbon and Hudson flyash were used as adsorbent respectively. The experimental procedure was similar to the one used in the multi-solute adsorption study . One binary system (benzene/toluene) and one 4-component system (toluene/benzene/phenol/MIBK) were investigated.

4.4.5. Effect of Inorganic Salts on Adsorption Kinetics

Hudson fly ash (20.0 g) or 0.4 grams of activated carbon were placed in 700 ml glass bottles equipped with a rubber-lined septum and plastic screw cap. The bottles were filled with a particular concentration of target organic pollutants. Experiments were run without and with the addition of 0.01 M NaCl and 0.01 M $AlCl_3$ activated carbon and Hudson fly ash chosen as adsorbents respectively. The bottles were shaken and aliquots were collected at a specific time intervals (5 min.,10 min.,20 min.,30min., 60 min., 90 min., 120 min. and 12 hours) and analyzed by gas chromatograph . The influent concentrations of traget compounds were increased until the system reached a study-state condition. The concentrations obtained were used as the influent concentrations in the study of the effect of concentration of inorganic salts on adsorption kinetics. Various concentrations of inorganic salts (0mM,2mM,4mM,6mM,8mM and 10mM) were added to the sorption system. Samples were prepared by the above mentioned procedure and samples were taken at the same time intervals.

4.5. Analytical Procedure

The Perkin-Elmer model 8500 gas chromatograph is the major instrument for the analysis of the samples. It is a dual channel, microprocessor-based gas chromatograph. The instrument can be flexibly configured with many options and accessories, and with a wide range of operating conditions, enabling it to be set up to suit specific requirements. The instrument is made up of two main units; the analyser and keyboard unit, and the visual display unit (VDU). THe analyser unit consists of an analytical oven, and electronic compartment and a pneumatic compartment. Inside the oven are two columns, each of which is connected to an injector at the top and a dector at the bottom. A sample mixture enters the carrier gas stream via the injector, and moves onto the column where separation takes place. After passing through the column, the sample components enter the detector and produce an electrical signal, which can be used to measure the quantity of each component present. There are five panels in the pneumatic panels which control the flow of gases to the analytical system. The electronics unit contains the power supplies and printed circuit board which control the instrument. There are three types of keys on the keyboard: function keys, soft keys and numeric keys. The function keys have set functions, which do not change during the operation of the instrument. The function of the soft keys change during the operation of the instrument. There are ten numeric keys labelled from zero to nine, a minus sign and a decimal point. The Visual Display Unit is used, together with the keyboard on the chromatograph, to set up the instrument in accordance with the type of analysis required. The VDU is connected to the chromatograph by a multicore cable unit but is not mechanically attached. All GC parameters are entered and set up using the keyboard and VDU. The operator is prompted by questions from the screem, which also display the valid range for each entry.

The dector used in this research was Flame

Ionization Dector (FID) [see Figure 4.1]. The FID enable compounds that ionize in a hydrogen flame to be detected. Hydrogen introducted into the eluate from the column is burned in air introducted into the base of the detector to form a stable, noise-free flame. THe charged particles that are produced when an organic compound eluted from the column is burnt in the detector, migrate towards the collector electrode under the influence of a polarizing electric field applied to the jet of the detector. The quantity of electricity that is produced applied to the jet of detector. The quantity of elecrticity that is produced is proportional to the amount of compound present, and the resultant current is amplified and plotted on the recorder as a chromatogram. During the operation, the hydrogen pressure was set to 84 kpa (12 psig), and air pressure was set to 155 kps (22 psig) in this research. The FID has the folluwing specifications:

Operating Temperature Range : 100^{o}C to 450^{o}C can be set in 1 deg C increments.

Sensitivity : Better than 0.015 coulombs g^{-1} carbon.

Minimum Detectability (singal to noise ratio 2:1) : 5 x 10^{-12} g carbon/sec.

Linearity : Greater than 10^{6}

Attenuation Control : Controlled via the keyboard with values of x1 to x4096 in powers of 2

Input ranges : High(x1) and Low(x20)

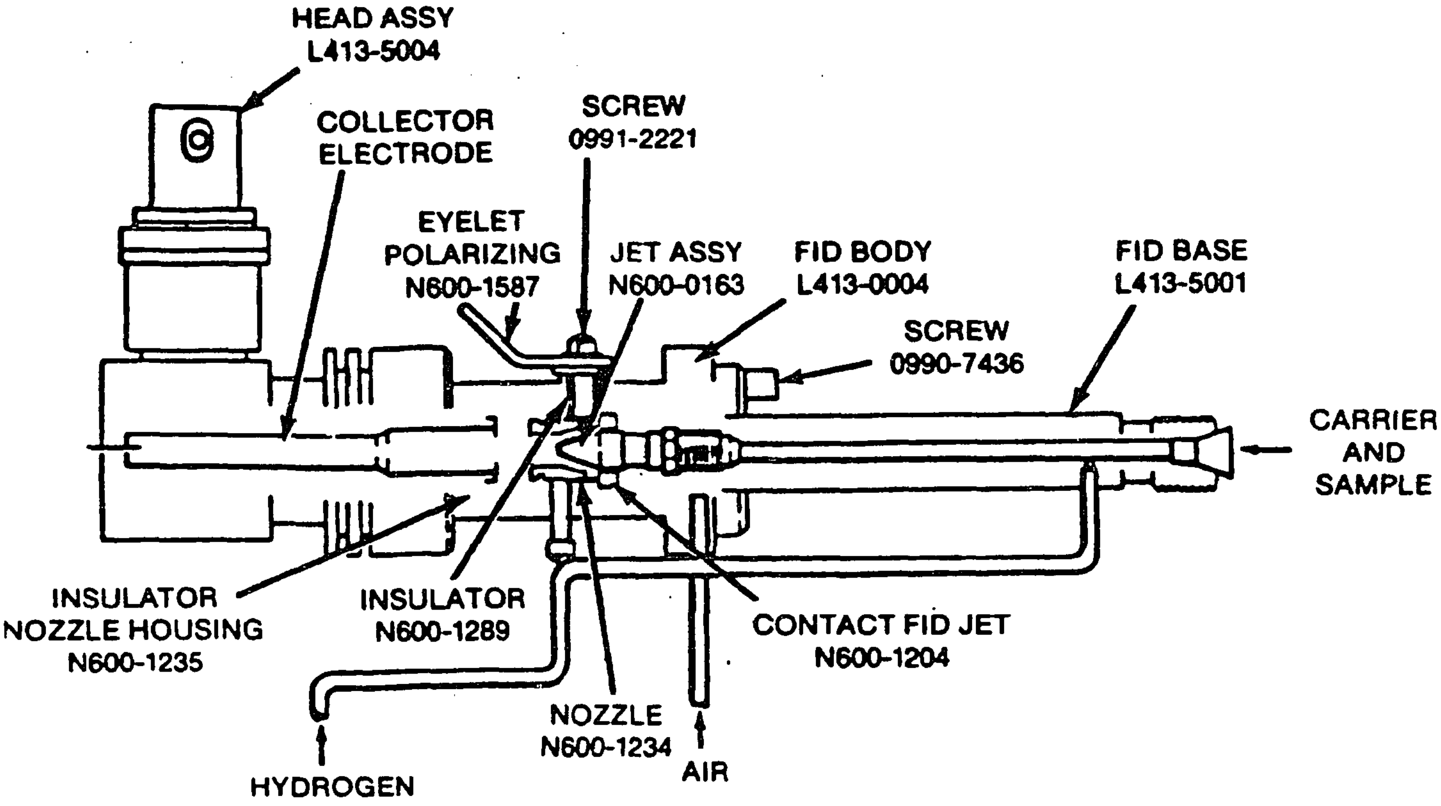


Figure 4.1 Cutway view of FID

High=$5x10^{-12}$ ampers FDS on screen or a 1mv recorder on attenudation x 1.

Output range : 10 V and 1mV.

Time constant : 45 ms

The packed column used in this research had the following specifications :

1%, sp,1000, 16/80 carbonpack-b, 6 ft long, 1/8 "OD, custom column injection configuration.

The following instrument conditions are set up for analysis:

Oven Temperature : 180^{o}C

Injection Temperature : 230^{o}C

Detector Temperature : 230^{o}C

Iso Time : 5 min.

SECTION V

RESULTS AND DISCUSSIONS

In this section, the results and discussions are presented in the following sequence :

5.1 Adsorbability improved using inorganic salts

5.2 pH effect on adsorption

5.3 Effect of inorganic salts on single solute adsorption equilibria

5.4 Effect of inorganic salts on multi-solute adsorption equilibria

5.5 Effect of inorganic salts on kinetics of adsorption

5.6 Correlation of adsorption capacity with concentration of inorganic salt

5.7 Correlation of soption rate constant with concentration of inorganic salt

5.1.Adsorbability Improvement Using Inorganic Salts.

A logical beginning for this research was the determination of whether or not inorganic salts effect the adsorption of organic compound onto flyash and activated carbon. Previous investigation (8) has shown the optimum adsorbent dose on the adsorption of organic compounds for flyash and activated carbon is 20 grams of flyash per 700 ml of organic waste, Figure 5.1 shows the same dose, after the addition of a particular inorganic salt into the sorption system. Figure 5.2 shows that the optimum adsorbent dose for activated carbon is 0.4 grams of activated carbon per 700 ml of organic waste, with and without the inorganic

Figure 5.1 Adsorption Dose Test

Flyash, phenol 50 ppm, 5mM NaCl

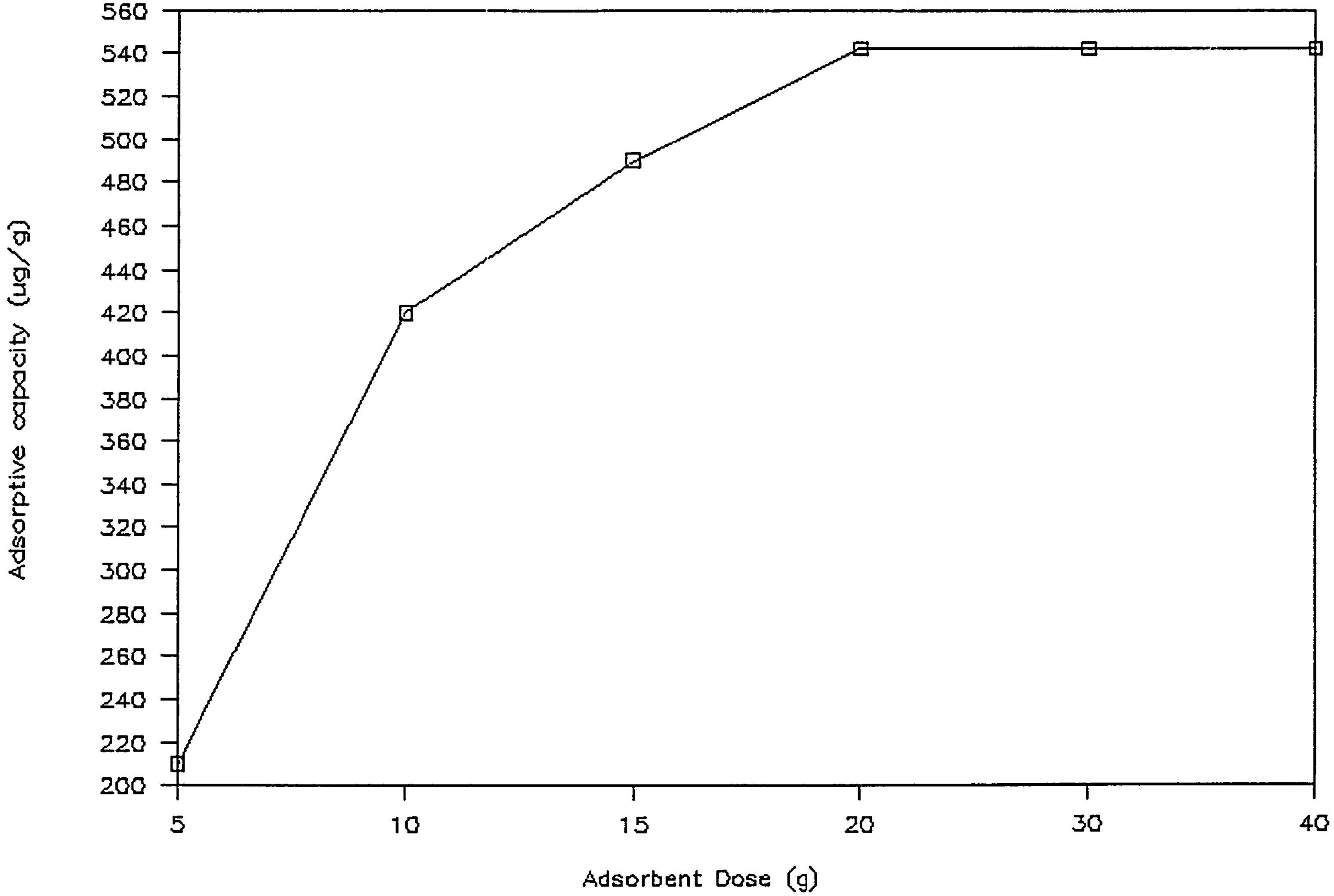
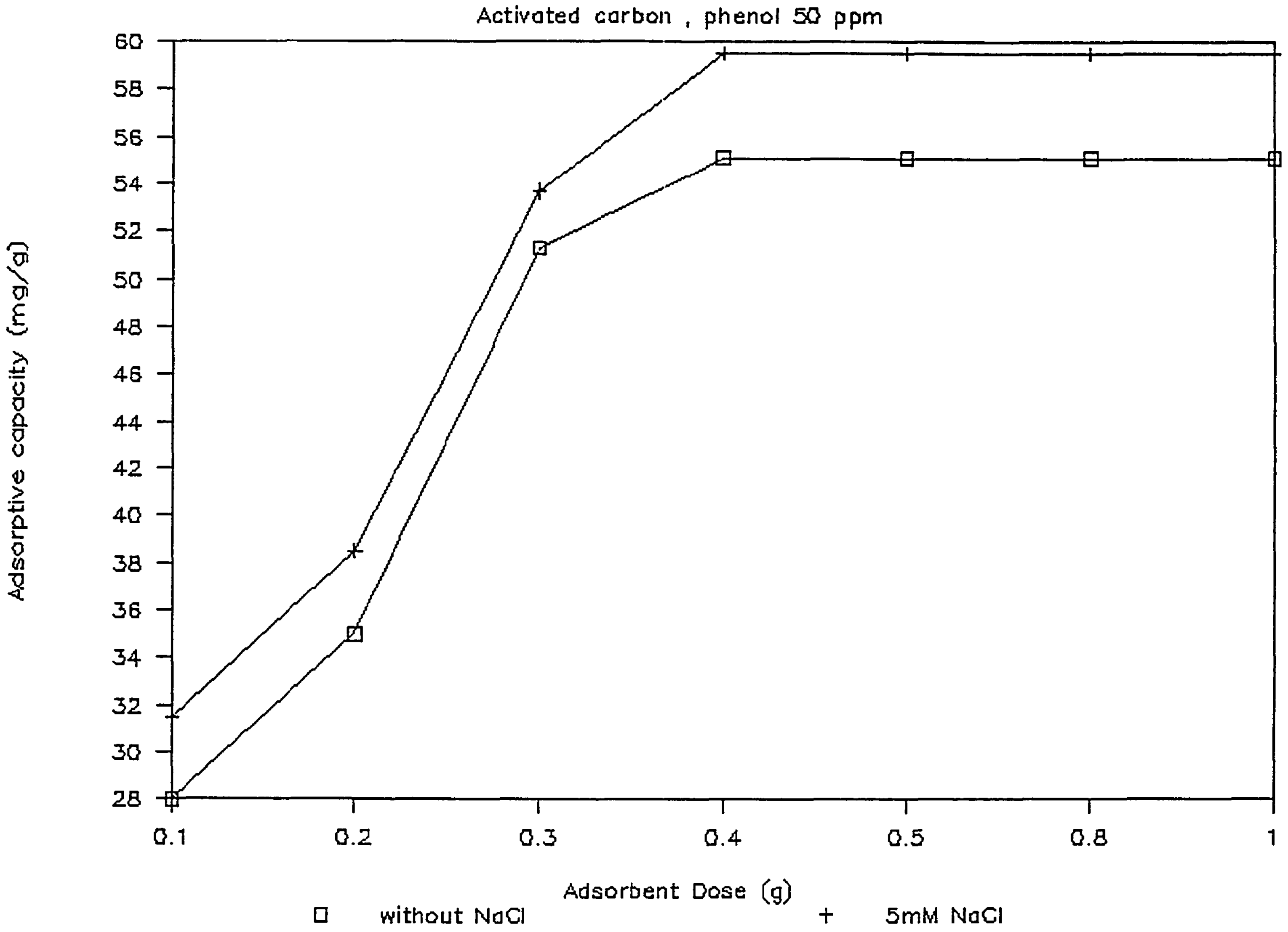


Figure 5.2 Adsorption Dose Test



salt added. Hence, throughout this present study (batch experiment) these same doses have been used. Single dosage experiments were carried out by contacting 700 ml aliquots of stock solutions with and without specific concentrations of inorganic salt for each compound with 20 g of flyash or 0.4 g of activated carbon in a glass media bottle provided with a rubber lined septum and plastic screw cap. The bottles were agitated by a shaker for 12 hours in order to achieve an equilibrium concentration. Each mixture was allowed to settle overnight. The samples were analyzed using a Perkin-Elmer Model 8500 Flame Ionization Detector Gas Chromatograph.

Table 5.1 lists the micrograms of sorbate removed per gram of sorbent (activated carbon and flyash) as well as percent reductions of sorbate with about 5 mM of inorganic salts and without any salt added. Table 5.1 shows the effectiveness of inorganic salt strongly depends on the chemical characteristics of the adsorbate. A higher percent reduction of sorbate will have lower residual pollutant molecules remaining in the solution, therefore a lower effective improvement in the addition of inorganic salts is achieved. Activated carbon has a higher adsorptive capacity than virgin flyash. However, with the addition of inorganic salts, flyash performs at a higher efficiency than activated carbon. For a specific adsorbent, toluene is more readily adsorbed than phenol without salts. However, phenol has a greater improvement of capacity adsorbed by

Table 5.1

Adsorbability Improvement Using Inorganic Salts

Adsorbent Used: Hudson Flyash

Target Compound: Toluene

Initial Conc.	No Salts			Addition of Inorganic Salts				
	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)	Salt Type	Conc. (mM)	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)
53.3	30.6	42.6	0.72	NaCl	6.20	29.3	45.0	0.84
45.6	26.9	41.0	0.65	CaCl2	5.53	24.2	46.9	0.75
37.8	22.0	41.8	0.55	AlCl3	6.20	18.5	51.0	0.68

Target Compound: Benzene

Initial Conc.	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)	Salt Type	Conc. (mM)	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)
58.8	36.6	37.7	0.78	NaCl	4.90	34.7	41.0	0.84
43.3	26.8	38.1	0.58	CaCl2	5.50	23.8	45.0	0.68
42.6	26.2	38.5	0.57	AlCl3	5.10	20.0	53.0	0.79

Target Compound: Phenol

Initial Conc.	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)	Salt Type	Conc. (mM)	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)
40.4	32.9	18.6	0.26	NaCl	7.06	29.7	26.5	0.37
46.9	38.5	17.9	0.29	CaCl2	5.60	33.3	29.0	0.47
89.5	72.5	19.0	0.59	AlCl3	4.97	61.3	31.5	[illegible]

Adsorbent Used: Activated Carbon

Target Compound: Toluene

Initial Conc.	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)	Salt Type	Conc. (mM)	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)
54.7	8.5	84.5	80.9	NaCl	5.04	7.9	85.5	81.9
74.2	11.2	84.9	110.3	CaCl2	5.80	10.8	85.4	110.9
46.9	7.1	84.8	69.6	AlCl3	5.54	6.9	85.3	70.0

Target Compound: Benzene

Initial Conc.	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)	Salt Type	Conc. (mM)	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)
39.9	8.0	79.9	55.8	NaCl	6.40	6.6	83.5	58.3
51.1	10.5	79.5	71.1	CaCl2	5.70	9.2	82.0	73.3
76.5	14.5	81.1	108.5	AlCl3	4.90	14.1	81.6	109.2

Target Compound: Phenol

Initial Conc.	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)	Salt Type	Conc. (mM)	Final Conc.	% of Reduction	Adsorp. Cap.(mg/g)
48.4	18.8	61.1	51.8	NaCl	6.80	16.5	65.9	55.8
83.6	32.2	61.5	90.0	CaCl2	5.40	30.1	64.0	93.6
103.0	39.2	61.9	111.6	AlCl3	5.10	37.8	63.3	114.1

sorbent with the addition of inorganic salts than toluene.

5.2.pH Effect on Adsorption

Previous research (8) (1988) indicated that washed flyash shows better adsorptive capacities than unwashed flyash. Therefore, flyash has been washed prior to use.

The effect of pH on adsorption is a well established concept. The addition of inorganic salts may significantly change the pH value in solution. The pH of a solution from which adsorption occurs may influence the extent of adsorption. Hence, in the presence of inorganic salts, it was necessary to determine the effect of pH on flyash and activated carbon performance and also to evaluate the optimum pH condition for the system. Adjustment to acidic conditions was made using sulfuric acid, while adjustment to basic conditions was made using potassium hydroxide as the buffer. The adsorptive capacity of flyash and activated carbon on target aromatic compounds (toluene, benzene, phenol) with the addition of about 5mM concentration of inorganic salts (NaCl, $CaCl_2.2H_2O$, $AlCl_3$) is shown in Figures A1 to A18. Results show a very interesting phenomena; namely, that flyash has a different adsorption behavior than activated carbon. For flyash, results indicate that the adsorption capacity increases with increasing pH up to a certain pH value and then decreases at higher pH levels. In contrast, with activated carbon , adsorption capacity shows an optimal behavior, displaying a reduction in adsorptive capacity. Above the salt saturation point (i.e., upon salt precipitation or supersaturation) adsorptive capacity increases again. The possible precipitation of metallic hydroxide can be evaluated from Figure 5.3$^{(11)}$, the difference may be due to the fact that activated carbon possess greatly different surface characteristics than flyash. During the precipitation of metallic hydroxides in the presence of activated carbon, the organic pollutant - inorganic salt system may contribute a small amount of adsorptive capacity thus making the carbon surface more active in adsorbing organic molecules.

Figures A_1 to A_{18} show that the adsorption of organic compounds onto flyash and activatied carbon is highly pH sensitive. Results show that activated carbon and Hudson flyash favor a neutral pH range (6 - 8) in the presence of sodium chloride and calcium chloride, while in the presence of alumium chloride, the adsorbents favor a pH range (4 - 5). This may be due to the fact that the ion charge balance in the solution system can exhibit the highest adsorption property of the adsorbents. It seems that the pH value for the dissociation of sodium chloride and calcium chloride in aqueous state is a neutral range (6 - 8), while the a dissolution of aluminum chloride in aqueous is in an acidic pH range (4 - 5). In a series of isotherm batch tests, the pH was adjusted to an optimum value prior to obtaining gas chromatographic data . In order to prevent a drastic pH change during adsorption , three drops of

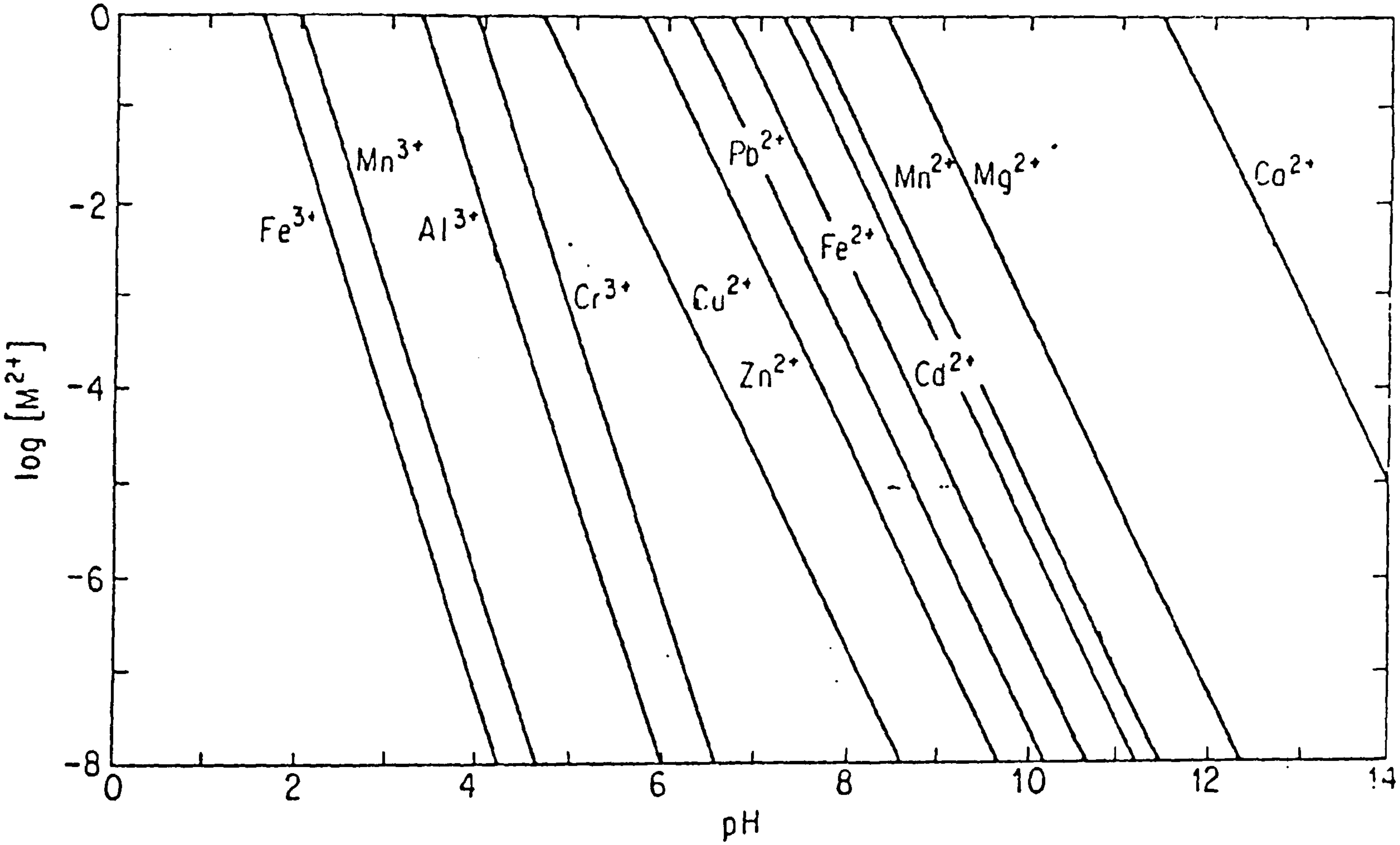


Figure 5.3 Logarithmic Concentration Diagram Showing the Solubility of Various Metallic Hydroxides.

buffer solution were added to the solution system prior to each experiment.

5.3. Effect of Inorganic Salts on Single Solute Adsorption Equilibria

A series of batch studies were performed with two adsorbents (Hudson flyash and activated carbon). Benzene, toluene, and phenol were selected as adsorbates. The inorganic salts used were monovalent/sodium chloride (NaCl), divalent/calcium chloride ($CaCl_2.2H_2O$), and trivalent/aluminum chloride ($AlCl_3$) compounds. A scan of physical property, the above salts were completely dissolved in water in the range of salt concentration investigated in this research. Sodium chloride and calcium chloride were completely dissociate to cation and anion in water. Amhydrous aluminum chloride can have a violent chemical reaction with water to form aluminum hydroxide. The dissociation of aluminum hydroxide in water is dependent on the pH value of the solution.(45)

$$Al(OH)_3 + 3\ H^+ \text{---->} Al^{3+} + 3H_2O$$

An experiment was conducted to check the possible occurrence of chemical reaction to enchance or hinder the adsorption of adsorbent during the investigation in this research. Without the presence of adsorbents, two identical bottles were prepared with and without the presence 0.01 M of inorganic salt, and were filled with the same influent concentration of target organic pollutant respectively.

Bottles were shaken for 12 hours and samples were analyzed by gas chromatography. Table 5.2 shows the concentration of organic pollutants between the two bottles remains the same. It indicates that under the dilute concentration of organic compounds and inorganic salt, the water molecule swept out the possible chemical reaction that is expected.

Table 5.3 list the micrograms of sorbate removed per gram of flyash (adsorptive capacity), percent recuction of sorbate, pH and solution conductivity charge of flyash, toluene and NaCl salt as a example . Salts concentration was determined by titration. Data from Table 5.3 shows a linear relationship between salt concentration and effluent concentration for the organic pollutant species. From the linear regression 0,2,4,6,8,10 minimolarity of inroganic salts effluent concentration, the percentage of reduction and adsorptive capacity were calculated.

The adsorption characteristics of the adsorbents on the target organic compound has been analyzed and evaluated using the Freundlich isotherm equation. This model is most useful for dilute soltuions over small concentration ranges. In addition, the Freundlich isotherm is frequently used in feasibility studies for industrial applications. The equation for the isotherm is :

$$q = X/M = K_F(C)^{1/n}$$

where :

q = adsorptive capacity of unit weight of sorbent material,(mg/g)

Table 5.2 Isotherm Data Without Adsorbents

Sorbate	Inorganic Salts	Concentration	pH
phenol	———	149.7ppm,($1.59*10^{-3}$M)	7.7
phenol	0.01M $CaCl_2*2H_2O$	149.5ppm,($1.59*10^{-3}$M)	7.5
phenol	———	121.0ppm,($1.29*10^{-3}$M)	6.0
phenol	0.01M $FeCl_3*6H_2O$	120.8ppm,($1.28*10^{-3}$M)	2.8
phenol	———	142.8ppm,($1.52*10^{-3}$M)	7.5
phenol	0.01M $AlCl_3$	142.7ppm,($1.52*10^{-3}$M)	4.5
MIBK	———	133.5ppm,($1.33*10^{-3}$M)	7.7
MIBK	0.01M $CaCl_2*2H_2O$	132.2ppm,($1.32*10^{-3}$M)	7.6
MIBK	———	157.6ppm,($1.58*10^{-3}$M)	7.5
MIBK	0.01M $FeCl_3*6H_2O$	156.4ppm,($1.56*10^{-3}$M)	2.6
MIBK	———	145.7ppm,($1.46*10^{-3}$M)	7.6
MIBK	0.01M $AlCl_3$	146.8ppm,($1.48*10^{-3}$M)	4.3
IPA	———	131.5ppm,($2.63*10^{-3}$M)	7.4
IPA	0.01M $CaCl_2*2H_2O$	130.8ppm,($2.62*10^{-3}$M)	7.4
IPA	———	140.0ppm,($2.80*10^{-3}$M)	7.1
IPA	0.01M $FeCl_3*6H_2O$	139.8ppm,($2.80*10^{-3}$M)	2.7
IPA	———	134.4ppm,($2.69*10^{-3}$M)	7.4
IPA	0.01M $AlCl_3$	135.2ppm,($2.70*10^{-3}$M)	4.4

Table 5.3
Flyash Used : Hudson Flyash
Inorganic Salt : NaCl ; Target Compound : Toluene

Salt Conc. before Adsorp.	Eff. Conc.(ppm)	% of Removal	Adsorp. Cap.(mg/g)	PH before Adsorp.	PH after Adsorp.	Salt Conc. after Adsorp.	Conductivity before Adsorp.	Conductivity after Adsorp.
Influent Concentration: 101.5 ppm								
-------	58.9	42.0	1.491	6.47	7.26	--------	1.5*100umho	2.2*100umho
1.83 mM	57.0	43.8	1.557	6.86	7.56	1.83	3.3	3.6
3.74 mM	56.5	44.3	1.575	6.67	7.41	3.74	5.3	5.5
6.63 mM	56.0	44.8	1.592	6.59	7.28	6.63	8.0	8.3
8.31 mM	55.3	45.5	1.617	6.32	7.08	8.31	9.3	9.5
10.05 mM	54.8	46.0	1.634	6.48	7.34	10.05	11.4	11.6
Influent Concentration: 81.5 ppm								
-------	47.7	41.5	1.183	6.40	7.20	--------	1.3	2.0
2.03 mM	46.3	43.2	1.232	6.60	7.40	2.03	3.5	3.7
3.68 mM	45.6	44.0	1.256	6.86	7.54	3.68	5.0	5.2
6.50 mM	45.1	44.7	1.274	6.78	7.50	6.50	7.2	7.4
8.03 mM	44.6	45.3	1.291	6.75	7.53	8.03	9.0	9.2
10.02 mM	44.1	45.9	1.309	6.88	7.39	10.02	11.4	11.8
Influent Concentration: 60.3 ppm								
-------	35.3	41.4	0.875	6.54	7.08	--------	1.3	2.0
2.44 mM	34.1	43.4	0.917	6.12	6.92	2.44	3.7	3.9
4.12 mM	33.4	44.6	0.941	6.40	7.40	4.12	5.6	5.7
5.79 mM	32.6	45.9	0.969	6.53	7.23	5.79	7.0	7.2
7.71 mM	32.2	46.6	0.983	6.45	7.40	7.71	8.6	8.8
9.73 mM	31.9	47.1	0.994	6.28	7.02	9.73	10.8	11.0
Influent Concentration: 37.9 ppm								
-------	22.0	41.9	0.556	6.60	6.90	--------	1.2	2.0
2.40 mM	21.1	44.3	0.586	6.35	7.04	2.40	2.6	4.0
3.66 mM	20.6	45.6	0.605	6.71	7.23	3.66	5.4	5.6
5.69 mM	20.3	46.4	0.616	6.33	7.02	5.69	6.9	7.0
7.63 mM	19.5	48.5	0.644	6.90	7.15	7.63	8.5	8.6
9.65 mM	19.1	49.6	0.658	6.23	6.50	9.65	10.7	10.8
Influent Concentration: 26.2 ppm								
-------	16.5	41.5	0.409	6.46	7.12	--------	1.2	1.9
2.40 mM	16.0	43.8	0.427	6.43	7.17	2.40	3.6	3.8
3.80 mM	15.6	44.7	0.441	6.54	7.05	3.80	5.4	5.6
5.50 mM	15.2	46.1	0.455	6.78	7.33	5.50	6.8	7.0
7.70 mM	15.0	46.8	0.462	6.76	7.29	7.70	8.5	8.6
9.38 mM	14.4	46.9	0.483	6.67	7.34	9.38	10.4	10.6

X = weight of pollutants adsorbed, (mg)

M = weight of sorbent used, (g)

C = equilibrium inpurity concentration remaining in the solution,(mg/L)

K_F= empirical constant equal to intercept, known as capacity factor

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

K_F and n are constants depending on temperature, the characteristics of sorbent, and the substance to be adsorbed.

The adsorption isotherm of target compounds onto activated carbon and Hudson flyash at various concentrations of inorganic salts were shown in Figure B1 to B30. The regressed Freundlich parameters from above figures were summarized and listed in Table 5.4 to 5.7. The regression variances show that the experimental data was well represented by Freundlich Equation (variance generally less than 10^{-4}). From the regression of isotherm test data, adsorptive capacity calculated from the Freundlich parameters for adsorbents, adsorbates, and inorganic salts are shown in Table 5.8 to 5.11. By applying equilibrium concentration of target organic pollutant equal to 30 ppm and 10 ppm to the adsorption system of Hudson flyash and activated carbon respectively, plots of various concentrations of inorganic salts (0,2,4,6,8,10 mM) versus adsorptive capacity of target compounds onto Hudson flyash and activated carbon were shown in Figure C_1 to C_{10}.

Table 5.4
Freundlich Parameters for Adsorption of Pollutants
Onto Activated Carbon in the Presence of Inorganic Salts

Target Compound	Inorganic Salts	Salt Conc.(M)	Kf(mg/g)	1/n	Regression Varience
Toluene	NaCl	0	8.5624	1.053	7.76E-5
Toluene	NaCl	0.002	8.9949	1.048	9.27E-5
Toluene	NaCl	0.004	9.4907	1.036	1.17E-4
Toluene	NaCl	0.006	9.9403	1.028	1.50E-4
Toluene	NaCl	0.008	10.4712	1.018	1.84E-4
Toluene	NaCl	0.010	10.8893	1.014	3.203-8
Toluene	CaCl2.2H2O	0	9.2023	1.014	8.74E-5
Toluene	CaCl2.2H2O	0.002	9.5257	1.007	7.28E-5
Toluene	CaCl2.2H2O	0.004	9.8220	1.004	7.66E-5
Toluene	CaCl2.2H2O	0.006	10.1859	0.998	7.46E-5
Toluene	CaCl2.2H2O	0.008	10.5681	0.992	7.65E-5
Toluene	CaCl2.2H2O	0.010	10.9144	0.987	8.83E-5
Toluene	AlCl3	0	8.8858	1.034	2.38E-6
Toluene	AlCl3	0.002	8.9476	1.037	2.38E-6
Toluene	AlCl3	0.004	8.9763	1.043	2.49E-6
Toluene	AlCl3	0.006	9.0406	1.046	2.53E-6
Toluene	AlCl3	0.008	9.0594	1.053	2.76E-6
Toluene	AlCl3	0.010	9.1390	1.056	2.88E-6
Benzene	NaCl	0	7.0974	1.003	1.03E-4
Benzene	NaCl	0.002	7.5231	1.004	1.03E-4
Benzene	NaCl	0.004	8.0001	1.004	9.87E-5
Benzene	NaCl	0.006	8.5211	1.005	9.99E-5
Benzene	NaCl	0.008	9.1264	1.004	9.23E-5
Benzene	NaCl	0.010	9.7723	1.006	9.00E-5
Benzene	CaCl2.2H2O	0	6.8359	1.018	5.40E-5
Benzene	CaCl2.2H2O	0.002	7.2660	1.011	4.63E-5
Benzene	CaCl2.2H2O	0.004	7.6913	1.008	3.71E-5
Benzene	CaCl2.2H2O	0.006	8.2073	1.001	3.24E-5
Benzene	CaCl2.2H2O	0.008	8.7076	0.998	2.25E-5
Benzene	CaCl2.2H2O	0.010	9.3454	0.989	2.89E-5
Benzene	AlCl3	0	7.0843	0.996	7.25E-6
Benzene	AlCl3	0.002	7.2778	1.002	3.70E-6
Benzene	AlCl3	0.004	7.5093	1.008	1.23E-6
Benzene	AlCl3	0.006	7.7091	1.016	2.25E-6
Benzene	AlCl3	0.008	7.9561	1.023	6.57E-6
Benzene	AlCl3	0.010	8.2035	1.031	1.45E-6
Phenol	NaCl	0	2.7504	1.017	2.03E-6
Phenol	NaCl	0.002	2.9478	1.012	1.93E-6
Phenol	NaCl	0.004	3.1405	1.010	1.73E-6
Phenol	NaCl	0.006	3.3986	1.006	1.52E-6
Phenol	NaCl	0.008	3.6585	0.997	7.52E-7
Phenol	NaCl	0.010	3.8273	0.996	4.31E-7
Phenol	CaCl2.2H2O	0	2.6393	1.020	1.50E-4
Phenol	CaCl2.2H2O	0.002	2.7944	1.014	1.18E-4
Phenol	CaCl2.2H2O	0.004	2.9457	1.009	9.79E-5
Phenol	CaCl2.2H2O	0.006	3.1117	1.003	8.87E-5
Phenol	CaCl2.2H2O	0.008	3.2832	0.998	8.93E-5
Phenol	CaCl2.2H2O	0.010	3.4881	0.991	1.03E-4
Phenol	AlCl3	0	2.9214	0.986	1.04E-4
Phenol	AlCl3	0.002	3.0040	0.984	7.00E-5
Phenol	AlCl3	0.004	3.0882	0.983	4.32E-5
Phenol	AlCl3	0.006	3.1463	0.984	2.05E-5
Phenol	AlCl3	0.008	3.2591	0.980	1.22E-5
Phenol	AlCl3	0.010	3.3589	0.978	8.43E-6

Table 5.5
Freundlich Parameters for Adsorption of Pollutants
Onto Hudson Flyash in the Presence of Inorganic Salts

Target Compound	Inorganic Salts	Salt Conc.(M)	Kf(ug/g)	1/n	Regression Varience
Toluene	NaCl	0	23.659	1.020	2.24E-5
Toluene	NaCl	0.002	28.119	0.985	2.27E-5
Toluene	NaCl	0.004	31.623	0.964	3.75E-5
Toluene	NaCl	0.006	37.068	0.931	4.12E-5
Toluene	NaCl	0.008	41.783	0.908	7.57E-5
Toluene	NaCl	0.010	49.091	0.875	1.13E-4
Toluene	CaCl2.2H2O	0	24.774	1.002	7.14E-6
Toluene	CaCl2.2H2O	0.002	26.302	1.006	1.11E-5
Toluene	CaCl2.2H2O	0.004	29.716	0.993	4.47E-5
Toluene	CaCl2.2H2O	0.006	32.136	0.991	2.42E-5
Toluene	CaCl2.2H2O	0.008	36.391	0.976	7.26E-5
Toluene	CaCl2.2H2O	0.010	38.815	0.978	8.99E-5
Toluene	AlCl3	0	22.387	1.043	2.92E-7
Toluene	AlCl3	0.002	24.434	1.051	2.38E-8
Toluene	AlCl3	0.004	26.182	1.061	1.05E-7
Toluene	AlCl3	0.006	28.708	1.066	1.04E-7
Toluene	AlCl3	0.008	31.551	1.069	5.19E-8
Toluene	AlCl3	0.010	34.119	1.076	1.17E-8
Benzene	NaCl	0	21.037	1.002	1.56E-5
Benzene	NaCl	0.002	25.061	0.967	2.58E-5
Benzene	NaCl	0.004	29.444	0.938	1.04E-5
Benzene	NaCl	0.006	33.651	0.913	2.23E-5
Benzene	NaCl	0.008	39.264	0.882	3.63E-5
Benzene	NaCl	0.010	44.463	0.861	6.91E-5
Benzene	CaCl2.2H2O	0	23.067	0.988	1.62E-5
Benzene	CaCl2.2H2O	0.002	27.227	0.970	8.06E-5
Benzene	CaCl2.2H2O	0.004	32.508	0.948	1.21E-4
Benzene	CaCl2.2H2O	0.006	38.370	0.925	2.55E-4
Benzene	CaCl2.2H2O	0.008	45.394	0.904	3.04E-5
Benzene	CaCl2.2H2O	0.010	53.088	0.884	4.67E-4
Benzene	AlCl3	0	19.588	1.043	1.97E-4
Benzene	AlCl3	0.002	22.438	1.051	2.85E-4
Benzene	AlCl3	0.004	22.961	1.106	3.43E-4
Benzene	AlCl3	0.006	26.001	1.106	3.43E-4
Benzene	AlCl3	0.008	29.512	1.119	4.96E-4
Benzene	AlCl3	0.010	31.261	1.156	5.16E-4
Phenol	NaCl	0	9.258	0.971	1.92E-4
Phenol	NaCl	0.002	11.995	0.944	1.24E-4
Phenol	NaCl	0.004	15.241	0.918	1.36E-4
Phenol	NaCl	0.006	19.588	0.871	1.909-3
Phenol	NaCl	0.008	23.121	0.873	2.88E-4
Phenol	NaCl	0.010	27.797	0.854	4.24E-4
Phenol	CaCl2.2H2O	0	8.906	0.985	4.72E-4
Phenol	CaCl2.2H2O	0.002	11.748	0.966	3.71E-4
Phenol	CaCl2.2H2O	0.004	14.791	0.952	3.40E-4
Phenol	CaCl2.2H2O	0.006	18.155	0.941	3.02E-4
Phenol	CaCl2.2H2O	0.008	21.777	0.934	3.05E-4
Phenol	CaCl2.2H2O	0.010	26.061	0.924	3.08E-4
Phenol	AlCl3	0	7.985	1.030	1.11E-6
Phenol	AlCl3	0.002	9.984	1.037	1.04E-7
Phenol	AlCl3	0.004	12.302	1.046	4.21E-7
Phenol	AlCl3	0.006	14.125	1.059	5.35E-7
Phenol	AlCl3	0.008	16.482	1.070	4.48E-7
Phenol	AlCl3	0.010	19.011	1.079	3.24E-7

Results show that the addition of inorganic salts tend to increase adsorptive capacity (see Figure C_1 to C_{10}). The range of inorganic salt concentrations from these experiments was 0 to 10 mM. The results reveal that the adsorptive capacity of flyash for a specific compound is higher for trivalent salts than for monovalent salts. For example the adsorptive capacity of Hudson Flyash (carbon content 1.9%) with 30 ppm toluene in the presence of 10 mM inorganic salt are 1,329 ug/g, 1,079 ug/g and 963 ug/g for aluminum chloride, calcium chloride and sodium chloride, respectively. While investigating the adsorptive capacity of activated carbon for a specific compound, the solution response is opposite. Monovalent salt displays a higher adsorptive capacity than divalent salt and trivalent salt. For example, the adsorptive capacity of activated carbon with 10ppm toluene in the presence of 10 mM salts are 112 mg/g, 105 mg/g, 103 mg/g for sodium chloride, calcium chloride, aluminum chloride, respectively.

This may be explained by the adsorption mechanism in the presence of salts. The mechanisms proposed to explain the observed effects of salts on the adsorption of organics can be grouped into three categories : (1) Adsorbate-salt interaction in solution; (2) Adsorbate-salt interaction on surface ; (3)Adsorbent-salt interactions.

Part of the studies were extended in order to examine adsorption effects without adsorbent. The concentration of various organic compounds were observed to

Table 5.6
Freundlich Parameters for Adsorption of Pollutants
Onto Activated Carbon in the Presence of Inorganic Salts

Target Compound	Inorganic Salts	Salt Conc. (M)	Kf(mg/g)	1/n	Regression Varience
MIBK	NaCl	0	4.0785	1.013	4.46E-7
MIBK	NaCl	0.002	4.2015	1.021	3.02E-6
MIBK	NaCl	0.004	4.4402	1.023	1.24E-8
MIBK	NaCl	0.006	4.6709	1.026	2.06E-7
MIBK	NaCl	0.008	4.9534	1.028	3.84E-7
MIBK	NaCl	0.010	5.2541	1.031	3.42E-7
MIBK	CaCl2.2H2O	0	4.4874	0.973	3.36E-5
MIBK	CaCl2.2H2O	0.002	4.6665	0.972	1.80E-5
MIBK	CaCl2.2H2O	0.004	4.8339	0.970	8.87E-6
MIBK	CaCl2.2H2O	0.006	5.0107	0.970	7.47E-6
MIBK	CaCl2.2H2O	0.008	5.2239	0.976	1.23E-5
MIBK	CaCl2.2H2O	0.010	5.4412	0.965	2.69E-5
MIBK	AlCl3	0	4.9102	0.936	1.98E-4
MIBK	AlCl3	0.002	4.8707	0.949	1.36E-4
MIBK	AlCl3	0.004	4.8372	0.961	8.69E-5
MIBK	AlCl3	0.006	4.8150	0.973	5.20E-5
MIBK	AlCl3	0.008	4.7808	0.985	2.88E-5
MIBK	AlCl3	0.010	4.7446	0.999	2.21E-5
IPA	NaCl	0	0.4985	0.994	5.07E-6
IPA	NaCl	0.002	0.4893	1.010	1.07E-5
IPA	NaCl	0.004	0.5306	1.001	1.59E-5
IPA	NaCl	0.006	0.5622	0.994	2.81E-5
IPA	NaCl	0.008	0.5739	1.000	1.59E-5
IPA	NaCl	0.010	0.5708	1.012	9.20E-6
IPA	CaCl2.2H2O	0	0.5794	0.928	2.32E-4
IPA	CaCl2.2H2O	0.002	0.5614	0.947	1.51E-4
IPA	CaCl2.2H2O	0.004	0.5467	0.964	9.10E-5
IPA	CaCl2.2H2O	0.006	0.5355	0.980	4.54E-5
IPA	CaCl2.2H2O	0.008	0.5242	0.996	1.83E-5
IPA	CaCl2.2H2O	0.010	0.5152	1.010	5.43E-6
IPA	AlCl3	0	0.4995	0.963	4.38E-6
IPA	AlCl3	0.002	0.5059	0.967	4.26E-6
IPA	AlCl3	0.004	0.5129	0.971	4.05E-6
IPA	AlCl3	0.006	0.5218	0.974	3.35E-6
IPA	AlCl3	0.008	0.5286	0.977	3.26E-6
IPA	AlCl3	0.010	0.5359	0.981	3.25E-6

Table 5.7
Freundlich Parameters for Adsorption of Pollutants
Onto Hudson Flyash in the Presence of Inorganic Salts

Target Compound	Inorganic Salts	Salt Conc.(M)	Kf(ug/g)	1/n	Regression Varience
MIBK	NaCl	0	16.59	0.880	2.29E-4
MIBK	NaCl	0.002	17.98	0.894	2.28E-4
MIBK	NaCl	0.004	19.50	0.906	2.35E-4
MIBK	NaCl	0.006	21.04	0.917	2.36E-4
MIBK	NaCl	0.008	22.86	0.925	2.48E-4
MIBK	NaCl	0.010	24.83	0.933	2.57E-4
MIBK	CaCl2.2H2O	0	11.48	0.985	4.83E-4
MIBK	CaCl2.2H2O	0.002	13.71	0.977	4.36E-4
MIBK	CaCl2.2H2O	0.004	16.14	0.970	4.04E-4
MIBK	CaCl2.2H2O	0.006	18.92	0.962	3.84E-4
MIBK	CaCl2.2H2O	0.008	21.88	0.956	3.76E-4
MIBK	CaCl2.2H2O	0.010	25.18	0.950	3.79E-4
MIBK	AlCl3	0	11.12	0.997	1.70E-5
MIBK	AlCl3	0.002	12.30	1.014	4.26E-6
MIBK	AlCl3	0.004	13.80	1.025	6.57E-6
MIBK	AlCl3	0.006	15.81	1.028	1.51E-6
MIBK	AlCl3	0.008	16.71	1.052	4.69E-6
MIBK	AlCl3	0.010	18.62	1.061	2.51E-6
IPA	NaCl	0	6.71	0.731	1.10E-4
IPA	NaCl	0.002	6.82	0.762	8.86E-5
IPA	NaCl	0.004	6.97	0.788	8.47E-5
IPA	NaCl	0.006	7.20	0.808	8.14E-5
IPA	NaCl	0.008	7.48	0.825	8.52E-5
IPA	NaCl	0.010	7.80	0.839	8.63E-5
IPA	CaCl2.2H2O	0	4.55	0.836	2.33E-4
IPA	CaCl2.2H2O	0.002	6.05	0.816	1.06E-4
IPA	CaCl2.2H2O	0.004	7.59	0.804	7.26E-5
IPA	CaCl2.2H2O	0.006	9.18	0.794	6.56E-5
IPA	CaCl2.2H2O	0.008	10.91	0.784	7.13E-5
IPA	CaCl2.2H2O	0.010	12.71	0.777	8.76E-5
IPA	AlCl3	0	2.44	1.016	6.57E-5
IPA	AlCl3	0.002	2.81	1.025	3.22E-5
IPA	AlCl3	0.004	3.51	1.012	9.56E-6
IPA	AlCl3	0.006	4.24	1.012	4.92E-6
IPA	AlCl3	0.008	5.04	1.021	2.41E-6
IPA	AlCl3	0.010	5.73	1.020	2.53E-6

remain the same with the addition of various concentration of inorganic salts. Table 5.2 shows these results. The reduction of solubility of organic compounds due to adsobate-salt interaction in soltuion before adsorption is not applicable to the observed phenomenon. Therefore the first proposed mechanism must be ruled out.

Adsorbate-salt interaction as a surface phenomenon can be explained by the adsorption behavior of activated carbon in the presence of salts. The surface of activated carbon is negatively charged. as a result, the concentration of cations near the surface will be higher than in the bulk solution. If adsorption takes place, the concentration of organic anions will also increase at the surface. This increase in interacting species at the surface can be expected to result in a shift in equilibrium from that of the bulk solution. The formation of organic-cation complex is significantly larger than the uncomplexed organic species; the attachment of larger complex ion on the surface of activated carbon is much easier than uncomplexed organic species. Therefore, adsorptive capacity is increased. Also, the possibility of formation of organic-cation complex, Na^+ is higher than Ca^{2+} and Al^{3+}. As such, NaCl imparts a greater improvement in adsorptive capacity in activated carbon-organic compound-salt solution system.

Adsorbent-salt interactions may explain the adsorption behavior of flyash in the presence of salts. The neutralization of electrostatic repulsion between adsorbate

Table 5.8

Adsorptive Capacity Calculated from Freundlich Equation

Adsorbent: Activated Carbon, Effluent Concentration: 10 ppm				
Adsorbate:		Toluene	Benzene	Phenol
Salts	Salts Conc. (mM)	Adsorp. Cap. (mg/g)	Adsorp. Cap. (mg/g)	Adsorp. Cap. (mg/g)
NaCl	0	96.73	71.46	28.56
NaCl	2	100.46	75.92	30.34
NaCl	4	103.11	80.74	32.25
NaCl	6	106.02	86.19	34.53
NaCl	8	109.14	92.11	36.42
NaCl	10	112.20	99.08	38.77
CaCl2.2H2O	0	95.03	71.25	27.64
CaCl2.2H2O	2	96.80	74.52	28.86
CaCl2.2H2O	4	99.13	78.34	30.07
CaCl2.2H2O	6	101.32	82.26	31.33
CaCl2.2H2O	8	103.63	86.59	32.71
CaCl2.2H2O	10	106.00	91.03	34.18
AlCl3	0	96.09	70.11	28.30
AlCl3	2	97.43	73.11	28.98
AlCl3	4	99.10	76.49	29.68
AlCl3	6	100.50	79.98	30.32
AlCl3	8	102.35	83.88	31.12
AlCl3	10	103.96	88.10	31.89

Table 5.9

Adsorptive Capacity Calculated from Freundlich Equation

Adsorbent: Hudson Flyash , Effluent Concentration: 30 ppm				
Adsorbate:		Toluene	Benzene	Phenol
Salts	Salts Conc. (mM)	Adsorp. Cap. (ug/g)	Adsorp. Cap. (ug/g)	Adsorp. Cap. (ug/g)
NaCl	0	759.73	635.41	251.98
NaCl	2	802.15	670.86	297.13
NaCl	4	838.22	714.65	345.36
NaCl	6	880.02	750.69	379.45
NaCl	8	916.69	789.33	450.48
NaCl	10	963.33	829.97	508.04
CaCl2.2H2O	0	748.29	664.11	254.06
CaCl2.2H2O	2	805.32	735.57	313.42
CaCl2.2H2O	4	869.32	816.03	377.41
CaCl2.2H2O	6	935.33	892.22	445.93
CaCl2.2H2O	8	1007.52	983.80	521.95
CaCl2.2H2O	10	1079.39	1073.05	604.15
AlCl3	0	778.46	680.18	266.09
AlCl3	2	871.04	800.64	341.18
AlCl3	4	967.59	948.33	432.45
AlCl3	6	1075.08	1118.63	519.83
AlCl3	8	1196.68	1327.08	627.87
AlCl3	10	1329.04	1594.24	749.37

and adsorbent and by the formation of adsorbent-salt-adsorbate complexes make the organic compound more readily adsorbed by flyash. Also, Al^{3+} has a higher electron charge which neutralizes the repusion between adsorbent and adsorbate, than either Ca^{2+} and Na^{+}. This would explain why $AlCl_3$ displays a greater degree of adsorptive capacity improvement in the flyash-organic compound-salt solution system.

The results also show that the improvement of adsorption capacity by the addition of specific inorganic salts at a certain concentration of target compound and salts is more effective for flyash than activated carbon. For example, the adsorptive capacity of Hudson flyash with 10 ppm toluene and 10 mM NaCl is 368.3 ug/g, and for 10 ppm toluene without NaCl is 247.7 ug/g shows a 48.6% capacity increase. The adsorptive capacity of activated carbon with 10 ppm toluene and 10 mM NaCl is 112.2 mg/g and 10 ppm toluene without NaCl is 96.73 mg/g ,which is only a 16%, increase. We conclude that the remaining unadsorbed organic molecules in flyash is much greater than in activated carbon.Since the salts concentration of diluent (see Table 5.3) remained unchanged during the batch adsorption experiments, we can conclude that the salt itself does not participate in the sorption process. Also, the slight variation in pH and solution conductivity supports that anions dissolved from inorganic salts do not affect the solution process.

Previous investigation (8) has shown that the lower

Table 5.10

Adsorptive Capacity Calculated from Freundlich Equation

Adsorbent: Activated Carbon, Eff. Conc.: 10 ppm			
Adsorbate:		MIBK	IPA
Salts	Salts Conc. (mM)	Adsorp. Cap. (mg/g)	Adsorp. Cap. (mg/g)
NaCl	0	42.02	4.92
NaCl	2	44.10	5.01
NaCl	4	46.87	5.32
NaCl	6	49.59	5.54
NaCl	8	52.83	5.74
NaCl	10	56.43	5.87
CaCl2.2H2O	0	42.17	4.91
CaCl2.2H2O	2	43.75	4.97
CaCl2.2H2O	4	45.11	5.03
CaCl2.2H2O	6	46.76	5.11
CaCl2.2H2O	8	49.43	5.19
CaCl2.2H2O	10	50.19	5.27
AlCl3	0	42.38	4.59
AlCl3	2	43.31	4.69
AlCl3	4	44.22	4.80
AlCl3	6	45.25	4.92
AlCl3	8	46.18	5.01
AlCl3	10	47.33	5.13

Table 5.11

Adsorptive Capacity Calculated from Freundlich Equation

Adsorbent: Hudson Flyash ,Eff. Conc.: 30 ppm			
Adsorbate:		MIBK	IPA
Salts	Salts Conc. (mM)	Adsorp. Cap. (ug/g)	Adsorp. Cap. (ug/g)
NaCl	0	330.91	80.63
NaCl	2	376.13	91.06
NaCl	4	424.92	101.67
NaCl	6	475.95	112.42
NaCl	8	531.39	123.74
NaCl	10	593.10	135.33
CaCl2.2H2O	0	327.27	78.14
CaCl2.2H2O	2	380.35	97.07
CaCl2.2H2O	4	437.23	116.90
CaCl2.2H2O	6	498.78	136.67
CaCl2.2H2O	8	565.16	156.99
CaCl2.2H2O	10	637.26	178.59
AlCl3	0	330.21	77.29
AlCl3	2	386.99	91.78
AlCl3	4	450.74	109.68
AlCl3	6	521.69	132.50
AlCl3	8	598.28	162.39
AlCl3	10	687.39	184.00

the water solubility (the higher the Kow value) of target compound, the higher the adsorptive capacity adsorbed onto the sorbents. The addition of inorganic salts in the adsorption system also follows the same pattern; toluene possesses the lowest water solubility (highest Kow value), attains the highest adsorbability among the target compounds. For example, in the presence of 10 mM of NaCl, the adsorptive capacity of toluene, benzene, MIBK,phenol and IPA onto activated carbon are 112.20 mg/g, 99.08 mg/g, 56.43 mg/g, 38.07 mg/g and 5.87 mg/g respectively (calculated based on equilibrium concentration = 10 mg/l), while the water solubility of the target compounds increases follow the above sequence (see Table 4.2).

5.4. Multi-solute Adsorption Equilibria

Because the existence of multi-component in industrial wastewater stream and ground water is fairly common, it was felt necessary to examine the effect of inorganic salts on multi-component adsorption systems. The role that inorganic salts perform in multi-component adsorption systems, may be a significant factor in helping to establish an accurate design of a sorption plant. Competition for adsorption sites occurs when a wide spectrum of contaminants are present in the solution . The system becomes more complicated with the addition of inorganic salts. The interactions among adsorbent, adsorbates and inorganic salts raise the multi-solute adsorption system to a higher level of sophistication. To find out how the inorganic salts quantitatively effect the adsorption capacity of adsorbents is the objective of this study. The results of a series of adsorption studies in multi-component mixture , with and without the presence of inorganic salts, by activated carbon and flyash are presented and discussed.

In single-solute adsorption equilibria study has shown the applicability of Freundlich equation, in the presence of a low concentration of inorganic salts (salts' concentration less than 0.01 M). Results also show a significant improvement of adsorptive capacity of adsorbents (either activated carbon or flyash).

The most widely acceptable method for prediction of multi-solute adsorption equilibria is the Ideal Adsorbed Solution theory (IAST) of Myers and Pransnitz$^{(26)}$ for adsorption of gaseous mixtures. Radke and Prausnitz $^{(27)}$ extended this method to dilute liquid solution. The big advantage of this thoery is that only single-solute data are required. Therefore, the aim of the study is to show that a satisfactory prediction of the behavior of complex mixture can be achieved by mathematical models which require only single solute data. Based on that, the five target compounds which have been investigated in single-solute equilibria were selected.

The multi-component adsorptive behavior with and without the presence of inorganic salts by activated carbon and flyash of the following combination were examined.

(1). Benzene and Toluene

(2). Phenol and Toluene

(3). Methyl isobutyl ketone and Toluene

(4). Isopropyl alcohol and Methyl isobutyl ketone

(5). Isopropyl alcohol and Toluene

(6). Benzene, Toluene and Phenol

(7). Benzene, Methyl isobutyl ketone, and Toluene

(8). Isopropyl alcohol, Methyl isobutyl alcohol, and Toluene

(9). Benzene, Methyl isobutyl ketone, Toluene, and Phenol

(10). Benzene, Methyl isobutyl ketone, Toluene, and Phenol

(11). Isopropyl alcohol, Benzene, Methyl isobutyl ketone, Toluene, and Phenol

From the results of single-solute study with the addition of inorganic salts, NaCl and $AlCl_3$ has the highest adsorptive capacity performance when activated carbon and flyash were used as sorbent material respectively. Therefore, 0.01 M of NaCl and $AlCl_3$ in multi-solute system were studied in activated carbon and flyash separately.

A. Calculation of adsorptive capacity (q of X/M) from experimental measurement. Data obtsined from the experiment has been utilized to calculate the adsorptive capacity of sorbents using mass balance equation :

$$q = X/M = (Ci-Ce)* V/M$$

where :

$q, X/M$ = adsorptive capacity (mg/g) or (ug/g)

$$= \frac{\text{weight of solute adsorbed (mg or ug)}}{\text{weight of sorbent used (g)}}$$

Ci = influent concentration, ppm

Ce = equilibrium concentration, ppm

V = volume of the reactor, (l)

M = weight of sorbent used, (g)

The linear regression data were obtained by the regression of equilibrium concentration versus adsorptive capacity on logarithmic scale.

B. The Freundlish parameters apply to equation (2-38 to 2-43) gets equation (2-44) is used for the calculation of adsorptive capacity (X/M, q):

$$C_{oi} - q_i \left(\frac{M}{V} \right) \frac{q_i}{\sum_{j=1}^{N} q_j} \left[\frac{\sum_{j=1}^{N} q_j n_i}{n_i K_{Fi}} \right]^{ni}$$

Where : C_{oi} = Influent concentration of component i in multi- component system.

q_i = Solid phase concentration of solute i at single-solute system (mass/mass)

n_i, K_{Fi} = Freundlich parameter for component i in single solute system.

N = Number of components.

M/V = Sorbent dose.

M = Weight of sorbent used.

V = Volume of solution.

i = Species "i"

j = Species "j"

N nonlinear simultaneous equation with N unknow solved to get the adsorptive capacity of N species at equilibrium state.

5.4.1. Competitive Adsorption of Toluene and Benzene.

The first case examined was the adsorption of a mixture containing toluene and benzene. This pair of compounds was selected because toluene and benzene both are aromatic compound and performed the highest adsorbability in single solute while comparing with other target compounds. Isotherm tests were performed parallelly with and without

0.01M NaCl by mixing equal concentration of each of the compound (benzene and toluene) at various concentration ranges (10 mg/l to 80 mg/l). A linear expression was obtained by the regression of equilibrium concentration versus adsorptive capacity. Regression coefficients ($R^2 > 0.95$) shows the data well represented by linear relationship. Freundlish parameters obtained from single solute study , without and with 0.01 M NaCl or $AlCl_3$ (see Table 5.4 to 5.7), were used in the calculation of IAST mathematical model.

Table 5.12 shows that the adsorptive capacity of activated carbon (experimental value) on toluene and benzene during the multi-component system are 41.31 mg/g and 51.57 mg/g (effluent concentration = 10 mg/l) respectively, whereas the adsorptive capacity of the same activated carbon on the same compounds during single-solute system are 71.46 mg/g and 96.74 mg/g respectively (values obtained from Table 5.4 using equilibrium concentration = 10 mg/l). Table 5.13 also shows that the presence of 0.01 M NaCl in benzene/toluene solution system, the adsorptive capacity of activated carbon (experimental value) on toluene and benzene during the multi-component system are 52.02 mg/g and 66.11 mg/g (effluent concentration = 10 mg/l) respectively, whereas the adsorptive capacity of the same activated carbon on the same compound during single-solute with the presence of 0.01 M NaCl are 99.08 mg/g, and 112.46 mg/g , respectively (values obtained from Table 5.4

Table 5.12 : **Competitive adsorption of** Benzene & Toluene
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**			
	Experimental Value		**IAST**	
	Benzene	Toluene	Benzene	Toluene
1	6.57	7.83	6.90	8.39
2	10.43	12.69	13.80	16.78
3	14.29	17.55	20.70	25.17
4	18.15	22.41	27.60	33.56
5	22.00	27.70	34.50	41.95
10	41.31	51.57	69.00	83.90

$R^2 = 0.967$

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**			
	Experimental Value		**IAST**	
	Benzene	Toluene	Benzene	Toluene
1	9.45	10.31	9.46	9.51
2	14.18	16.51	18.93	19.02
3	18.91	22.71	28.38	28.53
4	23.64	28.91	37.84	38.04
5	28.37	35.11	47.30	47.55
10	52.02	66.11	94.60	95.10

$R^2 = 0.950$

using equilibrium concentration = 10 mg/l). The effect of inorganic salt on benzene/toluene and activated carbon adsorption system, the addition of 0.01M NaCl can increase the adsorptive capacity of benzene and toluene by 25.92 % and 28.19 % respectively, while comparing to the same system without inorganic salt. Table 5.13 shows that the adsorptive capacity of Hudson flyash (experimental data) on benzene and toluene during the multi-component system are 514.10 ug/g, and 639.21 ug/g (effluent concentration = 30 mg/l) respectively, whereas the adsorptive capacity of the same flyash on the same compound on single-solute system are 680.18 ug/g and 777.38 ug/g respectively (values obtained from Table 5.5 using equilibrium concentration = 30 mg/l). Table 5.13 also shows that the presence of 0.01 M $AlCl_3$ in benzene/toluene solution system, the adsorptive capacity of Hudson flyash on benzene and toluene during the multi-solute system are 749.30 ug/g and 938.73 ug/g respectively, whereas the adsorptive capacity of the same flyash on the same compounds in single-solute system with the presence of 0.01 M $AlCl_3$ in solution are 1594.2 ug/g and 1325.5 ug/g respectively. (values obtained from Table 5.5 using equilibrium concentration = 30 mg/l). The effect of inorganic salt on benzene/toluene and Hudson flyash system, the presence of 0.01 M $AlCl_3$ can increase the adsorptive capacity of benzene and toluene by 45.74 % and 46.87 % respectively, while comparing with the same system without the presence of $AlCl_3$.

Table 5.13 : **Competitive adsorption of** Benzene & Toluene
Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	Adsorptive Capacity (ug / g)			
	Experimental Value		IAST	
	Benzene	Toluene	Benzene	Toluene
5	100.35	110.96	102.70	115.13
10	183.10	216.61	205.40	230.30
15	265.85	322.26	308.10	345.45
20	348.00	427.91	410.80	460.60
25	431.35	533.56	513.50	575.75
30	514.10	639.21	616.20	690.90

R^2=0.996

Sorbent : Hudson Flyash **Inorganic Salt :** 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	Adsorptive Capacity (ug / g)			
	Experimental Value		IAST	
	Benzene	Toluene	Benzene	Toluene
5	137.05	165.98	147.65	169.17
10	259.50	320.53	295.30	338.30
15	381.95	475.08	442.95	507.45
20	504.40	629.63	590.60	676.60
25	628.85	784.18	738.25	845.75
30	749.30	938.73	885.90	1014.90

R^2 = 0.997

Data indicates that the individual compound in the mixture are each adsorbed to a lesser extent when compare with their relative adsorbabilities in the single component tests. It also reveals that the addition of inorganic salts, flyash performs at a high efficiency than activated carbon , either on single solute or two-solue adsorption system.

5.4.2 Competitive Adsorption of Toluene and Phenol

The pair of compounds was selected to compare the variance of adsorptive capacity of toluene, while competing with different compounds in the solution under the condition of with and without the addition of inorganic salts. Isotherm tests were performed like previous binary system with and without the addition of inorganic salts at the same various concentration range (10 mg/l to 80 mg/l). Table 5.14 and 5.15 show the same pattern as was observed in the other (Toluene/Benzene) binary system. Data again indicates clearly that a competition for the adsorption sites takes place when more than one sorbate are present in the system. And the enchancement of adsorptive capacity of individual target compound, by adding inorganic salts in system. Toluene performed a higher adsorptive capacity onto adsorbents when compete with phenol than with benzene in a binary system. It can be observed in both cases of with and without inorganic salts in the sorption system. For example , in the presence of 0.01 M NaCl, toluene has adsorptive capacity of 73.44 mg/g and 66.11 mg/g onto activated carbon in toluene-phenol and toluene-benzene binary system

Table 5.14 : **Competitive adsorption of** Phenol & Toluene
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**			
	Experimental Value		**IAST**	
	Phenol	Toluene	Phenol	Toluene
1	2.60	8.20	2.62	8.32
2	4.53	14.25	5.24	16.65
3	6.46	20.30	7.86	24.96
4	8.39	26.35	10.48	33.28
5	10.32	32.40	13.10	41.60
10	19.97	62.65	26.25	83.20

$R^2 = 0.985$

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**			
	Experimental Value		**IAST**	
	Phenol	Toluene	Phenol	Toluene
1	3.53	9.45	3.76	9.40
2	5.85	16.65	7.52	18.80
3	8.17	23.67	11.28	28.20
4	10.49	30.78	15.04	37.60
5	12.81	37.89	18.80	47.00
10	24.41	73.44	37.60	94.00

$R^2 = 0.975$

Table 5.15 : **Competitive adsorption of** Toluene & Phenol
Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**			
	Experimental Value		**IAST**	
	Toluene	Phenol	Toluene	Phenol
5	117.45	36.53	120.15	40.00
10	227.45	62.88	240.03	80.00
15	337.45	89.23	360.45	120.00
20	447.45	113.58	480.60	160.00
25	557.45	141.93	600.75	200.00
30	667.45	165.28	720.90	240.00

$R^2 = 0.992$

Sorbent : Hudson Flyash **Inorganic Salt :** 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**			
	Experimental Value		**IAST**	
	Toluene	Phenol	Toluene	Phenol
5	171.82	88.20	174.25	96.10
10	341.27	173.00	348.50	192.20
15	490.72	257.80	522.75	288.30
20	650.17	342.60	697.00	384.40
25	809.62	427.40	871.25	480.50
30	969.07	512.20	1045.50	576.60

$R^2 = 0.997$

respectively, this indicates benzene is more efficient sorbate than phenol because phenol is a higher water solubility than benzene, in other word, benzene has a higher competition capability than phenol in binary competition adsorption system . Table 5.15 shows the addition of 0.01 M AlCl3 can significantly increase the adsorptive capacity of phenol onto Hudson flyash in toluene-phenol binary system. Data implies that the formation of adsorbent-sorbate-salt complex enchances the adsorbability of phenol onto flyash. The presence of inorganic salts also shows a considerable improvement in adsorptive capacity of adsorbents.(see Table 5.14 and 5.15).

5.4.3 Competitive Adsorption of Toluene and MIBK

This pair was selected to compare the competition adsorption of aromatic compound (toluene) and alphatic compound (MIBK). Isotherm tests were followed the same procedure performed the experiment parallelly with and without the addition of inorganic salts, at the same various concentration ranges.

In single-solute adsorption system, toluene performs a higher adsorptive capacity than MIBK (see Table 5.4 to 5.7). Table 5.16 and 5.17 also show the same pattern as was observed in the other binary systems. Refer to Table 5.12,5.13,5.14,and 5.15, among the toluene/phenol, toluene/MIBK, and toluene/benzene binary adsorption system, data shows toluene performs the highest adsorbability of the three target compounds. Data also indicates MIBK is a

Table 5.16 : **Competitive adsorption of** MIBK & Toluene
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**			
	Experimental Value		**IAST**	
	MIBK	Toluene	MIBK	Toluene
1	3.81	7.48	3.82	8.52
2	6.76	12.80	7.64	17.01
3	9.71	18.12	11.46	25.56
4	12.66	23.44	15.28	34.08
5	15.61	28.76	19.10	42.60
10	30.36	55.36	38.20	85.20

$R^2 = 0.987$

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**			
	Experimental Value		**IAST**	
	MIBK	Toluene	MIBK	Toluene
1	4.75	9.08	5.02	9.51
2	9.56	15.98	10.04	19.02
3	14.13	22.88	15.06	28.53
4	18.70	29.78	20.08	38.04
5	23.27	36.68	25.10	47.55
10	46.12	71.18	50.20	95.10

$R^2 = 0.986$

Table 5.17 : **Competitive adsorption of** MIBK & Toluene

Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**			
	Experimental Value		**IAST**	
	MIBK	Toluene	MIBK	Toluene
5	52.92	110.71	55.07	115.94
10	95.57	216.71	110.14	231.88
15	138.22	322.71	165.21	347.82
20	180.87	428.71	220.28	463.76
25	223.52	534.71	275.35	579.70
30	266.17	640.71	330.42	695.64

$R^2 = 0.995$

Sorbent : Hudson Flyash **Inorganic Salt :** 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**			
	Experimental Value		**IAST**	
	MIBK	Toluene	MIBK	Toluene
5	94.95	165.17	100.55	174.50
10	182.70	323.87	201.10	349.0
15	270.95	482.57	301.65	523.50
20	359.20	641.27	402.20	698.00
25	447.45	799.97	502.75	872.50
30	535.70	958.67	603.30	1047.00

$R^2 = 0.995$

slightly higher efficiency sorbate than phenol, but a lower efficiency than benzene. Adsorptive capacity of toluene onto adsorbents perform the highest capacity in toluene/phenol binary system among the above mentioned binary system. For example, toluene has adsorptive capacity of 667.45 ug/g, 640.71 ug/g and 639.21 ug/g on toluene/phenol, toluene/MIBK, and toluene/benzene binary system onto Hudson flyash respectively. The adsorption system in the presence of inorganic salts also shows the same result (see Table 5.16 and 5.17).

The addition of inorganic salts again shows the improvement of adsorptive capacity of sorbents on the adsorption of binary system. The extent of improvement of adsorptive capacity of a specific compound onto a specific sorbent somehow follows the same trend which was obtained from single solute isotherm sorption studies.

5.4.4. Competitive Adsorption of IPA and MIBK

The pair was selected to check the competition adsoeption of two alphatic compounds. Also, check the difference of adsorptive capacity of MIBK onto the sorbents while competing with toluene (the highest adsorbability onto sorbents) and IPA (the lowest adsorbability on to sorbents) in selected target compounds in binary adsorption system. Table 5.18 and 5.19 show MIBK has a relatively higher adsorptive capacity than IPA onto the sorbents, with and without the presence of inorganic salts in solution. This follows the same pattern in single-solute adsorption

Table 5.18 : **Competitive adsorption of** IPA & MIBK
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	Adsorptive Capacity (mg /g)			
	Experimental Value		IAST	
	IPA	MIBK	IPA	MIBK
1	0.43	3.51	0.44	3.92
2	0.78	6.71	0.88	7.84
3	1.13	9.91	1.32	11.76
4	1.48	13.11	1.76	15.68
5	1.83	16.31	2.20	19.60
10	3.58	32.31	4.40	39.20

$R^2 = 0.991$

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	Adsorptive Capacity (mg / g)			
	Experimental Value		IAST	
	IPA	MIBK	IPA	MIBK
1	0.53	4.75	0.55	5.05
2	1.01	9.47	1.10	10.10
3	1.49	14.19	1.65	15.15
4	1.97	18.91	2.20	20.20
5	2.45	23.63	2.75	25.25
10	4.85	47.23	5.50	50.55

$R^2 = 0.991$

Table 5.19 : Competitive adsorption of IPA & MIBK
Adsorbent : Hudson Flyash

Equi. Concn. (**mg/l**)	**Adsorptive Capacity** (ug / g)			
	Experimental Value		IAST	
	IPA	MIBK	IPA	MIBK
5	12.08	53.90	12.21	54.59
10	21.83	96.90	24.42	109.18
15	31.58	139.90	36.63	163.77
20	41.33	182.90	48.84	218.36
25	51.08	225.90	61.05	272.95
30	60.83	268.90	73.26	327.54

$R^2 = 0.986$

Sorbent : Hudson Flyash **Inorganic Salt :** 0.01 M $AlCl_3$

Equi. Concn. (**mg/l**)	**Adsorptive Capacity** (ug / g)			
	Experimental Value		**IAST**	
	IPA	MIBK	IPA	MIBK
5	23.56	96.49	27.25	99.05
10	41.81	185.89	54.50	198.10
15	60.06	275.29	81.75	297.15
20	78.31	364.69	109.00	396.20
25	96.56	454.09	136.25	495.25
30	114.81	543.49	163.50	594.30

$R^2 = 0996$

system. Compare with the competitive adsorption system of MIBK/toluene, adsorptive capacity of MIBK onto sorbents has slightly higher in IPA/MIBK system than in toluene/MIBK system. For example, the adsorptive capacity of MIBK onto activated carbon during the MIBK/IPA adsorption system and MIBK/toluene system are 32.31 mg/g and 30.36 mg/g respectively (values obtained from Table 5.16 and 5.18 with a effluenct concentration = 10 mg/l). The addition of inorganic salts also improves the adsorptive capacity of sorbents in this binary sorption system. Data reveals flyash performs a higher improvement efficiency than activated carbon in the presence of inorganic salts. For example , comparing the solution without salts, the presence of 0.01 M NaCl can improve the adsorptive capacity of MIBK onto activated carbon in MIBK/IPA sorption system , from 32.31 mg/g to 47.23 mg/g, i.e. 46 % efficiency improvement(based on effluent concentration = 10 ppm). While in the presence of 0.01 M $AlCl_3$ can significantly improve the adsorptive capacity of MIBK onto flyash in the same sorption system from 96.90 ug/g to 185.89 ug/g, i.e., 92 % efficiency improvement (based on the same effluent concentration).This also follw the same pattern as in single-solute system.

5.4.5. Competitive Adsorption of IPA and Toluene

The pair is selected to check the competitive adsorption of highest adsorbability (toluene) and lowest adsorbability (IPA) of the selected compounds in this study. Table 5.20 and 5.21 show data follows the same

Table 5.20 : **Competitive adsorption of** IPA & Toluene
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**			
	Experimental Value		**IAST**	
	IPA	Toluene	IPA	Toluene
1	0.40	7.91	0.41	8.46
2	0.74	14.88	0.82	16.92
3	1.08	21.85	1.23	25.38
4	1.42	28.82	1.64	33.84
5	1.76	35.79	2.05	42.30
10	3.46	70.64	4.10	84.60

$R^2 = 0.991$

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**			
	Experimental Value		**IAST**	
	IPA	Toluene	IPA	Toluene
1	0.53	9.98	0.55	10.50
2	0.97	17.52	1.10	21.00
3	1.41	25.06	1.65	31.50
4	1.85	32.60	2.10	42.00
5	2.29	40.14	2.65	52.50
10	4.49	77.84	5.50	105.00

$R^2 = 0.996$

Table 5.21 : **Competitive adsorption of** IPA & Toluene
Adsorbent : Hudson Flyash

Equi. Concn. (**mg/l**)	**Adsorptive Capacity** (ug / g)			
	Experimental Value		**IAST**	
	IPA	Toluene	IPA	Toluene
5	11.78	116.25	12.39	118.43
10	20.58	227.50	24.78	236.86
15	29.38	338.75	37.17	355.29
20	38.18	450.00	49.56	473.72
25	46.98	561.25	61.95	592.15
30	55.78	672.50	74.34	710.58

R^2 = 0994

Sorbent : Hudson Flyash **Inorganic Salt** : 0.01 M $AlCl_3$

Equi. Concn. (**mg/l**)	**Adsorptive Capacity** (ug / g)			
	Experimental Value		**IAST**	
	IPA	Toluene	IPA	Toluene
5	23.56	177.30	28.99	182.10
10	41.21	336.45	57.98	364.20
15	58.86	495.60	86.97	546.30
20	76.51	654.75	115.96	728.40
25	94.16	813.90	144.95	910.50
30	111.81	973.05	173.94	1092.60

R^2 = 0991

pattern as was observed in the other binary systems. Summarizing from the previous four sets of binary adsorption systems,the adsorptive capacity of adsorbents on toluene performs the highest adsorptive capacity during the IPA/toluene competitive system. For example, in the presence of 0.01 M $AlCl_3$, the adsorptive capacity of toluene onto Hudson flyash during the IPA/toluene, phenol/toluene, MIBK/Toluene, and benzene/toluene binary systems are 973.05 ug/g, 969.07 ug/g, 958.67 ug/g, and 938.73 ug/g respectively (values obtained from Table 5.13- 5.19 with effluent concentration = 30 mg/l). It's apparent that IPA has the highest solubility in water among the selected compounds takes the lowest adsorbability, Therefore, in toluene/IPA adsorption system, toluene can perform the highest adsorptive capacity onto sorbents. The sorption behavior follows the same trend as the system without the presence of salts.

5.4.6. Competitive Adsorption of Benzene, Toluene and Phenol

Equal concentration of benzene, toluene and phenol were mixed together at various concentration ranges and their competition effect onto Hudson flyash and Activated carbon with and without the addition of inorganic salts were investigated. Data (Table 5.22 and 5.23) indicates that an increasing number of compounds 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 decreases. For example, in the

Table 5.22 : **Competitive adsorption of** Benzene , Toluene & Phenol
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**					
	Experimental Value			**IAST**		
	Benzene	Toluene	Phenol	Benzene	Toluene	Phenol
1	6.50	7.30	2.40	6.95	8.13	2.61
2	10.00	11.98	3.92	13.90	16.26	5.22
3	13.50	16.66	5.44	20.85	24.39	7.83
4	17.00	21.34	6.96	27.80	32.52	10.44
5	21.00	26.02	8.48	34.75	40.65	13.05
10	38.00	49.42	16.08	69.50	81.30	26.10

R^3 = 0.981

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**					
	Experimental Value			**IAST**		
	Benzene	Toluene	Phenol	Benzene	Toluene	Phenol
1	8.92	8.69	3.45	9.94	10.07	3.80
2	12.99	14.75	5.53	19.88	20.14	7.60
3	17.06	20.81	7.61	29.82	30.21	11.40
4	21.13	26.87	9.69	39.76	40.28	15.20
5	25.20	32.93	11.77	49.70	50.35	19.00
10	45.55	63.23	22.17	99.40	100.70	38.00

R^3 = 0.972

Table 5.23 : **Competitive adsorption of** Benzene, Toluene & Phenol
Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**					
	Experimental Value			**IAST**		
	Benzene	Toluene	Phenol	Benzene	Toluene	Phenol
5	97.38	108.23	34.82	101.80	116.61	39.26
10	170.63	190.73	58.82	203.60	233.20	78.52
15	243.88	273.23	82.82	305.40	349.80	117.78
20	317.13	355.73	106.82	407.20	466.40	157.04
25	390.38	438.23	130.82	509.00	583.00	196.30
30	463.63	520.73	154.82	610.80	699.60	235.56

$R^2 = 0.994$

Sorbent : Hudson Flyash **Inorganic Salt :** 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**					
	Experimental Value			**IAST**		
	Benzene	Toluene	Phenol	Benzene	Toluene	Phenol
5	121.51	161.55	77.65	138.20	171.80	87.45
10	227.11	299.45	143.90	276.40	343.60	174.90
15	332.71	437.35	210.15	414.60	515.40	262.35
20	438.31	575.25	286.14	552.80	687.20	349.80
25	543.91	713.15	352.65	691.00	859.00	437.25
30	649.51	815.05	419.00	829.20	1030.80	524.70

$R^2 = 0997$

presence of 0.01 M $AlCl_3$ in solution, the adsorptive capacity of Hudson flyash on toluene in single component system is 1325.49 ug/g, whereas the same situation for two component system (benzene/toluene) and 3 component system (benzene/toluene/phenol) are 938.73 ug/g and 815.05 ug/g respectively (values obtained from Table 5.5, 5.13 and 5.23,using equilibrium concentration = 30 mg/l). The same pattern is also observed in the case of other compounds.

The improvement of adsorptive capacity onto sorbents in the presence of inorganic salts can be also observed in three-component system. For example, comparing with the sorption system without the addition of NaCl, the presence of 0.01 M NaCl can increase the adsorptive capacity of activated carbon on benzene, toluene, and phenol by 20 %, 28 %,and 38 % respectively (calculated based on effluent concentration = 10 ppm from Table 5.22).

5.4.7. Competitive Adsorption of Benzene, MIBK, and Toluene

Two aromatic sorbates and one alphatic sorbate were mixed with equal concentration to check up how the competitive adsorption takes place. Also, adsorption onto virgin activated carbon, virgin flyash, activated carbon with the addition of 0.01 M NaCl, and Hudson flyash with the addition of 0.01 M $AlCl_3$ in solution were investigated. Data (Table 5.24 and 5.25) follows the same pattern as was obtained in the case of other multi-solute system. Referring to benzene/phenol/toluene adsorption system, it reveals that when competing with the same solutes in three-component

Table 5.24 : **Competitive adsorption of** Benzene , MIBK & Toluene
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**					
	Experimental Value			**IAST**		
	Benzene	MIBK	Toluene	Benzene	MIBK	Toluene
1	6.55	3.20	7.33	7.12	3.78	8.39
2	9.76	5.81	11.91	14.24	7.56	16.78
3	12.97	8.42	16.49	21.36	11.34	25.17
4	16.18	11.03	21.07	28.48	15.12	33.56
5	19.39	13.64	25.65	35.60	18.90	41.95
10	35.44	26.69	48.55	71.20	37.80	83.90

R^3 = 0.968

Sorbent : Activated Carbon **Inorganic Salt** : 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**					
	Experimental Value			**IAST**		
	Benzene	MIBK	Toluene	Benzene	MIBK	Toluene
1	8.75	4.17	8.61	9.98	5.07	10.55
2	12.82	8.26	14.62	19.96	10.14	21.01
3	16.89	12.35	20.63	29.94	15.21	31.56
4	20.96	16.44	26.64	39.92	20.28	42.20
5	25.03	20.53	32.65	49.90	25.35	52.75
10	45.38	40.98	62.70	99.80	50.70	105.50

R^3 = 0.963

Table 5.25 : **Competitive adsorption of** Benzene, MIBK & Toluene
Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug /g)**					
	Experimental Value			**IAST**		
	Benzene	MIBK	Toluene	Benzene	MIBK	Toluene
5	96.88	44.56	106.36	102.70	55.07	118.43
10	169.32	84.14	183.31	205.40	110.14	236.90
15	242.38	118.31	260.26	308.10	165.21	355.35
20	315.13	155.19	337.21	410.80	220.28	473.80
25	387.88	192.06	414.46	513.50	275.35	592.25
30	460.63	228.94	491.11	616.20	330.42	710.70

$R^3 = 0.994$

Sorbent : Hudson Flyash **Inorganic Salt :** 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**					
	Experimental Value			**IAST**		
	Benzene	MIBK	Toluene	Benzene	MIBK	Toluene
5	124.50	80.04	162.10	139.20	91.03	171.10
10	224.85	140.04	291.65	278.40	182.06	342.20
15	325.20	200.04	421.20	417.60	273.09	513.30
20	425.55	260.04	551.55	556.80	364.12	684.40
25	525.90	320.04	680.30	696.00	455.15	855.50
30	626.25	380.04	809.85	835.20	546.18	1026.60

$R^3 = 0.996$

system, MIBK has a higher competitive capability onto the available sorption sites than phenol. This is due to MIBK has a relatively lower solubility in water than phenol. For example, in the presence of 0.01 M NaCl, the adsorptive capacity of activated carbon on MIBK and phenol during adsorption system of MIBK/toulene/benzene and phenol/toluene/benzene are 40.98 mg/g, and 22.17 mg/g respectively (see Table 5.24).

The effect of addition of inorganic salts shows a significant improvement of adsorptive capacity of adsorbents. For example, without the presence of inorganic salt, the adsorptive capacity of toluene,benzene, and MIBK onto Hudson flyash are 499.11 ug/g, 460.63 ug/g and 228.94 ug/g respectively. Whereas, the addition of 0.01 M $AlCl_3$ in the solution, the adsorptive capacity of toluene, benzene and MIBK onto Hudson flyash increase to 809.85 ug/g, 626.65 ug/g, and 380.04 ug/g respectively. That's 65 %, 36% and 66% efficiency improvement on toluene, benzene, and MIBK respectively.

5.4.8. Competitive Adsorption of IPA, MIBK and Toluene

The objective of this experiment was to check the competition adsorption of one aromatic solute and two aliphatic solutes in three-component adsorption system. Experimental procedure was follow as previously mentioned. Data (Table 5.26 and 5.27) indicates the adsorptive capacity of adsorbents on toluene during the adsorption system of IPA/MIBK/toluene system is higher than during the

Table 5.26 : **Competitive adsorption of** IPA, MIBK & Toluene
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**					
	Experimental Value			**IAST**		
	IPA	MIBK	Toluene	IPA	MIBK	Toluene
1	0.38	3.33	6.71	0.35	3.84	8.52
2	0.69	6.16	11.86	0.70	7.68	17.04
3	1.00	8.99	17.01	1.05	11.52	25.56
4	1.31	11.82	22.16	1.40	15.36	34.08
5	1.62	14.65	27.31	1.75	19.20	42.60
10	3.17	28.80	53.06	3.50	38.40	85.20

R^3 = 0.979

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**					
	Experimental Value			**IAST**		
	IPA	MIBK	Toluene	IPA	MIBK	Toluene
1	0.51	4.69	8.75	0.54	5.07	10.75
2	0.88	8.82	14.88	1.08	10.14	21.50
3	1.25	12.95	21.01	1.62	15.21	32.25
4	1.62	17.08	27.14	2.16	20.28	43.00
5	1.99	21.21	33.27	2.70	25.35	53.75
10	3.84	41.86	63.92	5.40	50.70	107.50

R^3 = 0.984

Table 5.27 : **Competitive adsorption of** IPA, MIBK & Toluene
Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**					
	Experimental Value			**IAST**		
	IPA	MIBK	Toluene	IPA	MIBK	Toluene
5	10.24	47.07	114.88	12.50	54.59	117.59
10	18.14	86.64	198.93	25.00	109.18	235.18
15	26.04	126.22	282.98	37.50	163.77	352.77
20	33.94	165.79	367.03	50.00	218.36	470.36
25	41.84	205.36	451.08	62.50	272.95	587.95
30	49.74	244.94	535.13	75.00	327.54	705.54

$R^3 = 0.987$

Sorbent : Hudson Flyash **Inorganic Salt :** 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**					
	Experimental Value			**IAST**		
	IPA	MIBK	Toluene	IPA	MIBK	Toluene
5	20.48	80.58	159.64	28.19	98.35	176.50
10	35.06	143.68	297.29	56.38	196.70	353.00
15	49.66	206.78	434.94	84.57	295.05	529.50
20	64.26	269.88	572.59	112.76	393.40	706.00
25	78.86	332.98	710.24	140.95	491.75	882.50
30	93.46	396.08	847.89	169.14	590.10	1059.00

$R^3 = 0.995$

other three-component systems which was previously studied. For example,the adsorptive capacity of Hudson flyash on toluene in IPA/MIBK/toluene system, benzene/phenol/toluene system and phenol/benzene/toluene system are 535.5 ug/g, 520.73 ug/g and 491.11 ug/g respectively. This implies that the solubility effect makes the sorbate less efficient, and consequently less efficient use of the available surface area. IPA shows the highest solubility among the five target compounds, i.e., IPA has the lowest competitive adsorption capability among those solutes, therefore, providing more available adsorption sites for toluene to utilize,as a result , increase the adsorptive capacity of sorbents onto toluene.

The inorganic salts show a improvement of sorption efficiency in this sorption system too. Summarizing the data from the three sets of three-component systems in this study, under the effect of the addition of inorganic salts, Hudson flyash performs a higher efficiency improvement of each target compound in three-component systems than activated carbon does. For example, comparing with the system of IPA/MIBK/toluene without the addition of NaCl, the efficiency improvement (under the addition of 0.01 M NaCl) of IPA,MIBK and toluene, are 18%,45% and 20% respectively (calculated based on equilibrium concentration = 10 mg/l from Table 5.26). Whereas, the same sorption system, the efficiency improvement (under the addition of 0.01 M $AlCl_3$) of IPA, MIBK, and toluene onto Hudson flyash increases to

88%, 62% and 58% respectively(data based on equilibrium concentration = 30 mg/l from Table 5.27).

5.4.9. Competitive Adsorption of IPA,Benzene,MIBK and Toluene and Competitive Adsorption of Benzene, MIBK, Toluene and Phenol

Two sets of four-component adsorption system were examined to explore the adsorption mechanisms take place when two aromatic compounds and two alphatic compounds and three aromatic compounds and two alphatic compounds are mixed together. Data (Table 5.28, 5.29, 5.30, and 5.31) follows the same trend as was obtained in the case of other multi- component systems. Again, it indicates an increasing number of compounds in a system, increases the competition among the solutes for adsorption sites, as a result of which the adsorptive capacity of the sorbent on that particular compound decreases. For example, in the presence of 0.01 M NaCl, the adsorptive capacity of activated carbon on phenol in the single component system was 37.92 mg/g (based on equilibrium concentration = 10 mg/l). Whereas the same conditions for the two-component system (phenol/toluene), three-component system (benzene/toluene/phenol) and four-component system (phenol/MIBK/benzene/toluene) are 24.41 mg/g, 22.17 mg/g and 19.71 mg/g respectively. The same pattern was also observed in the case of other target compounds.

As the other cases of multi-component systems, the addition of inorganic salts in four-component sorption

Table 5.28: **Competitive adsorption of** IPA, Benzene, MIBK and Toluene
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**							
	Experimental Value				**IAST**			
	IPA	Benzene	MIBK	Toluene	IPA	Benzene	MIBK	Toluene
1	0.33	6.00	2.91	6.20	0.35	7.20	3.94	8.39
2	0.61	8.95	5.44	10.60	0.70	14.40	7.88	16.78
3	0.89	11.90	7.91	15.00	1.05	21.60	11.82	25.17
4	1.17	14.85	10.38	19.40	1.40	28.80	15.76	33.56
5	1.45	17.80	12.85	23.80	1.80	36.00	19.70	41.95
10	2.85	32.55	25.20	45.80	3.50	72.00	39.40	83.90

R^4 = 0.970

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**							
	Experimental Value				**IAST**			
	IPA	Benzene	MIBK	Toluene	IPA	Benzene	MIBK	Toluene
1	0.49	7.82	3.64	8.08	0.55	10.02	5.08	10.40
2	0.84	11.75	6.94	14.05	1.10	20.04	10.16	20.80
3	1.19	15.68	10.24	20.02	1.65	30.06	15.24	31.20
4	1.54	19.61	13.54	25.99	2.10	40.08	20.32	41.60
5	1.89	23.54	16.84	31.96	2.65	50.10	25.40	52.20
10	3.64	43.19	33.34	61.91	5.50	100.20	50.80	104.00

R^4 = 0.968

Table 5.29 : **Competitive adsorption of** IPA,Benzene,MIBK & Toluene

Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**							
	Experimental Value				**IAST**			
	IPA	Benzene	MIBK	Toluene	IPA	Benzene	MIBK	Toluene
5	8.44	84.92	41.67	90.82	10.52	104.95	54.12	120.95
10	15.69	149.20	74.17	166.12	21.04	209.99	108.24	241.90
15	22.94	213.50	106.67	241.42	31.56	314.85	162.36	362.85
20	30.19	277.80	139.17	316.72	42.08	419.80	216.48	483.80
25	37.44	342.10	171.67	392.02	52.60	524.75	270.60	604.75
30	44.69	406.40	204.17	467.32	63.12	629.70	324.72	725.70

$R^4 = 0.985$

Sorbent : Hudson Flyash **Inorganic Salt** : 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**							
	Experimental Value				**IAST**			
	IPA	Benzene	MIBK	Toluene	IPA	Benzene	MIBK	Toluene
5	17.87	114.72	75.30	146.07	29.45	139.00	92.10	176.50
10	28.72	210.22	129.40	266.52	58.89	278.00	184.20	353.00
15	39.57	305.72	183.50	386.97	88.35	417.00	276.30	529.50
20	50.42	401.22	237.60	507.42	117.80	556.00	368.40	706.00
25	61.27	496.72	291.70	627.87	147.25	695.00	460.50	882.50
30	72.12	592.22	345.80	748.32	176.70	834.00	552.60	1059.00

$R^4 = 0.987$

Table 5.30 : **Competitive adsorption of** Benzene , MIBK , Toluene , & Phenol
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**							
	Experimental Value				**IAST**			
	Benzene	MIBK	Toluene	Phenol	Benzene	MIBK	Toluene	Phenol
1	5.85	2.96	6.66	2.24	7.12	3.93	8.39	2.74
2	8.25	5.09	10.64	3.55	14.24	7.96	16.78	5.58
3	10.65	7.22	14.62	4.86	21.36	11.89	25.17	8.32
4	13.05	9.35	18.60	6.17	28.48	15.82	33.56	11.06
5	15.45	11.48	22.58	7.48	35.60	19.75	42.00	13.80
10	27.45	22.13	42.48	14.03	71.20	39.30	83.90	27.40

R^4 = 0.971

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**							
	Experimental Value				**IAST**			
	Benzene	MIBK	Toluene	Phenol	Benzene	MIBK	Toluene	Phenol
1	7.63	3.54	7.33	2.97	10.02	4.91	10.65	3.48
2	11.26	6.64	12.93	4.83	20.04	9.82	21.30	6.96
3	14.89	9.74	18.53	6.69	30.06	14.73	31.95	10.44
4	18.52	12.84	24.13	8.55	40.08	19.64	42.60	13.92
5	22.15	15.94	29.73	10.41	50.10	24.55	53.25	17.40
10	40.30	31.44	57.73	19.71	100.20	49.10	106.50	34.80

R^4 = 0.968

Table 5.31 : **Competitive adsorption of** Benzene,MIBK, Toluene & Phenol
Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**							
	Experimental Value				**IAST**			
	Benzene	MIBK	Toluene	Phenol	Benzene	MIBK	Toluene	Phenol
5	83.11	41.64	95.96	31.07	103.15	54.41	119.10	39.51
10	146.11	70.39	166.61	55.25	206.30	108.82	238.20	79.02
15	209.11	99.14	237.26	79.42	309.45	163.23	357.30	118.53
20	272.11	127.89	307.91	103.60	412.60	217.64	476.40	158.04
25	335.11	156.64	378.56	127.77	515.75	272.05	595.50	197.55
30	398.11	185.39	449.21	151.95	618.90	326.46	714.60	237.06

R^4 = 0.996

Sorbent : Hudson Flyash **Inorganic Salt** : 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**							
	Experimental Value				**IAST**			
	Benzene	MIBK	Toluene	Phenol	Benzene	MIBK	Toluene	Phenol
5	118.03	77.32	146.78	74.94	159.32	89.15	172.05	85.30
10	209.88	128.42	266.58	128.84	318.60	178.30	344.10	170.60
15	301.73	179.52	386.38	182.74	477.90	267.45	516.15	255.90
20	393.58	230.62	506.18	236.64	637.20	356.60	688.20	341.20
25	485.43	281.72	625.98	290.54	796.50	445.75	860.25	426.50
30	577.28	332.82	745.78	344.44	955.80	534.90	1032.30	511.80

R^4 = 0.994

system also shows a significant enchancement of adsorptive capacity of each target compound. The extent of improvement of individual component in multi-component sorption system, is strongly dependent on the characteristics of sorbents and sorbates. Data shows a range of 25 % to 125 % of improvement of adsorptive capacity of sorbents on individual compound in the two sets of four-component sorption system (data calculated based on equilibrium concentration = 10 mg/l for activated carbon, and 30 mg/l for Hudson flyash).

5.4.10. Competitive adsorption of IPA, Benzene, MIBK, Toluene and Phenol

Equal amounts of the five target compounds in this study were mixed together at various concentration ranges. Experiments were performed based on adsorption onto activated carbon and Hudson flyash with and without inorganic salts added. Once again, data (Table 5.32 and 5.33) prove the same pattern as in the case of other multi-component systems; i.e. the more number of solutes in the system, the lower competitive efficiency of each compound. Summarizing from Table 5.12 to 5.33, the competitive adsorption capability in multi-component system of the five target compounds, under the condition of with and without addition of inorganic salts, follows the following sequence:

toluene > benzene > MIBK > phenol > IPA

The sequence also demonstrates in single-solute adsorption system, it indicates that the lower the solubility in water of the compound, the higher adsorptive capacity is performed

Table 5.32 : **Competitive adsorption of** IPA , Benzene , MIBK , Toluene & Phenol
Adsorbent : Activated Carbon

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg /g)**									
	Experimental Value					**IAST**				
	IPA	Benzene	MIBK	Toluene	Phenol	IPA	Benzene	MIBK	Toluene	Phenol
1	0.29	5.78	2.49	6.10	1.92	0.43	7.20	4.00	8.19	2.70
2	0.53	8.01	4.14	9.60	3.04	0.86	14.40	8.00	16.38	5.40
3	0.77	10.24	5.79	13.10	4.16	1.29	21.60	12.00	24.57	8.10
4	1.01	12.47	7.44	16.60	5.28	1.72	28.80	16.00	32.76	10.80
5	1.25	14.70	9.09	20.10	6.40	2.54	36.00	20.00	40.95	13.50
10	2.45	25.85	17.34	37.60	12.00	4.30	72.00	40.00	81.90	27.00

R^5 = 0.959

Sorbent : Activated Carbon **Inorganic Salt :** 0.01M NaCl

Equi. Concn. (mg/l)	**Adsorptive Capacity (mg / g)**									
	Experimental Value					**IAST**				
	IPA	Benzene	MIBK	Toluene	Phenol	IPA	Benzene	MIBK	Toluene	Phenol
1	0.45	6.59	2.99	7.10	2.58	0.56	9.94	4.88	10.60	3.48
2	0.75	9.53	5.14	11.23	4.11	1.12	19.88	9.76	21.20	6.96
3	1.05	12.47	7.29	15.36	5.64	1.68	29.82	14.64	31.80	10.44
4	1.35	15.41	9.44	19.49	7.17	2.24	39.76	19.52	42.40	13.92
5	1.65	18.35	11.59	23.62	8.70	2.80	49.70	24.40	53.00	17.44
10	3.12	33.05	22.34	44.27	16.35	5.60	99.40	48.80	106.00	34.80

R^5 = 0.973

Table 5.33 :: **Competitive adsorption of** IPA, Beneze, MIBK, Toluene & Phenol
Adsorbent : Hudson Flyash

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug /g)**									
	Experimental Value					**IAST**				
	IPA	Benzene	MIBK	Toluene	Phenol	IPA	Benzene	MIBK	Toluene	Phenol
5	8.24	79.90	38.12	85.63	29.23	11.92	104.80	53.64	119.60	40.82
10	14.14	139.20	61.87	152.98	45.38	23.84	209.60	107.28	239.20	81.64
15	20.04	198.50	85.62	220.33	61.53	35.76	314.40	160.92	358.80	122.46
20	25.94	257.80	109.37	287.68	77.68	47.68	419.20	214.56	478.40	163.28
25	31.84	317.10	133.12	355.03	93.83	59.60	524.00	268.20	598.00	204.10
30	37.74	376.40	156.87	422.38	109.98	71.52	628.80	321.84	717.60	244.92

R^5 = 0.987

Sorbent : Hudson Flyash **Inorganic Salt :** 0.01 M $AlCl_3$

Equi. Concn. (mg/l)	**Adsorptive Capacity (ug / g)**									
	Experimental Value					**IAST**				
	IPA	Benzene	MIBK	Toluene	Phenol	IPA	Benzene	MIBK	Toluene	Phenol
5	15.62	108.04	65.30	135.29	68.16	29.50	133.10	89.55	178.00	85.65
10	25.40	197.84	109.40	247.74	112.66	59.00	266.20	179.10	356.00	171.30
15	34.60	287.64	153.50	360.19	157.16	88.50	399.30	268.65	534.00	256.95
20	43.80	377.44	197.60	472.64	201.66	118.00	532.40	358.20	712.00	342.60
25	53.00	467.24	241.70	585.09	246.16	147.50	665.50	447.75	890.00	428.25
30	62.20	557.04	285.80	697.54	290.66	177.00	798.60	537.30	1068.00	513.90

R^5 = 0.988

in single-solute system, and the higher competitive capability in multi-component systems onto the sorbents. For a specific compound, multi-component equilibrium onto virgin activated carbon, virgin flyash, activated carbon with the presence of 0.01 M NaCl in solution and Hudson flyash with the presence of 0.01 M $AlCl_3$ in solution, were shown in Figure E1 to E20. Figures demonstrate the more compounds (sclutes) in adsorption system, the lower the adsorptive capacity of adsorbents (either with or without the presence of inorganic salts). On a particular compound , Table 5.34 and 5.35 shows that an increasing number of compounds (sorbates) in a system, the utilization of adsorption sites decreases. For example, the system of activated carbon in the presence of 0.01 M NaCl , the percentage of utilization of adsorption sites are 55.84 %, 52.48 % , 48.77% and 38.21 % on two-system (toluene/benzene), three-solute system (toluene / benzene / phenol), four-solute system (toluene/benzene/phenol/MIBK), and five-solute system (toluene/benzene/phenol/MIBK/IPA) respectively. This indicates the existence of considerable interaction among the solutes and this interaction increases as the number of components in the system increases. The interaction and competition among the sorbate molecules retard the sorbate molecules attaching onto the adsorption sites, making the sorbent can not make full utilization of its available adsorption sites and consequently decreases the adsorptive capacity of sorbents. Data (Table 5.12 to 5.33) also

Table 5.34 Multi-solute Competitive Adsorption

Sorbent : Activated Carbon

Compound	Single Solute System(mg/g)	Two-solute System(mg/g)	Three-solute System(mg/g)	Four-solute System(mg/g)	Five-solute System(mg/g)
Toluene	96.73	51.57	47.42	42.48	37.60
Benzene	71.46	41.31	38.00	27.45	25.85
Phenol	28.60		16.08	14.03	12.00
MIBK	42.02			22.13	17.34
IPA	4.92				2.45
		92.88	103.50	106.09	95.24
Overall Sorbent Capacity	243.73	168.19	196.79	238.81	243.73
Utilization of Adsorp. Site		55.22%	52.59%	44.42%	39.08%

Sorbent : Activated Carbon Inorganic Salt : 0.01 M NaCl

Compound	Single-solute System(mg/g)	Two-solute System(mg/g)	Three-solute System(mg/g)	Four-solute System(mg/g)	Five-solute System(mg/g)
Toluene	112.46	66.11	63.23	57.73	44.27
Benzene	99.08	52.02	45.55	40.30	33.05
Phenol	37.92		22.17	19.71	16.35
MIBK	56.43			31.44	22.34
IPA	5.87				3.12
		118.23	130.95	149.18	119.13
Overall Sorbent Capacity	311.76	211.54	249.46	305.89	311.76
Utilization of Adsorp.Site		55.84%	52.48%	48.77%	38.21%

Adsorptive capacity of activated carbon on each target compound has been calculated (using C= 10 mg/l) from Table 5.4 and 5.6

Table 5.35 Multi-solute Competitive Adsorption

Sorbent : Hudson Flyash

Compound	Single Solute System (ug/g)	Two-solute System(ug/g)	Three-solute System(ug/g)	Four-solute System(ug/g)	Five-solute System(ug/g)
Toluene	777.38	639.21	520.73	449.21	422.38
Benzene	680.18	514.10	463.63	398.11	376.40
Phenol	265.28		154.82	151.95	109.98
MIBK	330.21			185.39	156.87
IPA	77.29				37.74
		1153.31	1138.18	1184.66	1103.37
Overall Sorbent Capacity	2130.34	1457.56	1722.84	2053.05	2130.34
Utilization of Adsorp.Site		79.12%	66.12%	57.70%	51.79%

Sorbent : Hudson Flyash Inorganic Salt : 0.01 M $AlCl_3$

Compound	Single Solute System(ug/g)	Two-solute System(ug/g)	Three-solute System(ug/g)	Four-solute System(ug/g)	Five-solute System(ug/g)
Toluene	1325.49	938.73	815.05	745.78	697.54
Benzene	1594.24	749.30	649.51	577.28	557.04
Phenol	746.14		419.00	344.44	290.66
MIBK	687.39			332.82	285.80
IPA	184.00				62.20
		1688.03	1883.56	2000.32	1893.24
Overall Sorbent Capacity	4537.26	2919.73	3665.87	4353.26	4537.26
Utilization of Adsorp.Site		57.81%	51.38%	45.95%	41.73%

Adsorptive capacity of Hudson Flyash on each target compound has been calculated (using C = 30 mg/l) from Table 5.5 and 5.7

reveals that the experimental values can't well match the values calculated from Ideal Adsorbed Solution Theory (IAST) at higher equilibrium concentrations as well as in lower adsorbability of compounds. This also due to the higher competition and interaction among the solute molecules at a higher concentration in the sorption solution.

From above multi-component study, the sorption behavior of multi-solute system, in the presence of small amount of inorganic salts, follows the same pattern as the idential multi-solute system without salts does.

5.4.11. Effect of Concentration of Inorganic Salts on Multi-component Adsorption

The objective of this study is to examine the concentration of inorganic salts effect on the competitive adsorption systems. The concentration of inorganic salts studied in this investigation is at the range of 0 to 0.01 M. A specific and equal amonut of mixture target compound was conducted to the sorption system at a various concentrations of inorganic salts. The effluent concentration of each target compound was examined and the adsorptive capacity was calculated. Table 5.36 and 5.37 show the results of effect of inorganic salts on adsorption of two-component (benzene/toluene) adsorption system onto activated carbon and Hudson flyash respectively. Results reveal that the increases of concentration of inorganic salts the increases of adsorptive capacity of each traget

Table 5.36 Effect of Concentration of Inorganic Salt on Multi-component Adsorption

ADSORBENT : ACTIVATED CARBON				
INFLUENT CONCENTRATION = 30 mg/l				
concentration of inorganic salt	COMPONUDS			
	Benzene		Toluene	
	Effluent concentration (mg/l)	Adsorptive capacity (mg / g)	Effluent concentration (mg/l)	Adsorptive capacity (mg /g)
NaCl, 0mM	9.96	35.07	7.71	39.01
NaCl, 2mM	9.54	35.81	7.26	39.80
NaCl, 4mM	8.85	37.01	7.05	40.16
NaCl, 6mM	8.28	38.01	6.78	40.64
NaCl, 8mM	7.86	38.75	6.45	41.21
NaCl, 10mM	7.56	39.27	6.21	41.63

Table 5.37 Effect of Concentration of Inorganic Salt on Multi-component Adsorption

ADSORBENT : HUDSON FLYASH				
INFLUENT CONCENTRATION = 30 mg/l				
concentration of inorganic salt	COMPOUNDS			
	Benzene		Toluene	
	Effluent concentration (mg/l)	Adsorptive capacity (ug / g)	Effluent concentration (mg/l)	Adsorptive capacity (ug / g)
$AlCl_3$, 0mM	18.75	393.75	17.25	446.25
$AlCl_3$, 2mM	18.12	415.80	16.71	465.15
$AlCl_3$, 4mM	17.61	433.65	16.14	485.10
$AlCl_3$, 6mM	17.16	449.40	15.42	510.30
$AlCl_3$, 8mM	16.62	468.30	14.79	532.35
$AlCl_3$, 10mM	16.11	486.15	14.40	546.00

compound onto sorbents. This follows the same pattern in single compound study ; i.e., the higher the concentration of inorganic salts presenting in solution, the higher the adsorptive capacity is performed onto sorbents. Table 5.38 and 5.39 show the results of effect of concentration of inorganic salts on adsorption of four-component (benzene/toluene/MIBK/phenol) adsorption system onto activated carbon and Hudson flyash respectively. The adsorptive capacity of each target compound increases with the increases of concentration of inorganic salts. This also follows the same trend of two-component sorption systems. Figure E21 to E24 plots the concentration of inorganic salt versus the adsorptive capacity of individual compound, in the multi-component sorption system. For a specific concentration of inorganic salt and a specific sorbent, the adsorptive capacity of individual target compound is increasing with the decreasing of the number of compounds in competitive adsorption systems. For example, with 30 ppm influent concentration of toluene, in the presence of 4 mM NaCl of solution, the adsorptive capacity of toluene onto activated carbon are 40.16 mg/g and 38.75 mg/g during two-component and four-component adsorption respectively (see Table 5.36 and 5.37).

Table 5.38 Effect of Concentration of Inorganic Salt on Multi-component Adsorption

ADSORBENT : ACTIVATED CARBON								
INFLUENT CONCENTRATION = 30 mg/l								
concentration of inorganic salt	COMPOUNDS							
	Benzene		MIBK		Toluene		Phenol	
	Effluent Concn. (mg/l)	Adsorptive Capacity (mg/g)	Effluent Concn. (mg/l)	Adsorptive Capacity (mg/g)	Effluent Conc. (mg/l)	Adsorptive Capacity (mg/g)	Effluent Concn. (mg/l)	Adsorptive Capacity (mg/g)
NaCl,0mM	11.70	32.03	13.35	28.88	8.70	37.28	16.80	23.10
NaCl,2mM	11.10	33.08	12.84	30.02	8.25	38.06	16.20	24.39
NaCl,4mM	10.50	34.13	12.51	30.61	7.86	38.75	15.51	25.36
NaCl,6mM	10.05	34.91	11.82	31.82	7.53	39.32	14.94	26.36
NaCl,8mM	9.84	35.28	11.25	32.81	7.41	39.53	14.55	27.04
NaCl,10mM	9.15	36.49	10.80	33.60	7.05	40.16	14.25	27.56

Table 5.39 Effect of Concentration of Inorganic Salt on Multi-component Adsorption

ADSORBENT : HUDSON FLYASH								
INFLUENT CONCENTRATION = 30 mg/l								
concentration of inorganic salt	COMPOUNDS							
	Benzene		MIBK		Toluene		Phenol	
	Effluent Conc. (mg/l)	Adsorptive Capacity (ug/g)	Effluent Concn. (mg/l)	Adsorptive Capacity (ug/g)	Effluent Concn. (mg/l)	Adsorptive Capacity (ug/g)	Effluent Concn. (mg/l)	Adsorptive Capacity (ug/g)
AlCl3, 0mM	20.40	336.00	23.70	220.50	19.65	362.25	24.60	189.00
$AlCl_3$, 2mM	19.95	351.75	22.98	245.70	19.08	382.20	23.91	213.15
$AlCl_3$, 4mM	19.44	369.60	22.56	260.40	18.36	407.40	23.46	228.90
$AlCl_3$, 6mM	18.75	393.75	22.23	271.95	17.94	422.10	22.98	245.70
$AlCl_3$, 8mM	18.33	408.45	21.90	283.50	16.95	456.75	22.44	264.60
$AlCl_3$,10mM	17.85	425.25	21.54	296.10	16.26	480.90	21.63	292.95

5.5 Kinetics of Adsorption

The effect of inorganic salts on the kinetics of adsorption is worthwlile to explore, because the removal rate of organic compound from dilute aqueous solution by solid adsorbents is a efficiency determining factor in water sorption treatment plant. In single solute isotherm study, the slight change of concentration of inorganic salts during adsorption process, implies inorganic salts has a kind of "catalystic effect" on adsorbents. Previous investigation(8) has examined the kinetic effect of organic compounds onto flyash. A comparative kinetic study of virgin adsorbents with and without addition of inorganic salts is performed in this study . Results and discussion of this study is presented herein.

5.5.1.Effect of Contact time on Adsorption

The optimum contact time between the aqueous solution of the organic compounds and the sorbents is strongly dependent on the chemical characteristics and influent concentation of sorbates. Generally speaking, the higher the influent concentration of the target compound, the lower the optimum contact time. Because the concentration gradient between the liquid phase and solid phase in aqueous solution is the driving force in determining the contact time to reach equliibrium state of the system. A higher influent concentration of target compound means a higher concentration gradient between two phases, relatively, a shorter time for a higher influent concentration to reach the equilibrium state. Water solubility of sorbate is the major factor effecting the optimum contact time. Previous investigation (8) has shown that a higher soluble compound needs a higher contact time to reach the equilibrium state. The addition of inorganic salts in the system makes the optimum tim shorter than without the addition of inorganic salts in the same system. In this study, with or without the presence of inorganic salts in solution, continuous contact time has been lasting for 12 hours to ensure the system at equilibrium state.

5.5.2. Calculation of Rate Constant

Rate constant is the expression of removal rate, it shows how fast the organic pollutants in aqueous solution can be removed by adsorbents. It is a important factor of determining the efficiency of the process. However, removal efficiency directly effects the operation and cost of the process. Previous investigation(8) has proved the adsorption rate follows the first order reversible kinetics. The aim of this study is to find out the applicability of first order reversible kinetics to the same sorption system, expect for the presence of small amount of inorganic salts in the process. If the first order reversible kinetics can apply to the adsorption system in the presence of inorganic salts, (as a matter of fact, it can be proved later), then consider the equilibrium situation of liquid phase (A) and solid phase (B), the following equation can be established :

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B$$

The following equations can also be derived by the study of kinetics.(8)

$$k_c = \frac{k}{k'} \tag{5-1}$$

$$k_c = \frac{X_{Ae} + C_{Bo}/C_{AO}}{1 - X_{Ae}} \tag{5-2}$$

$$\ln \left(1 - \frac{X_A}{X_{Ae}} \right) = -k_{overall} \times t \tag{5-3}$$

$$\ln \left(\frac{C_A - C_{Ae}}{C_{Ao} - C_{Ae}} \right) = -k_{overall} \times t \tag{5-4}$$

Where :

C_{AO} = initial concentration of the target organic compound in the soliution at time t= 0

C_{Bo} = initial concentration of the target organic compound on the sorbent, at time t= 0

C_A = concentration of the target organic compound in the solution at any time t

C_{Ae} = concentration of the target organic compound in the solution at equilibrium state

X_A = fractional conversion

X_{Ae} = fractional conversion in the solution at equilibrium state

k = first order adsorption rate constant (time $^{-1}$)

k' = first order desorption rate constant (time $^{-1}$)

k_c = equilibrium constant

$k_{overall}$ = overall reaction rate constant

Hence from eq.(5-3) , a plot of $\ln(1 - X_A / X_{Ae})$ versus t yields a slop equal to $k_{overall}$.

5.5.3. Kinetic Study of Single Compound Adsorption

In this study, phenol and MIBK were selected as target sorbates. The adsorption kinetic study onto target virgin activated carbon, virgin flyash, activated carbon with the addition of 0.01 M NaCl in solution, and flyash with 0.01 M $AlCl_3$ in solution were investigated. It is observed that the overall rate constant increases with the increasing influent concentration until it reaches the steady state. Therefore, to find the minimum influent concentration, that concentration (driving force) does not have any effect on the rate constant beyond this value, in the above mentioned four cases.

Data (Table 5.40 to 5.47) has shown that the minimum influent concentration of adsorption of phenol onto Hudson flyash and activated carbon is 200 mg/l and 1000 mg/l respectively. Whereas, the minimum influent concentration of adsorption of MIBK onto Hudson flyash and activated carbon is 200 mg/l and 400 mg/l respectively. In the case of inorganic salts presenting in the solution, the minimum influent concentration of adsorption of phenol onto Hudson flyash and activated carbon is 250 mg/l and 1000 mg/l respectively. Whereas, the minimum influent concentration of adsorption of MIBK onto Hudson flyash and activated carbon is 250 mg/l and 400 mg/l respectively.

Table 5.40 Adsorption Kinetics of Phenol onto Activated Carbon

Influent Concentration = 50 ppm				Influent Concentration = 500 ppm			
Time (min.)	Remaining conc.(ppm)	XA	ln(1-XA/XAe)	Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)
5	48.98	0.02028	-0.03252	5	437.40	0.1252	-0.5188
10	47.77	0.04459	-0.07580	10	425.85	0.1483	-0.6528
20	47.59	0.04807	-0.08121	20	418.80	0.1624	-0.7444
30	47.07	0.05851	-0.10070	30	411.35	0.1773	-0.8507
60	44.75	0.10490	-0.18840	60	405.70	0.1886	-0.9405
90	44.33	0.11340	-0.20540	90	396.55	0.2069	-1.1056
120	41.85	0.16310	-0.31060	120	386.10	0.2278	-1.3337
R=0.9833, $K_{overall}$= 0.1089 , XAe = 0.6108				R=0.9795, $K_{overall}$= 0.3105, XAe = 0.3094			
Influent Concentration = 150 ppm				Influent Concentration = 1000 ppm			
Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)	Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)
5	139.89	0.06741	-0.1301	5	902.62	0.09378	-0.7444
10	136.49	0.09005	-0.1779	10	890.60	0.1094	-0.8916
20	134.67	0.10220	-0.2046	20	880.40	0.1196	-1.0356
30	132.10	0.11930	-0.2433	30	872.00	0.1280	-1.1712
60	124.73	0.16850	-0.3638	60	864.60	0.1354	-1.3093
90	120.58	0.19610	-0.4385	90	853.60	0.1464	-1.5559
120	115.44	0.2304	-0.5396	120	841.20	0.1588	-1.9379
R=0.9956, $K_{overall}$= 0.1717 , XAe = 0.5525				R=0.9849, $K_{overall}$ = 0.4605, XAe = 0.1855			
Influent Concentration = 250 ppm				Influent Concentration = 1800 ppm			
Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)	Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)
5	225.55	0.0978	-0.2469	5	1701.63	0.05465	-0.7508
10	217.33	0.1307	-0.3459	10	1689.53	0.06137	-0.8989
20	212.03	0.1519	-0.4155	20	1679.28	0.06707	-1.0441
30	207.23	0.1711	-0.4827	30	1671.08	0.07162	-1.1776
60	202.55	0.1898	-0.5527	60	1663.63	0.07576	-1.3168
90	195.35	0.2186	-0.6713	90	1652.83	0.08176	-1.5606
120	188.55	0.2458	-0.7895	120	1640.16	0.08880	-1.9519
R=0.9772, $K_{overall}$ = 0.2121 , XAe = 0.4470				R=0.9845, $K_{overall}$ = 0.4623, XAe = 0.1035			

Table 5.41 Adsorption Kinetics of MIBK onto Activated Carbon

Time (min.)	Remaining Conc.(mg/l)	XA	ln(1-XA/XAe)
Influent Concentration = 50 ppm			
5	43.22	0.1356	-0.2184
10	42.21	0.1558	-0.2554
20	41.81	0.1638	-0.2705
30	40.40	0.1920	-0.3254
60	39.98	0.2204	-0.3839
90	38.08	0.2385	-0.4231
120	35.46	0.2908	-0.5461
R = 0.9855, $K_{overall}$ = 0.1284 per min. , XAe = 0.6912			
Influent Concentration =100ppm			
5	76.98	0.2302	-0.4407
10	74.80	0.2520	-0.4943
20	73.96	0.2604	-0.5158
30	71.71	0.2829	-0.5759
60	69.34	0.3066	-0.6434
90	67.37	0.3263	-0.7032
120	61.87	0.3813	-0.8916
R = 0.9810, $K_{overall}$= 0.1719 per min., XAe = 0.6462			
Influent Concentration = 200ppm			
5	147.30	0.2635	-0.8119
10	144.54	0.2773	-0.8795
20	143.12	0.2844	-0.9163
30	139.44	0.3033	-1.0216
60	135.54	0.3223	-1.1394
90	133.36	0.3332	-1.2140
120	126.06	0.3697	-1.5141
R = 0.9811, Koverall = 0.2714 per min., XAe = 0.4740			
Influent Concentration = 400ppm			
5	296.62	0.2577	-1.2208
10	292.52	0.2687	-1.3280
20	290.64	0.2734	-1.3783
30	284.76	0.2881	-1.5517
60	278.64	0.3034	-1.7719
90	275.64	0.3109	-1.9105
120	264.00	0.3400	-2.6593
R = 0.9656, Koverall = 0.5445 per min., XAe = 0.3656			
Influent Concentration =800ppm			
5	691.60	0.1355	-1.2040
10	686.96	0.1413	-1.3093
20	683.84	0.1452	-1.3863
30	677.68	0.1529	-1.5606
60	671.12	0.1611	-1.7838
90	667.76	0.1653	-1.8579
120	655.68	0.1804	-2.6882
R = 0.9541, Koverall = 0.5490 per min., XAe = 0.1936			

Data reveals that the determining factors of minimum influent concentration in sorption kinetic study are dependent on the characteristics of sorbent and sorbate. Results show that a higher water solubility sorbate (phenol) needs a higher influent concentration to reach steady state. The higher adsorptive capacity of sorbent (activated carbon), the lower influent concentration is required to approach the steady state. The plots of $\ln(1-X_A / X_{Ae})$ versus time of target compounds onto adsorbents with and without the presence of inorganic salts, at various influent concentrations , were shown in Figure F13 to F20. Figures demonstrate that the overall rate constant remains the same when influent concentration is beyond a specific value; i.e., minimum influent concentration. The regression coefficients ($R > 0.95$) also indicates the adsorption of the target compounds onto the sorbents in this study, under the condition with or without addition of inorganic salts, follows first order reversible kinetics.

Plots of remaining concentration in solution versus time at various influent concentrations of target compounds onto adsorbents, with and without the addition of inorganic salts were shown in Figure F1 to F8. These figures show that at a higher influent concentration (higher than the minimum influent concentration) of target compound drops abruptly in the very beginning adsorption time. Data (Table 5.40 to 5.47) also reveals that the higher the influent concentration , the lower the X_{Ae} value is obtained. This

Table 5.42 Adsorption Kinetics of phenol onto Hudson Flyash

Time (min.)	Remaining Conc.(mg/l)	XA	ln(1-XA/XAe)
Influent Concentration = 50ppm			
5	49.79	0.00413	-0.02173
10	49.58	0.00825	-0.04385
20	49.18	0.01642	-0.08927
30	48.65	0.02688	-0.15060
60	48.14	0.03725	-0.21530
90	47.50	0.04998	-0.30110
120	46.35	0.07307	-0.47800
R = 0.9886, $K_{overall}$ = 0.003656, XAe = 0.1923			
Influent Concentration = 100ppm			
5	99.36	0.00634	-0.03662
10	98.74	0.01265	-0.07424
20	97.48	0.02517	-0.15360
30	95.88	0.04121	-0.26530
60	94.29	0.05707	-0.38980
90	92.34	0.07662	-0.56550
120	88.80	0.11196	-0.92460
R = 0.9876, $K_{overall}$ = 0.007124, XAe = 0.1768			
Influent Concentration = 200ppm			
5	185.32	0.07342	-0.7895
10	184.18	0.07909	-0.8977
20	183.25	0.08375	-0.9872
30	182.23	0.08884	-1.0951
60	180.15	0.09925	-1.3606
90	177.66	0.11170	-1.8109
120	175.46	0.12270	-2.5133
R = 0.9835, $K_{overall}$ = 0.01382 , XAe = 0.1335			
Influent Concentration = 500ppm			
5	474.81	0.05039	-0.8164
10	472.77	0.05445	-0.9238
20	471.55	0.05689	-0.9997
30	469.75	0.06050	-1.1087
60	466.59	0.06682	-1.3471
90	462.08	0.07585	-1.8326
120	458.28	0.08343	-2.5779
R = 0.9784, $K_{overall}$ = 0.01408 , XAe = 0.0903			

Table 5.43 Adsorption Kinetics of MIBK onto Hudson Flyash

Time (min.)	Remaining Conc.(mg/l)	XA	ln(1-XA/XAe)
Influent Concentration =50ppm			
5	49.73	0.005415	-0.02398
10	49.46	0.010780	-0.04835
20	48.93	0.021480	-0.09871
30	48.24	0.035140	-0.16699
60	47.56	0.048690	-0.23960
90	46.73	0.065350	-0.33680
120	45.23	0.095500	-0.54130
R = 0.9880, $K_{overall}$ = 0.004138 per min., XAe = 0.2285			
Influent Concentration =150ppm			
5	148.77	0.008149	-0.03853
10	147.57	0.016190	-0.07807
20	145.16	0.032230	-0.16193
30	142.08	0.052780	-0.28080
60	139.04	0.073060	-0.41380
90	135.28	0.098120	-0.60710
120	128.49	0.143400	-1.09360
R = 0.9782, $K_{overall}$ = 0.008298 per min., XAe = 0.2156			
Influent Concentration =200ppm			
5	180.20	0.09901	-0.8533
10	178.74	0.10630	-0.9571
20	177.50	0.11250	-1.0555
30	176.12	0.11940	-1.1776
60	173.34	0.13330	-1.4828
90	170.02	0.14990	-2.0325
120	167.74	0.16130	-2.7333
R = 0.9877, $K_{overall}$ = 0.01545 per min., XAe = 0.1725			
Influent Concentration =500ppm			
5	467.17	0.06566	-0.8440
10	464.64	0.07073	-0.9519
20	462.28	0.07545	-1.0642
30	459.97	0.08006	-1.1874
60	455.36	0.08928	-1.4916
90	449.90	0.10020	-2.0402
120	445.95	0.10810	-2.7806
R = 0.9869, $K_{overall}$ = 0.01508 per min., XAe = 0.1152			

Table 5.44 Adsorption Kinetics of Phenol onto Activated Carbon,0.01MNaCl

Influent Concentration = 50 ppm				Influent Concentration = 500 ppm			
Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)	Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)
5	48.73	0.02531	-0.03791	5	425.65	0.1487	-0.5798
10	47.22	0.05566	-0.08447	10	411.95	0.1761	-0.7361
20	46.99	0.06009	-0.08664	20	403.80	0.1924	-0.8419
30	46.35	0.07295	-0.11340	30	394.90	0.2102	-0.9728
60	43.45	0.13090	-0.21350	60	388.30	0.2234	-1.0812
90	42.92	0.14150	-0.23320	90	377.45	0.2451	-1.2914
120	37.73	0.20350	-0.35520	120	366.50	0.2670	-1.6029
R=0.9838, $K_{overall}$ =0.1252 min^{-1}, XAe=0.6805				R=0.9819, $K_{overall}$ =0.3901 min^{-1}, XAe=0.338			
Influent Concentration = 100 ppm				Influent Concentration = 1000 ppm			
Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)	Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)
5	94.69	0.05307	-0.08556	5	893.00	0.1070	-0.7339
10	90.68	0.09319	-0.15540	10	876.30	0.1237	-0.9188
20	90.10	0.09902	-0.16610	20	866.40	0.1336	-1.0469
30	88.35	0.11650	-0.19850	30	855.50	0.1445	-1.2106
60	80.75	0.19250	-0.35310	60	847.50	0.1525	-1.3509
90	79.26	0.20740	-0.38640	90	834.30	0.1657	-1.6348
120	70.46	0.29540	-0.60950	120	819.10	0.1809	-2.1119
R=0.9811,$K_{overall}$ =0.2037 min^{-1}, XAe = 0.6472				R=0.9830, $K_{overall}$ = 0.5245 min^{-1}, XAe=0.2058			
Influent Concentration = 200 ppm				Influent Concentartion = 2000 ppm			
Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)	Time (min.)	Remaining Conc.(ppm)	XA	ln(1-XA/XAe)
5	174.12	0.1294	-0.3120	5	1876.28	0.06186	-0.7381
10	167.16	0.1642	-0.4155	10	1857.10	0.07145	-0.9238
20	162.42	0.1879	-0.4927	20	1845.94	0.07703	-1.0498
30	158.18	0.2091	-0.5674	30	1833.40	0.08330	-1.2140
60	154.22	0.2289	-0.6425	60	1824.14	0.08793	-1.3548
90	148.04	0.2598	-0.7722	90	1808.98	0.09551	-1.6399
120	141.82	0.2909	-0.9221	120	1791.40	0.10430	-2.1202
R=0.9788,$K_{overall}$ =0.2345 min^{-1}, XAe=0.483				R= 0.9831, $K_{overall}$=0.5625 min^{-1}, XAe=0.1185			

Table 5.45 Adsorption Kinetics of MIBK onto Activated Carbon,0.01MNaCl

Time (min.)	Remaining Conc.(mg/l)	XA	ln(1-XA/XAe)
Influent Concentration = 50ppm			
5	41.93	0.1615	-0.2421
10	40.80	0.1840	-0.2810
20	40.35	0.1930	-0.2971
30	38.75	0.2253	-0.3567
60	37.24	0.2553	-0.4155
90	36.48	0.2704	-0.4463
120	33.48	0.3304	-0.5798
R= 0.9806, $K_{overall}$ = 0.1306 per min., XAe = 0.751			
Influent Concentration =100ppm			
5	75.42	0.2458	-0.4155
10	72.89	0.2711	-0.4700
20	72.16	0.2784	-0.4861
30	69.63	0.3037	-0.5447
60	67.10	0.3290	-0.6069
90	64.30	0.3570	-0.6714
120	58.50	0.4150	-0.8533
R= 0.9811, $K_{overall}$ = 0.1668 per min., XAe = 0.723			
Influent Concentration = 200ppm			
5	138.70	0.3065	-0.8795
10	135.24	0.3238	-0.9623
20	133.76	0.3312	-0.9997
30	129.78	0.3511	-1.1087
60	125.60	0.3720	-1.2379
90	123.18	0.3841	-1.3205
120	115.12	0.4244	-1.6607
R= 0.9795, $K_{overall}$ = 0.2989 per min., XAe = 0.524			
Influent Concentration = 400ppm			
5	281.44	0.2964	-1.3243
10	276.44	0.3089	-1.4482
20	274.84	0.3129	-1.4916
30	268.36	0.3291	-1.6874
60	261.40	0.3465	-1.9519
90	257.88	0.3553	-2.1202
120	245.28	0.3868	-3.1701
R= 0.9523, $K_{overall}$ = 0.6895 per min., XAe = 0.4038			
Influent Concentration = 800ppm			
5	666.08	0.1674	-1.3432
10	662.32	0.1721	-1.4271
20	659.20	0.1760	-1.5006
30	651.76	0.1853	-1.7037
60	645.60	0.1930	-1.9105
90	641.60	0.1980	-2.0715
120	626.48	0.2169	-3.1701
R= 0.9414, $K_{overall}$ = 0.6760 per min., XAe = 0.2265			

shows the limitation of adsorptive capacity of a specific dose of sorbents.

Figure F9 and F10 show the effect of inorganic salt (0.01 M NaCl) on the adsorption kinetics of phenol and MIBK onto activated carbon respectively. Adsorption is indicated by the decreasing concentration target compound remaining in the solution. Apparently, the addition of inorganic salts in the sorption system significantly increases the uptake rate of solute. Figure F11 and F12 show the effect of inorganic salt (0.01 M NaCl) on the overall rate constant for the adsorption of phenol and MIBK onto activated carbon respectively. The improvement of uptake rate by the addition of inorganic salts in the system is a result of the increase of overall rate constant.For example, the overall rate constant for the adsorption of phenol onto activated carbon are 0.46 $min.^{-1}$, and 0.54 $min.^{-1}$ without and with the presence of inorganic salt (0.01 M NaCl) respectively. The same pattern is also can be observed in the case of Hudson flyash and $AlCl_3$ (see Table 5.42,5.43, 5.46, and 5.47).

The calculation of adsorption and desorption rate constants were made by using equations (5-1) and (5-2). Table 5.48 and 5.49 show the sorption rate constants of target compounds (phenol and MIBK) onto activated and Hudson flyash respectively. At equilibrium state, when the sorbate concentration remaining in solution is greater than in sorbent; i.e., X_{Ae} is less than 0.5, the desorption rate

Table 5.46 Adsorption Kinetics of Phenol onto Hudson Flyash,0.01M AlCl$_3$

<table>
<tr><th>Time
(min.)</th><th>Remaining
Conc.(mg/l)</th><th>XA</th><th>ln(1-XA/XAe)</th></tr>
<tr><td colspan="4">Influent Concentration = 50ppm</td></tr>
<tr><td>5</td><td>49.56</td><td>0.00872</td><td>-0.02613</td></tr>
<tr><td>10</td><td>49.13</td><td>0.01741</td><td>-0.05287</td></tr>
<tr><td>20</td><td>48.27</td><td>0.03464</td><td>-0.10810</td></tr>
<tr><td>30</td><td>47.16</td><td>0.05671</td><td>-0.18370</td></tr>
<tr><td>60</td><td>46.07</td><td>0.07855</td><td>-0.26450</td></tr>
<tr><td>90</td><td>44.75</td><td>0.10540</td><td>-0.37390</td></tr>
<tr><td>120</td><td>42.29</td><td>0.15410</td><td>-0.60880</td></tr>
<tr><td colspan="4">R= 0.9872 , K$_{overall}$ = 0.004653 per min., XAe = 0.338</td></tr>
<tr><td colspan="4">Influent Concentration = 100ppm</td></tr>
<tr><td>5</td><td>98.78</td><td>0.01223</td><td>-0.0404</td></tr>
<tr><td>10</td><td>97.57</td><td>0.02432</td><td>-0.0819</td></tr>
<tr><td>20</td><td>95.16</td><td>0.04839</td><td>-0.1703</td></tr>
<tr><td>30</td><td>92.08</td><td>0.07923</td><td>-0.2962</td></tr>
<tr><td>60</td><td>89.03</td><td>0.10970</td><td>-0.4387</td></tr>
<tr><td>90</td><td>85.27</td><td>0.14730</td><td>-0.6478</td></tr>
<tr><td>120</td><td>78.48</td><td>0.2152</td><td>-1.1927</td></tr>
<tr><td colspan="4">R= 0.9758 , K$_{overall}$ = 0.009032 per min., XAe = 0.309</td></tr>
<tr><td colspan="4">Influent Concentration = 200ppm</td></tr>
<tr><td>5</td><td>175.98</td><td>0.1201</td><td>-0.6733</td></tr>
<tr><td>10</td><td>173.92</td><td>0.1304</td><td>-0.7603</td></tr>
<tr><td>20</td><td>172.20</td><td>0.1390</td><td>-0.8379</td></tr>
<tr><td>30</td><td>170.32</td><td>0.1484</td><td>-0.9301</td></tr>
<tr><td>60</td><td>166.52</td><td>0.1674</td><td>-1.1504</td></tr>
<tr><td>90</td><td>161.96</td><td>0.1902</td><td>-1.4983</td></tr>
<tr><td>120</td><td>157.92</td><td>0.2104</td><td>-1.9589</td></tr>
<tr><td colspan="4">R= 0.9916 , K$_{overall}$ = 0.010515 per min., XAe = 0.245</td></tr>
<tr><td colspan="4">Influent Concentration = 250ppm</td></tr>
<tr><td>5</td><td>220.20</td><td>0.1192</td><td>-0.8509</td></tr>
<tr><td>10</td><td>217.93</td><td>0.1283</td><td>-0.9597</td></tr>
<tr><td>20</td><td>216.43</td><td>0.1343</td><td>-1.0384</td></tr>
<tr><td>30</td><td>214.38</td><td>0.1425</td><td>-1.1552</td></tr>
<tr><td>60</td><td>210.65</td><td>0.1574</td><td>-1.4147</td></tr>
<tr><td>90</td><td>205.33</td><td>0.1787</td><td>-1.9587</td></tr>
<tr><td>120</td><td>201.05</td><td>0.1958</td><td>-2.9004</td></tr>
<tr><td colspan="4">R= 0.9705 , K$_{overall}$ = 0.01624 per min., XAe = 0.208</td></tr>
<tr><td colspan="4">Influent Concentration = 500ppm</td></tr>
<tr><td>5</td><td>458.18</td><td>0.08364</td><td>-0.8416</td></tr>
<tr><td>10</td><td>454.58</td><td>0.09085</td><td>-0.9623</td></tr>
<tr><td>20</td><td>452.82</td><td>0.09437</td><td>-1.0272</td></tr>
<tr><td>30</td><td>450.09</td><td>0.09981</td><td>-1.1363</td></tr>
<tr><td>60</td><td>444.60</td><td>0.11080</td><td>-1.4204</td></tr>
<tr><td>90</td><td>437.15</td><td>0.12570</td><td>-1.9310</td></tr>
<tr><td>120</td><td>430.35</td><td>0.13930</td><td>-2.9565</td></tr>
<tr><td colspan="4">R= 0.9628 , K$_{overall}$ = 0.01622 per min., XAe = 0.147</td></tr>
</table>

Table 5.47 Adsorption Kinetics of MIBK onto Hudson Flyash, 0.01M AlCl3

Time (min.)	Remaining Conc. (mg/l)	XA	ln(XA/XAe)
Influent Concentration = 50ppm			
5	49.43	0.01143	-0.03015
10	48.87	0.02270	-0.06081
20	47.73	0.04543	-0.12560
30	46.28	0.07431	-0.21440
60	44.86	0.10280	-0.31060
90	43.09	0.13820	-0.44470
120	39.91	0.20170	-0.74230
R = 0.9854, $K_{overall}$ = 0.005668 per min., XAe = 0.385			
Influent Concentration = 100ppm			
5	98.43	0.01566	-0.04499
10	96.90	0.03097	-0.09102
20	93.81	0.06194	-0.19120
30	89.89	0.10110	-0.33410
60	85.98	0.14020	-0.50080
90	81.17	0.18830	-0.75290
120	73.55	0.2645	-1.35940
R = 0.9871 , $K_{overall}$ = 0.01037 per min., XAe = 0.356			
Influent Concentration = 250ppm			
5	215.05	0.1398	-0.8675
10	212.40	0.1504	-0.9782
20	210.68	0.1573	-1.0584
30	208.43	0.1663	-1.1712
60	204.20	0.1832	-1.4271
90	197.90	0.2084	-2.0024
120	192.58	0.2297	-3.0576
R = 0.9640 , $K_{overall}$ = 0.01702 per min., XAe = 0.241			
Influent Concentration = 500ppm			
5	452.03	0.0959	-0.8795
10	448.40	0.1032	-0.9915
20	446.05	0.1079	-1.0729
30	443.00	0.1140	-1.1874
60	437.25	0.1255	-1.4482
90	428.65	0.1427	-2.0402
120	421.70	0.1566	-3.1011
R = 0.9648 , $K_{overall}$ = 0.01748 per min., Xae = 0.164			

Table 5.48 Rate Constants of Phenol and MIBK onto Activated Carbon

Compounds (Salts)	$K_{overall}$ (per min.)	K (per min.)	K' (per min.)
phenol (without salt)	0.4605	0.085	0.375
phenol (0.01 M NaCl)	0.5245	0.108	0.417
MIBK (without salt)	0.5445	0.199	0.345
MIBK (0.01 M NaCl)	0.6895	0.278	0.411

* Calculation based on influent concentration of phenol = 1000 mg/l and MIBK = 400 mg/l

* $K_{overall}$ = overall rate constant

* K = adsorption rate constant

* K' = desorption rate constant

Table 5.49 Rate Constants of Phenol and MIBK onto Hudson Flyash

Compounds (salts)	$K_{overall}$ (per min.)	K (per min.)	K' (per min.)
phenol (without salt)	0.01382	1.85×10^{-3}	1.19×10^{-2}
phenol (0.01 M $AlCl_3$)	0.01624	3.38×10^{-3}	1.28×10^{-2}
MIBK (without salt)	0.01545	2.67×10^{-3}	1.52×10^{-2}
MIBK (0.01 M $AlCl_3$)	0.01702	4.10×10^{-3}	1.29×10^{-2}

* calculation based on influent concentration of phenol = 250 mg/l and MIBK = 250 mg/l.

* $K_{overall}$ = overall rate constant

* K = adsorption rate constant

* K' = desorption rate constant

constant is higher than adsorption rate constant. Data indicates the addition of inorganic salts increases the overall rate constant, adsorption rate constant and desorption rate constant. For example, the kinetic adsorption of phenol onto activated carbon , the overall rate constant ,adsorption rate constant and desorption rate constant are 0.4605 min.^{-1},0.085 min.^{-1}, and 0.375 min.^{-1} respectively. Whereas in the presence of 0.01 MNaCl in the same sorption system, the overall rate constant, adsorption rate constant and desorption rate constant are 0.5245 min.^{-1} 0.01079 min.^{-1} and 0.4167 min.^{-1} respectively.(calculation based on influent concentration = 1000 ppm). The results reveal that the addition of inorganic salts significantly change the kinetic equilibrium state of the system.

5.5.4. Effect of Concentration of Inorganic Salts on Adsorption Kinetics

As the previous section mentioned, the rate constant remains constant after a specific influent concentration. In the presence of inorganic salt, the minimum influent concentration of phenol and MIBK onto activated carbon and flyash was also found in this study. Based on this, the objective of this section is to establish a relationship between the rate constant of target compounds and concentration of inorganic salts present in solution. With a specific concentrations beyond minimum influent concentrations ; kinetic studies were performed at various

Table 5.50 Effect of Concentration of Inorganic Salt on Adsorption Kinetic of Phenol onto Activated Carbon

INFLUENT CONCENTRATION = 1000 ppm			
Time (min.)	Remaining Conc.(mg/l)	XA	ln(1-XA/XAe)
Concentration of inorganic salt = NaCl, 2 mM			
5	901.5	0.0985	-0.7278
10	885.5	0.1145	-0.9189
20	876.0	0.1240	-1.0524
30	865.0	0.1350	-1.2333
60	860.0	0.1400	-1.3276
90	849.0	0.1510	-1.5733
120	836.0	0.1640	-1.9725
R = 0.9760, $K_{overall}$ = 0.4672 per min., XAe = 0.1905			
Concentration of inorganic salt = NaCl, 4 mM			
5	900.4	0.0996	-0.7117
10	881.2	0.1188	-0.9348
20	872.0	0.1280	-1.0624
30	861.0	0.1390	-1.2401
60	856.0	0.1440	-1.3326
90	845.0	0.1550	-1.5723
120	831.0	0.1690	-1.9952
R = 0.9721, $K_{overall}$ = 0.4731 per min., XAe = 0.1956			
Concentration of inorganic salt = NaCl, 6mM			
5	897.5	0.1025	-0.7195
10	880.0	0.1200	-0.9178
20	868.8	0.1312	-1.0690
30	859.0	0.1410	-1.2232
60	852.0	0.1480	-1.3499
90	841.0	0.1590	-1.6886
120	826.5	0.1735	-2.0277
R = 0.9762, $K_{overall}$ = 0.4909 per min., XAe = 0.1998			
Concentration of inorganic salt = NaCl, 8mM			
5	895.2	0.1048	-0.7272
10	878.0	0.1220	-0.9202
20	867.8	0.1322	-1.0552
30	856.5	0.1435	-1.2296
60	850.0	0.1500	-1.3457
90	838.0	0.1620	-1.6035
120	822.5	0.1775	-2.0814
R = 0.9780, $K_{overall}$ = 0.5078 per min., XAe = 0.2028			

Table 5.51 Effect of Concentration of Inorganic Salt on Adsorption Kinetics of MIBK onto Activated Carbon

INFLUENT CONCENTRATION = 400 ppm			
Time (min.)	Remaining Conc.(mg/l)	XA	ln(1-XA/XAe)
Concentration of inorganic salt = NaCl, 2mM			
5	293.28	0.2668	-1.2482
10	288.88	0.2778	-1.3563
20	287.04	0.2824	-1.4052
30	281.08	0.2973	-1.5823
60	275.00	0.3125	-1.8025
90	267.20	0.3320	-2.1824
120	260.00	0.3500	-2.7384
R = 0.9899, $K_{overall}$ = 0.6054 per min., XAe = 0.3742			
Concentration of inorganic salt = NaCl, 4mM			
5	290.36	0.2741	-1.2655
10	285.64	0.2859	-1.3816
20	283.84	0.2904	-1.4296
30	277.88	0.3053	-1.6076
60	272.00	0.3200	-1.8210
90	263.40	0.3415	-2.1539
120	255.60	0.3610	-2.9099
R = 0.9763, $K_{overall}$ = 0.6428 per min., XAe = 0.3818			
Concentration of inorganic salt = NaCl, 6mM			
5	288.00	0.2800	-1.2822
10	283.20	0.2920	-1.4005
20	281.04	0.2974	-1.4588
30	274.68	0.3133	-1.6529
60	269.12	0.3272	-1.8603
90	262.00	0.3450	-2.2102
120	253.00	0.3675	-2.9639
R = 0.9783, $K_{overall}$ = 0.6588 per min., XAe = 0.3875			
Concentration of inorganic salt = NaCl, 8mM			
5	281.12	0.2895	-1.3051
10	279.40	0.3015	-1.4232
20	277.44	0.3064	-1.4758
30	271.08	0.3223	-1.6683
60	264.72	0.3382	-1.9069
90	258.40	0.3540	-2.2185
120	248.80	0.3780	-3.0295
R = 0.9756, $K_{overall}$ = 0.6721 per min., XAe = 0.3972			

concentrations of inorganic salts (2mM, 4mM,6mM and 8mM). The effluent concentration was recorded during specific time intervals, and conversion factors calculated. Table 5.48 and 5.49 show the effect of concentration of NaCl on adsorption kinetics of phenol and MIBK onto activated carbon respectively. Data indicates increases of concentration of NaCl, increases the rate constant. Table 5.50 and 5.51 shows the same pattern of $AlCl_3$ effect on adsorption kinetics of phenol and MIBK onto Hudson flyash. Data also indicates the adsorption kinetics follows the first order reversible reaction. (regression coefficients greater than 0.96).

5.6 Correlation of Adsorption Capacity with Concentration of Inorganic Salts

In single solute study, the parameters of Freundlich equation were obtained by the regression of effluent concentration versus adsorptive capacity (see Figure B1-B30). To establish a satisfactory relationship between the concentration of inorganic salt and adsorptive capacity as a useful design factor of a sorption process is felt necessary. The linear correlation coefficient, R, is the most important factor to be determined in these regression. R is a indicator of how close the two variables are linearly correlated.(The value of R ranges from -1 to +1 , the absolut value of R approach 1 , it is indicating the two variables approaching a " perfect" linear correlatiin. If the absolute value of R approach to 0, it indicates a

Table 5.52 Effect of Concentration of Inorganic salt on Adsorption Kinetics of Phenol onto Hudson Flyash

INFLUENT CONCENTRATION = 250 ppm			
Time (min.)	Remaining Conc.(mg/l)	XA	ln(1-XA/XAe)
Concentration of inorganic salt = $AlCl_3$, 2mM			
5	228.32	0.0867	-0.8582
10	227.52	0.0899	-0.9056
20	226.05	0.0958	-1.0121
30	224.85	0.1006	-1.1039
60	219.80	0.1208	-1.6228
90	218.47	0.1261	-1.8193
120	215.17	0.1393	-2.5980
R = 0.9852, $K_{overall}$ = 0.01406 per min., XAe = 0.1505			
Concentration of inorganic salt = $AlCl_3$, 4mM			
5	226.82	0.0927	-0.8298
10	225.07	0.0997	-0.9325
20	223.77	0.1049	-1.0163
30	222.38	0.1105	-1.1152
60	219.90	0.1204	-1.3181
90	215.12	0.1395	-1.8874
120	211.52	0.1539	-2.7509
R = 0.9680, $K_{overall}$ = 0.01521 per min., XAe = 0.1644			
Concentration of inorganic salt = $AlCl_3$, 6mM			
5	225.05	0.0998	-0.8334
10	223.13	0.1075	-0.9392
20	221.73	0.1131	-1.0238
30	219.95	0.1202	-1.1426
60	217.00	0.1320	-1.3778
90	212.25	0.1510	-1.9346
120	208.63	0.1655	-2.7754
R = 0.9746, $K_{overall}$ = 0.01551 per min., XAe = 0.1765			
Concentration of inorganic salt = $AlCl_3$, 8mM			
5	222.35	0.1106	-0.8442
10	220.18	0.1193	-0.9543
20	218.70	0.1252	-1.0366
30	216.88	0.1325	-1.1488
60	213.38	0.1465	-1.4071
90	208.43	0.1663	-1.9464
120	204.30	0.1828	-2.8519
R = 0.9723, $K_{overall}$ = 0.01594 per min., XAe = 0.1940			

Table 5.53 Effect of Concentration of Inorganic Salt on Adsorption Kinetics of MIBK onto Hudson Flyash

INFLUENT CONCENTRATION =250 ppm			
Time (min.)	Remaining Conc.(mg/l)	XA	ln(1-XA/XAe)
Concentration of inorganic salt = $AlCl_3$, 2mM			
5	223.10	0.1076	-0.8581
10	221.05	0.1158	-0.9674
20	219.38	0.1225	-1.0665
30	217.55	0.1298	-1.1870
60	213.95	0.1442	-1.4782
90	210.35	0.1586	-1.8907
120	205.88	0.1765	-2.8979
R = 0.9865, $K_{overall}$ = 0.01587 per min., XAe = 0.1868			
Concentration of inorganic salt = $AlCl_3$, 4mM			
5	220.93	0.1163	-0.8676
10	218.73	0.1251	-0.9780
20	217.18	0.1313	-1.0638
30	215.30	0.1388	-1.1785
60	211.20	0.1552	-1.4875
90	207.30	0.1708	-1.9079
120	202.58	0.1897	-2.9212
R = 0.9688, $K_{overall}$ = 0.01604 per min., XAe = 0.2005			
Concentration of inorganic salt = $AlCl_3$, 6mM			
5	219.13	0.1235	-0.8606
10	217.02	0.1319	-0.9508
20	215.20	0.1392	-1.0512
30	213.35	0.1466	-1.1553
60	208.98	0.1641	-1.4559
90	204.38	0.1825	-1.9159
120	199.38	0.2026	-2.9323
R = 0.9678, $K_{overall}$ = 0.01626 per min., XAe = 0.2140			
Concentration of inorganic salt = $AlCl_3$, 8mM			
5	216.85	0.1326	-0.8670
10	214.55	0.1418	-0.9676
20	212.80	0.1488	-1.0516
30	210.75	0.1570	-1.1599
60	206.00	0.1760	-1.4678
90	201.13	0.1955	-1.9299
120	195.75	0.2170	-2.9728
R = 0.9667, $K_{overall}$ = 0.01652 per min., XAe = 0.2287			

neligible correlation). Tbale 5.54 and 5.55 present the linear regression of adsorptive capacity of activated carbon and Hudson flyash versus concentration of inorganic salt respectively. Adsorptive capacity was obtained from Table 5.8 to 5.11 which calculated from the regressed Freundlich parameter from Figure B_1 to B_{30}. The equilibrium concentration used are 10 mg/l and 30 mg/l for sorbent activated carbon and flyash respectively. Data shows a very satisfactory linear correlation between the concentration of salts and adsorptive capacity ($R > 0.99$). Therefore, for a specific range of equilibrium concentration and a particular inorganic salt, the adsorptive capacity of target compounds onto activated carbon and Hudson flyash can be easily calculated by using the linear equation from Table 5.54 and 5.55.

5.7. Correlation of Sorption Rate Constant with Concentration of Inorganic Salt

If the reaction rate follows the first order reversible reaction, the comparsion between equation (2-21) and equation (5-3) shows that the intraparticle diffusion coefficient (D_c) is a function of overall reaction rate constant ($K_{overall}$). It is convenient to use overall rate constant for the expression of reaction rate in steay of diffusion coefficient. Table 5.50 and 5.51 show the effect of concentration of sodium chloride on the adsorption of phenol and MIBK onto activated carbon respectively, while

Table 5.54 Linear Regression of Adsorptive Capacity of Activated Carbon versus Concentration of Inorganic Salts (0 -0.01 M)

Target Compounds	q (mg/g) versus concentration of inorganic salts (0-0.01 M)					
	NaCl		$CaCl_2 \cdot 2H_2O$		$AlCl_3$	
	Regression Coefficient	Linear Expression	Regression Coefficient	Linear Expression	Regression Coefficient	Linear Expression
Toluene	0.999	$q = 97.07+1518\ C_s$	0.999	$q = 94.78+1107\ C_s$	0.999	$q = 95.94+793\ C_s$
Benzene	0.996	$q = 70.53+2744\ C_s$	0.998	$q = 70.73+1986\ C_s$	0.998	$q = 69.62+1796\ C_s$
Phenol	0.999	$q = 28.33+1026\ C_s$	0.999	$q = 27.54+650\ C_s$	0.999	$q = 28.26+357\ C_s$
MIBK	0.996	$q = 41.43+1442\ C_s$	0.993	$q = 42.03+839\ C_s$	0.999	$q = 42.32+491\ C_s$
IPA	0.991	$q = 4.89+102\ C_s$	0.997	$q = 4.90+36\ C_s$	0.999	$q = 4.58+54\ C_s$

C_s = Concentration of inorganic salt (M)

Calculated based on equilibrium concentration = 10 ppm

Table 5.55 Linear Regression of Adsorptive Capacity of Hudson Flyash versus Concentration of Inorganic Salts

Target Compounds	q (ug/g) versus concentration of inorganic salts (0-0.01M)					
	NaCl		$CaCl_2.2H_2O$		$AlCl_3$	
	Regression Coefficient	Linear Expression	Regression Coefficient	Linear Expression	Regression Coefficient	Linear Expression
Toluene	0.999	$q = 760+20048\ C_s$	0.999	$q = 741+33258\ C_s$	0.997	$q = 762+54818C_s$
Benzene	0.999	$q = 634+19489\ C_s$	0.999	$q = 656+40936\ C_s$	0.989	$q = 627+90284C_s$
Phenol	0.994	$q = 245+25349\ C_s$	0.998	$q = 245+34922\ C_s$	0.996	$q = 250+48055C_s$
MIBK	0.998	$q = 325+26110\ C_s$	0.998	$q = 320+30941\ C_s$	0.997	$q = 318+35581C_s$
IPA	0.999	$q = 80 + 5461\ C_s$	0.999	$q = 77+10025\ C_s$	0.993	$q = 71+10974C_s$

C_s = Concentration of inorganic salts (M)

Calculated based on equilibriumconcentration = 30 ppm

Table 5.52 and 5.53 show the effect of concentration of aluminum chloride on the adsorption of phenol and MIBK onto Hudson flyash separately. Tables show the increasing of concentration of inorganic salt , increases of overall rate constant . As mentioned earlier, if the salt significantly affects the adsorption capacity, the observable reaction is not only a function of the intraparticule diffusion, but also a function of the adsorption capacity. A separative realtionship among adsorptive capacity, salt concentration, and overall reaction rate (or intraparticle diffusion coefficient) must be set up. Figure G_1 to G_4 demonstrate the relationship. As expected, the salt concentration significantly affects the adsorptive capacity , and the adsorption greatly affects the adsorption rate. Relatively, the effect of salt concentration on sorption rate individually is unimportant.

SECTION VI

CONCLUSIONS

The major finding and contribution of this study is summarized and some suggestion are offered for future research.

6.1. Conclusions

(1). The addition of inorganic salts change the pH value of the solution. The study of pH effect on adsorption shows flyash has a different adsorption behavior than activated carbon. For flyash, the adsorption capacity increases with increasing pH up to a certain pH value and then decreases at higher pH levels. For activated carbon, the adsorptive capacity increases with increasing pH up to a optimum pH value then decreases, but pH value above the salt saturation point, adsorptive capacity increases again.

(2). Activated carbon and flyash favor a neutral pH value (6-8) in the presence of sodium chloride and calcium chloride, while in the presence of aluminum chloride, the adsorbents favor a lower pH range (4-5).

(3). Within the examined concentrations of inorganic salts, the addition of inorganic salts enhance the adsorptive capacity. The adsorptive capacity of flyash for organic compounds, aluminum chloride is the most effective, calcium less effective than aluminum chloride, and sodium chloride the least effective. The adsorption of target compounds onto activated carbon; sodium chloride is the most effective, calcium chloride slightly less effective than sodium chloride, and aluminum chloride the least effective.

(4).The improvement of adsorptive capacity by the addition of specific inorganic salts at a certain concentrations of target compounds and inorganic salt, flyash is more effective than activated carbon.

(5). There are no reactions between inorganic salts and organic molecules prior to the adsorption. The adsorptive capacity of adsorbents may be enhanced due to the adsorbate-salt interaction on the sorbent surface and the formation of adsorbent-salt-adsorbate complexes.

(6). The anion concentration of inorganic salt does not change during the sorption process.

(7). Within the examined concentration range of inorganic salts, the adsorptive capacity of adsorbents can be established as a linear expression with the salt concentration at a specified equilibrium concentration.

(8). The higher the water solubility of a compound , the lesser the adsorption capacity. The sorption system in the presence of inorganic salts also shows the same relation.

(9). The effect of inorganic salts on multi-component sorption systems almost follows the same pattern as single solute systems do.

(10). Except for the increasing of adsorptive capacity, the multi-solute system in the presence of inorganic salts behave in the same pattern as the same system without salt.

(11). In the presence of small concentrations of inorganic salts, the adsorption kinetics of activated carbon and flyash follows the first order reversible reaction.

(12). Inorganic salts can significantly affect the adsorption capacity and rate, but salt concentration does not greatly affect the reaction rate constant individually.

6.2. Expected Contribution

It must be recognized that flyash is not comparable with activated carbon on the basis of adsorptive capacity. To make flyash an attractive alternative to more costly activated carbon, the addition of inexpensive inorganic salts as a means of improving efficiency is being considered. Based on this, the contribution of this study will be:

Theoretical : The establishment of an experimental data base to help quantify and further explain the adsorption mechanism for flyash and activated carbon systems as well as develop a mechanistic understanding of the role inorganic salts as an adsorbent enhancer.

Industrial :

(1). A potentially cost effective approach to enhance the adsorptive capacity of a waste by product (flyash), i.e., finding a commercial use for flyash.

(2). Establish design guidelines for adsorption system based on flyash and activated carbon.

(3). Enhance present state-of-the-art understanding of the adsorption process of mixed systems (organic/inorganic).

(4). Ascetrain potential economic significance of mixed systems.

(5). Determine if presence or addition inorganic salts can act as an adsorption catalyst.

6.3. Recommendations

The study has explored the sorption mechanism in the presence of inorganic salts, and has investigated the effect of inorganic salts on adsorption capacity and rate during the process in batch study. Some further experimental work for additional understanding might include :

(1). Adsorption thermodynamics study in the presence of inorganic salts helping to identify the sorption forces and energies during the sorption process. Possibility of chemisorption in the presence of inorganic salts might also be examined in such a study.

(2). Multi-solute kinetics study in presence of inorganic salts can yield a better understanding of the effect of inorganic salts on adsorption rate.

(3). Dynamic studies (continuous flow column) would move more closely to simulating actual field conditions.

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APPENDIX- 'A'

EFFECT OF pH ON ADSORPTION

Fig A1, PH effect on Adsorption.

Flyash, Benzene, NaCl, 4.91mM

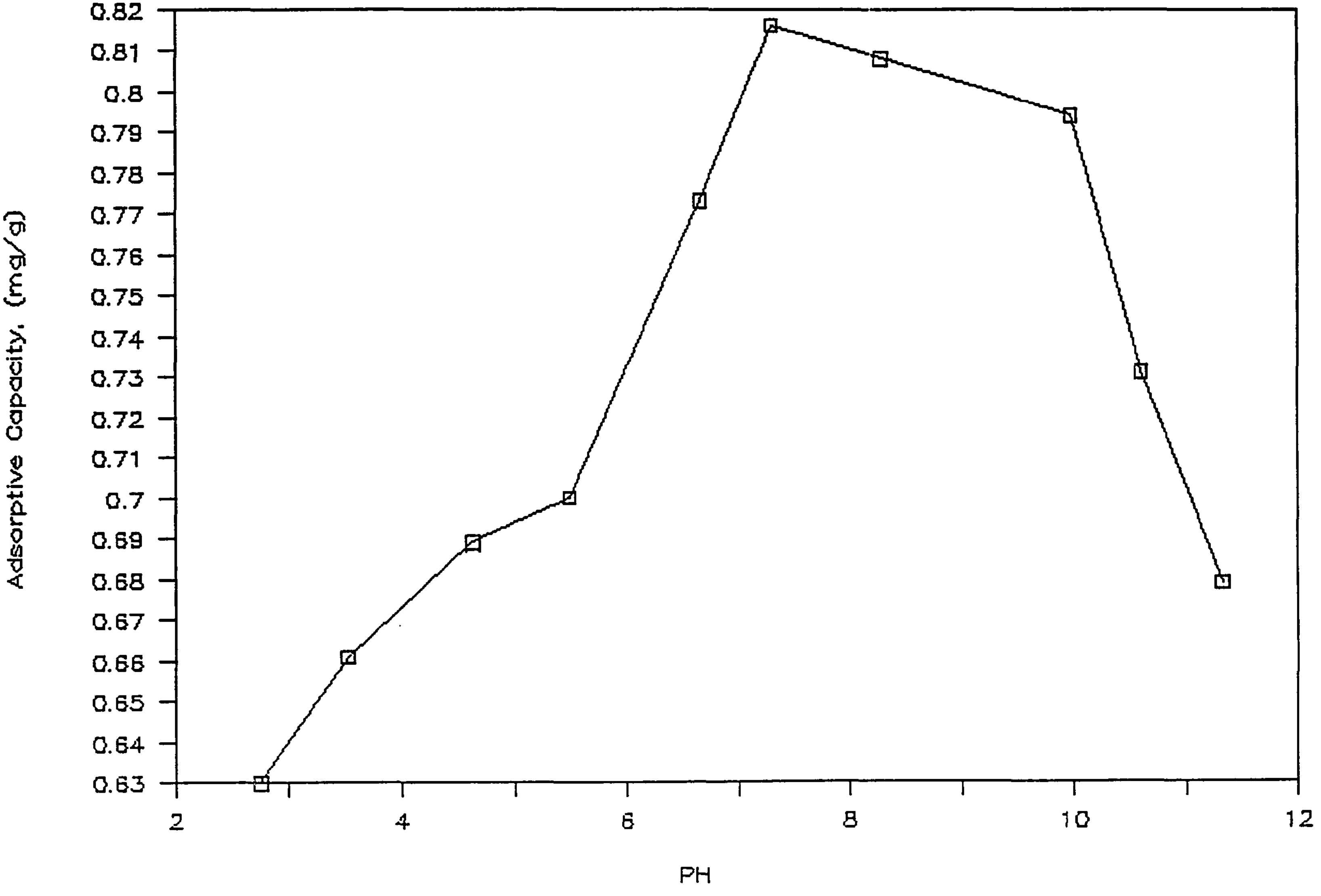
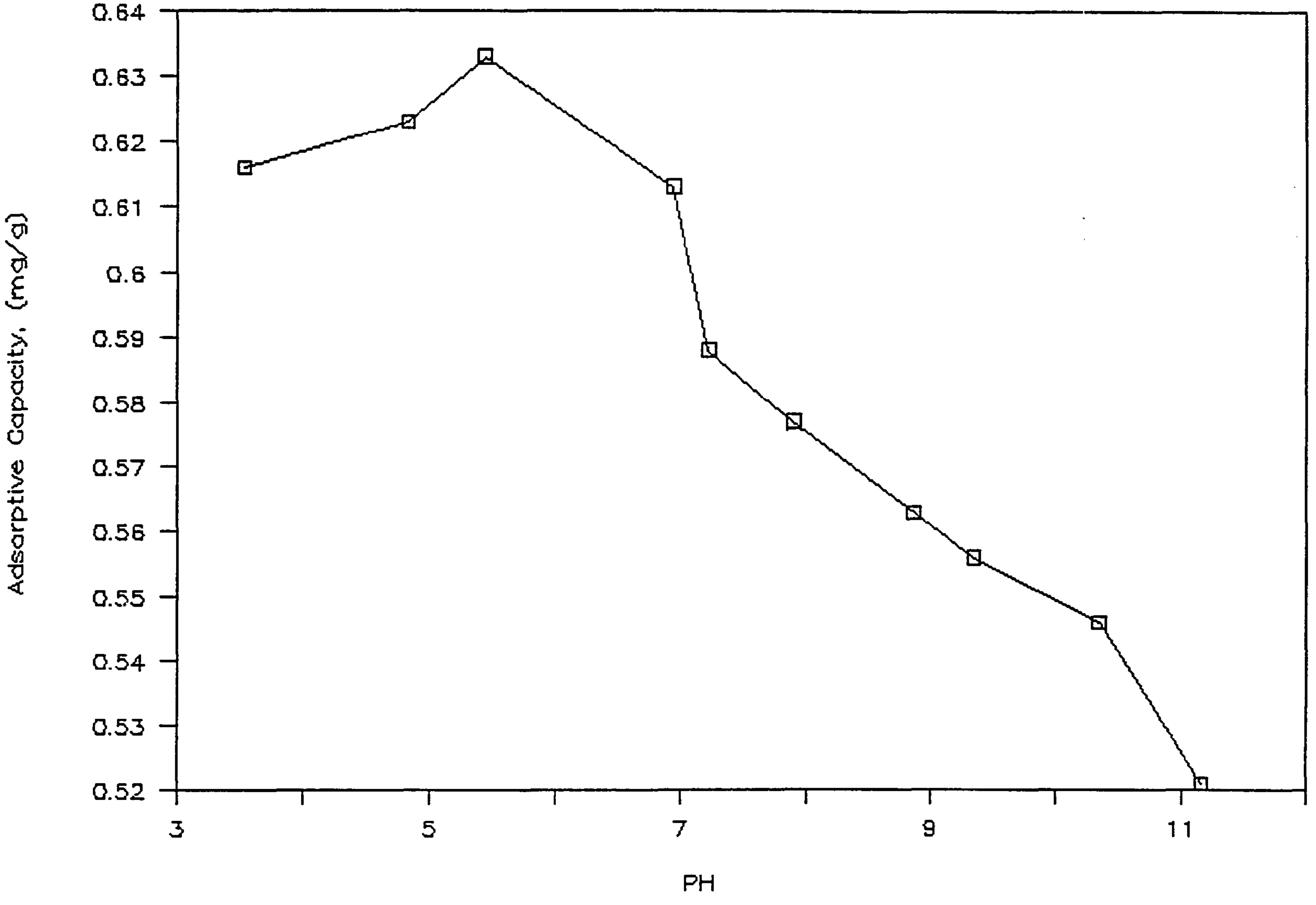


Fig A2, PH effect on Adsorption.

Flyash, Benzene, CaCl2, 5.33mM



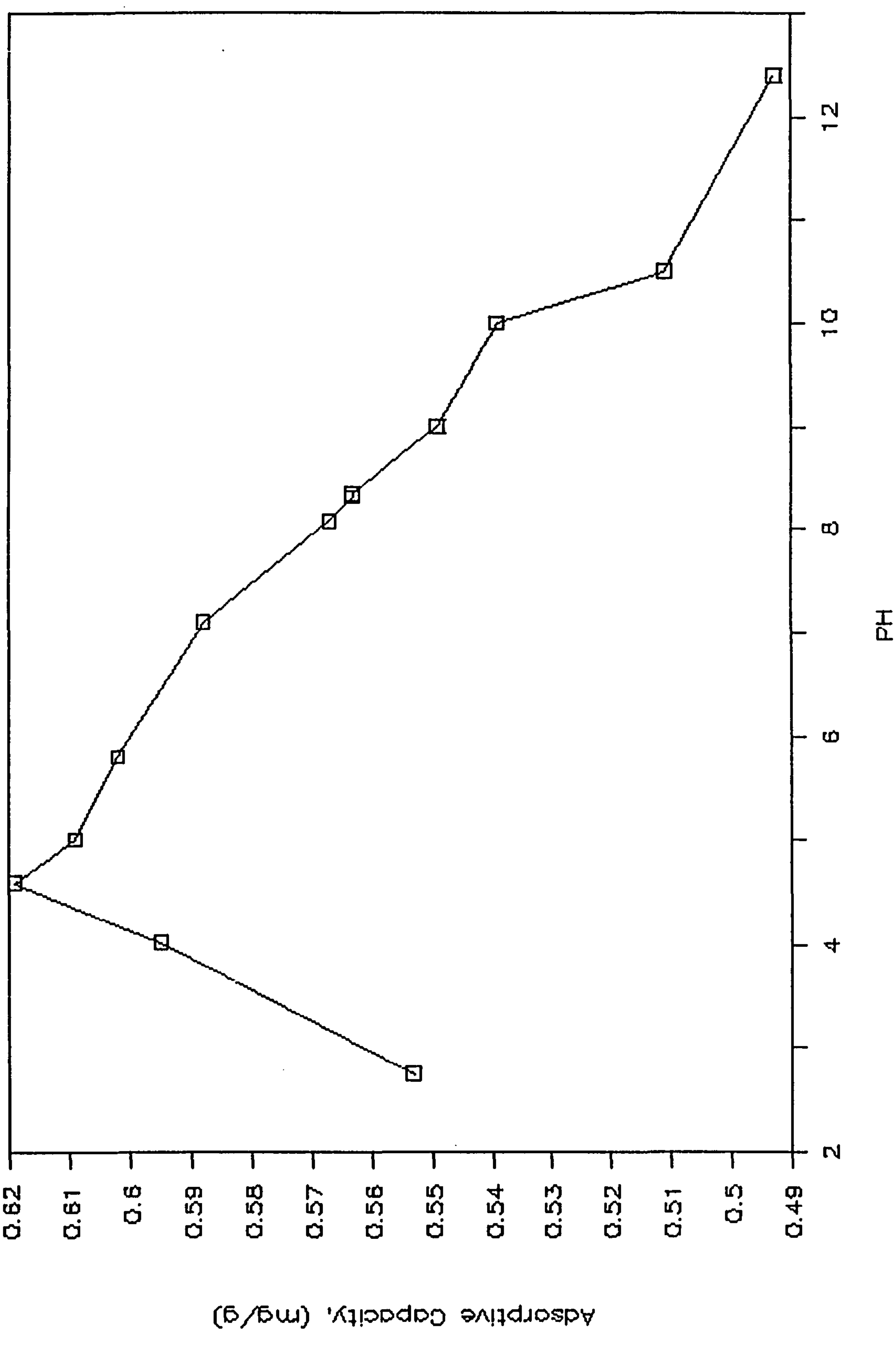
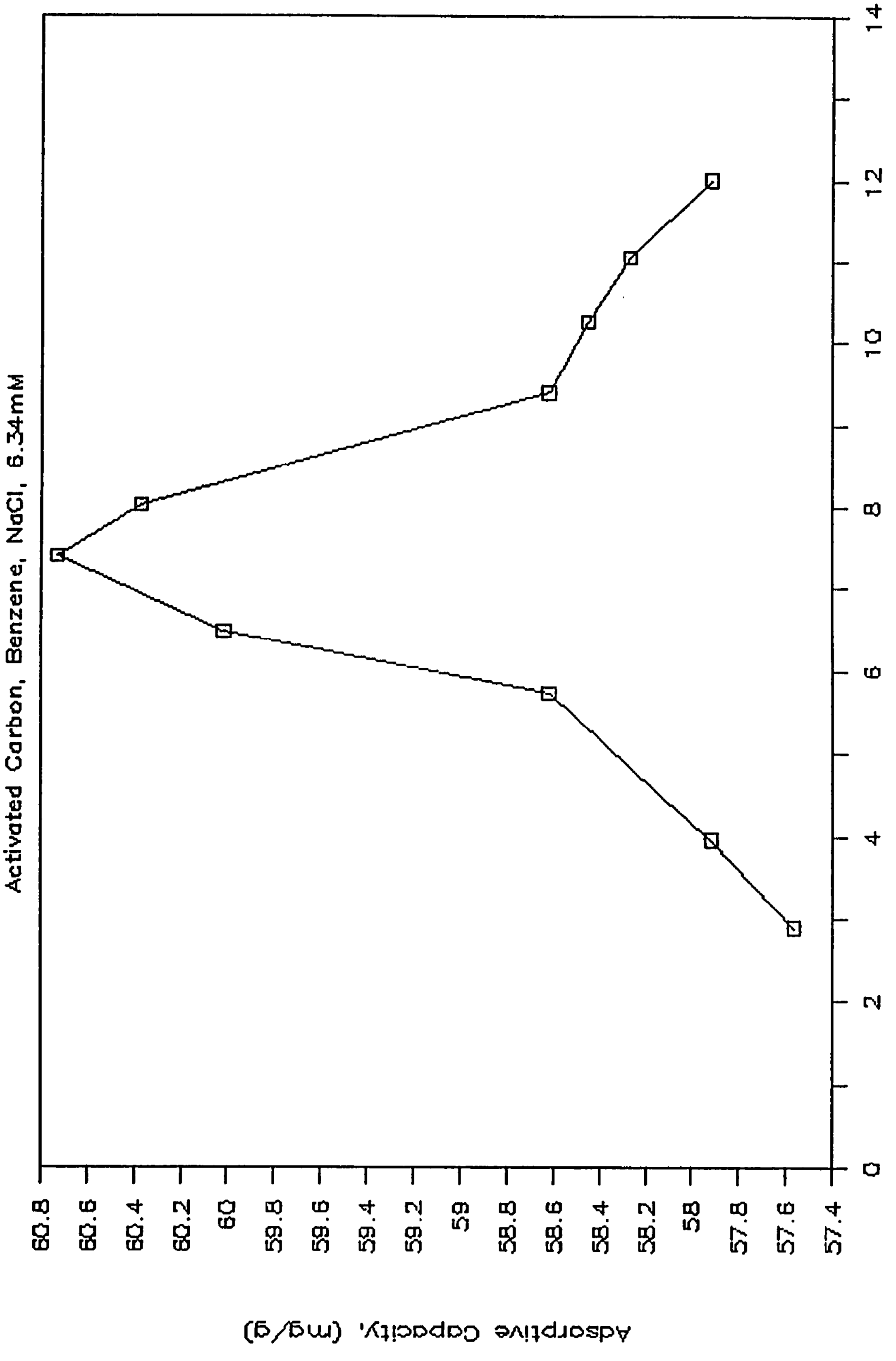


Fig A3, PH effect on Adsorption.

Flyash, Benzene, AlCl3, 6.2mM

Fig A4, PH effect on Adsorption.



Activated Carbon, Benzene, NaCl, 6.34mM

Fig A5, PH effect on Adsorption.

Activated Carbon, Benzene, CaCl2, 5.7mM

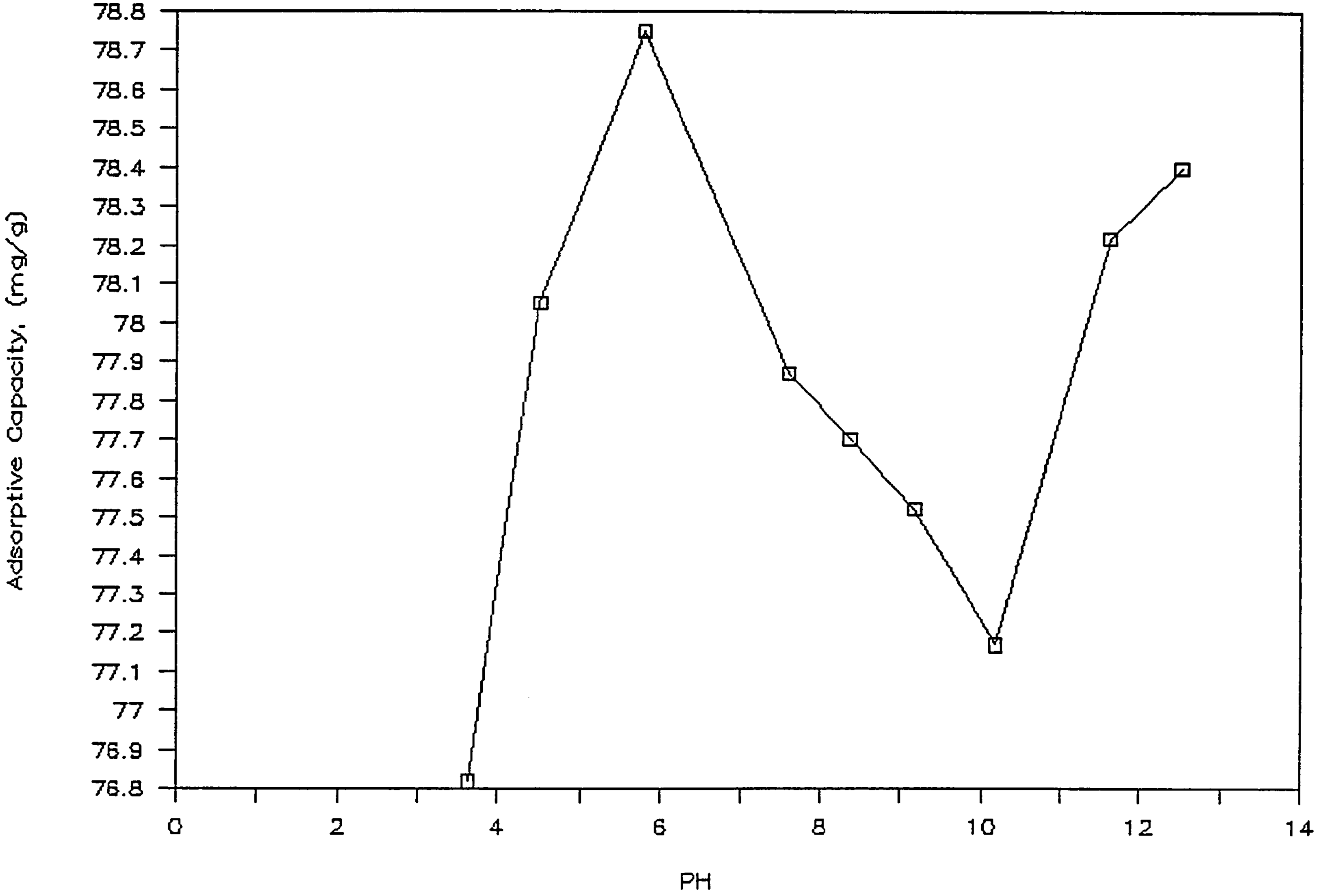


Fig A6, PH effect on Adsorption

Activated Carbon, Benzene, AlCl3,4.93mM

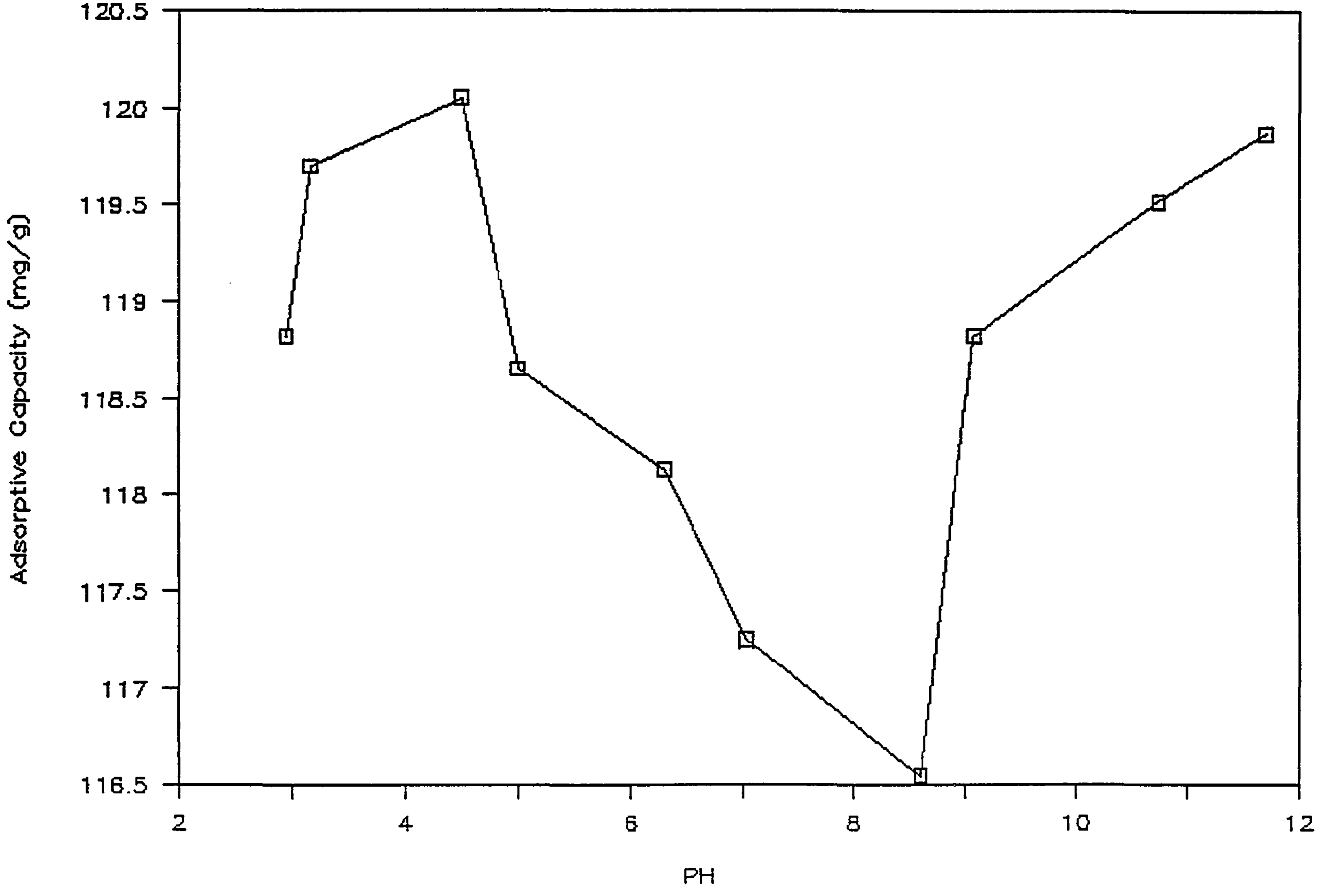
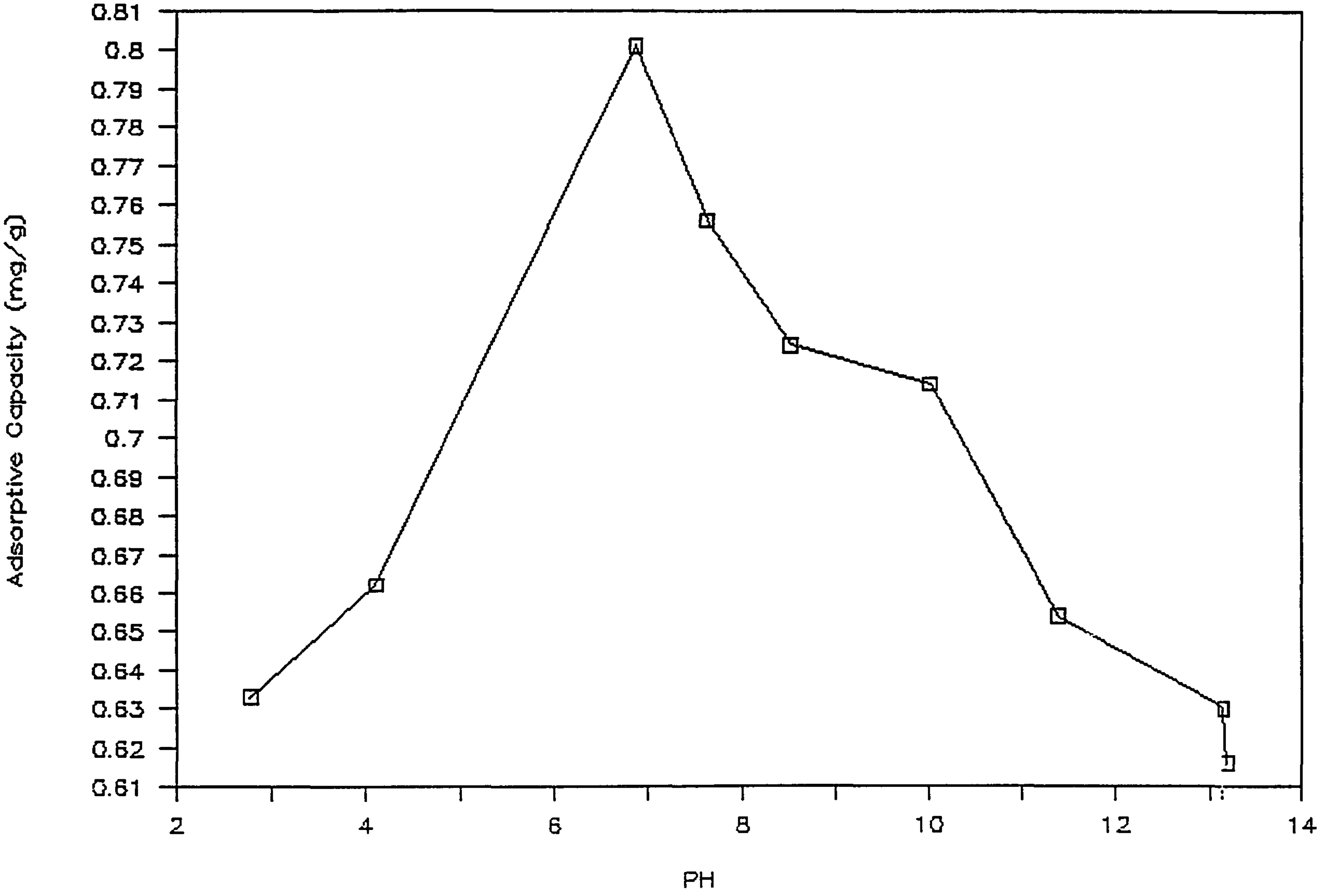


Fig A7, PH effect on Adsorption

Flyash, Toluene, NaCl, 6.2mM



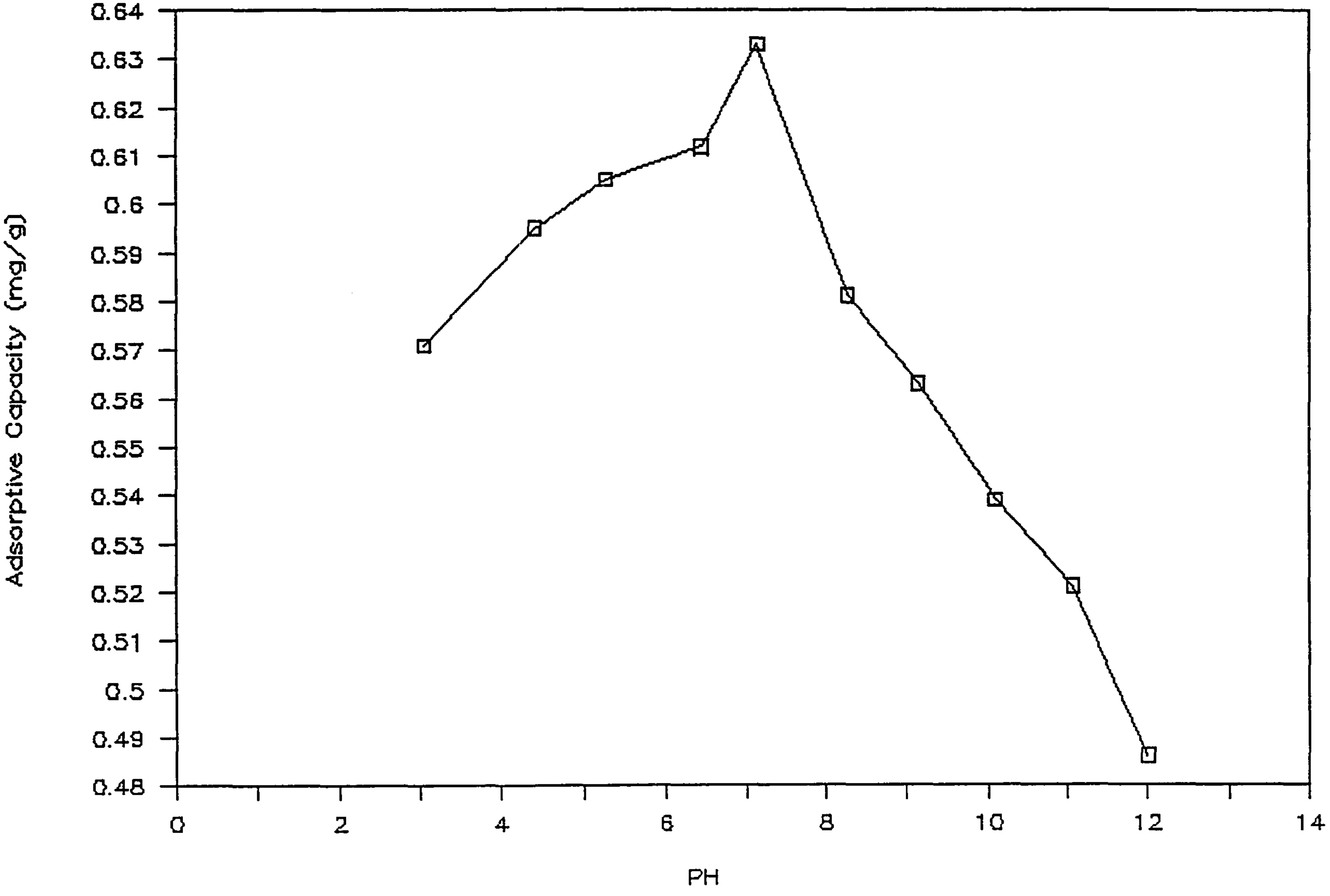


Fig A8, PH effect on Adsorption

Flyash, Toluene, CaCl2, 5.53mM

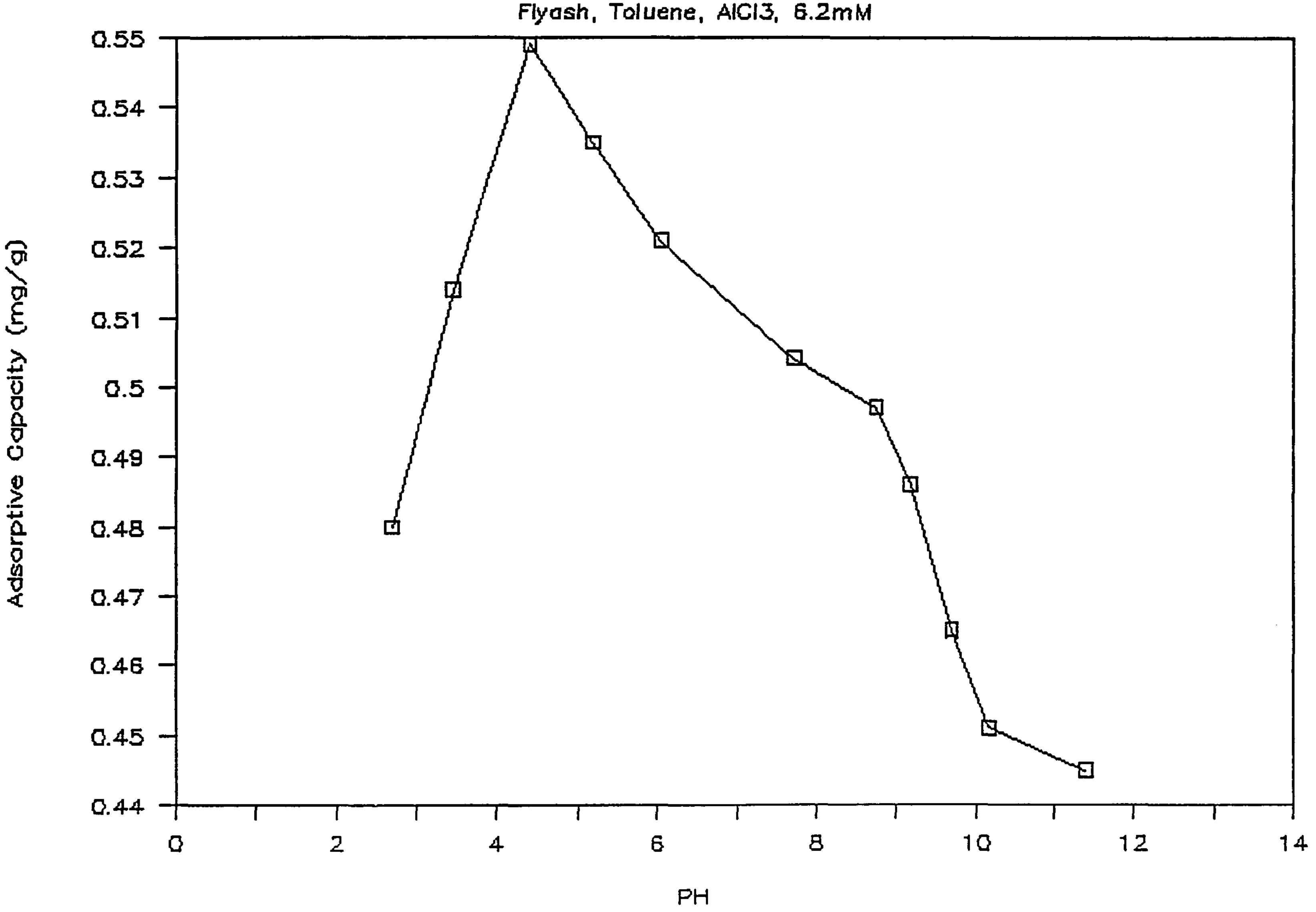


Fig A9, PH effect on Adsorption

Fig A10, PH effect on Adsorption

Activated Carbon, Toluene, NaCl, 5.04mM

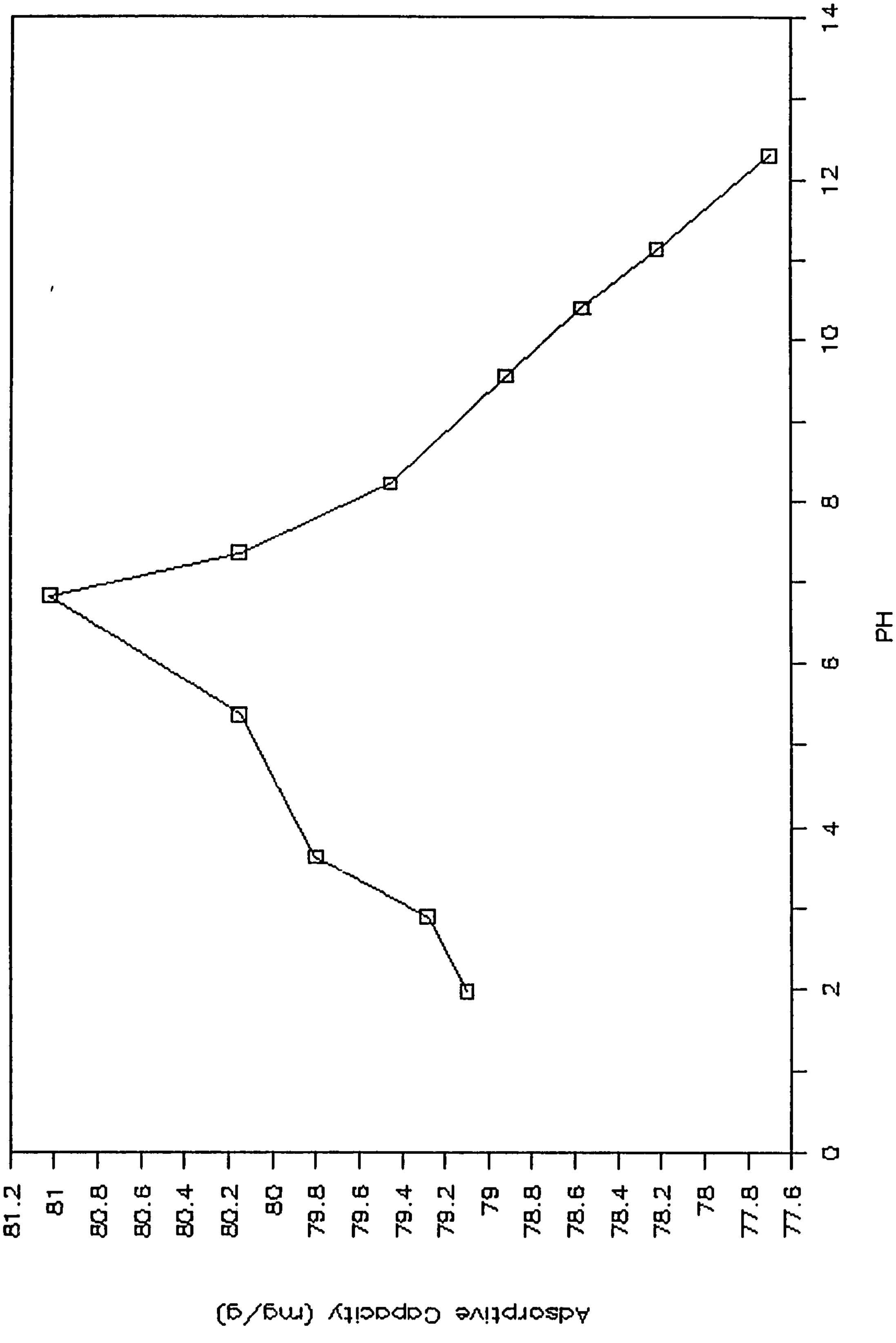
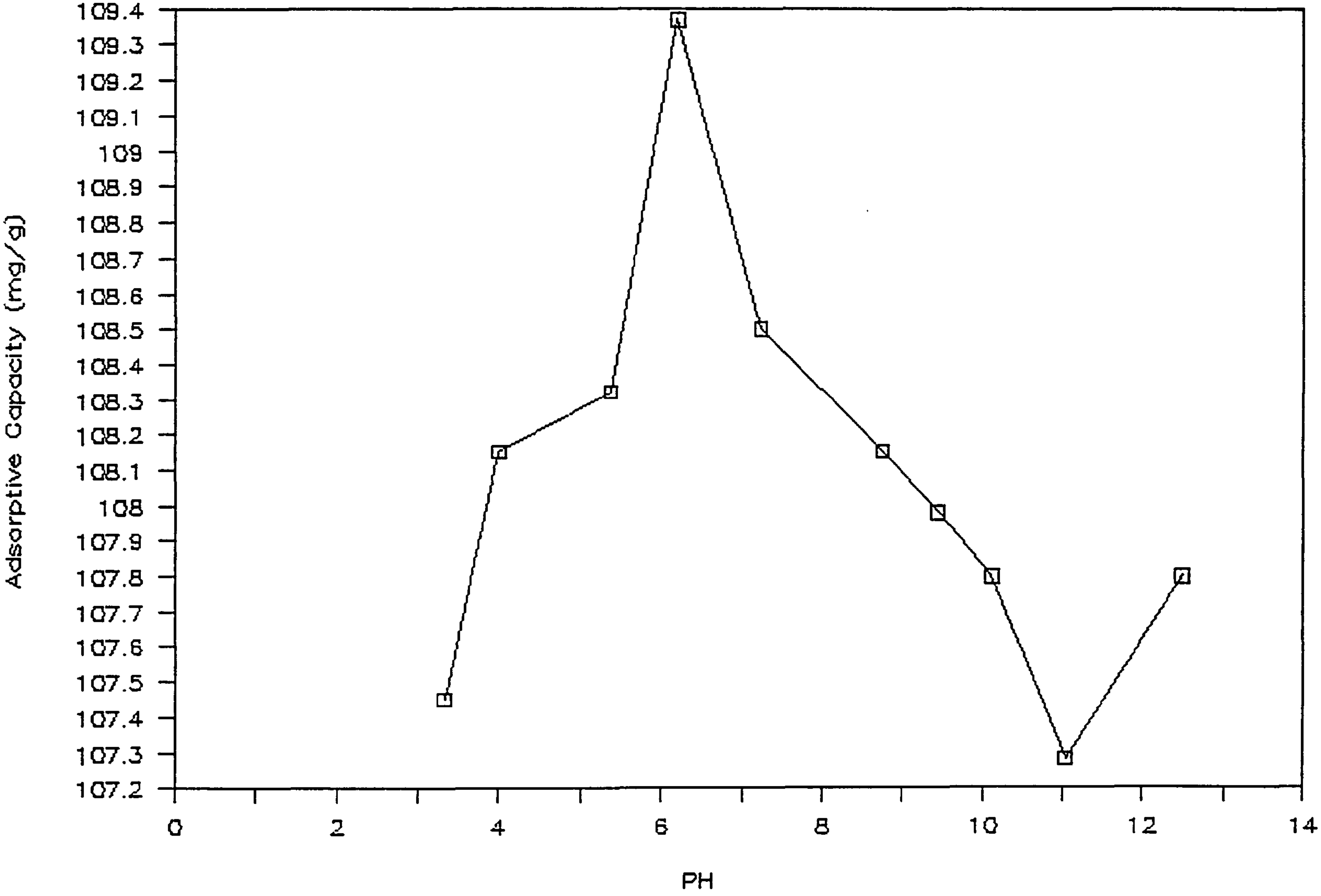


Fig A11, PH effect on Adsorption

Activated Carbon, Toluene, CaCl2, 5.8mM



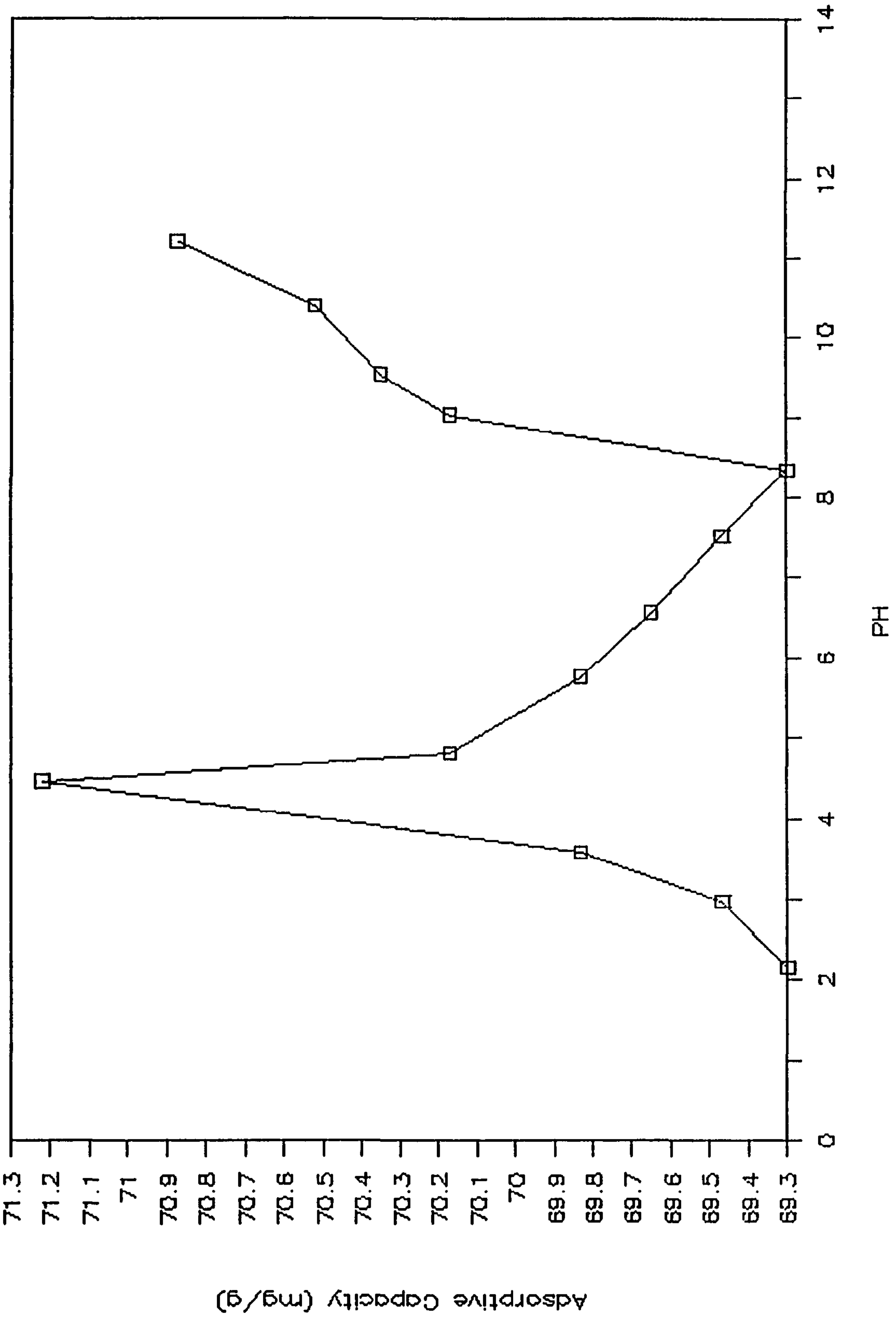


Fig A12, PH effect on Adsorption

Activated Carbon, Toluene, AlCl3, 5,5mM

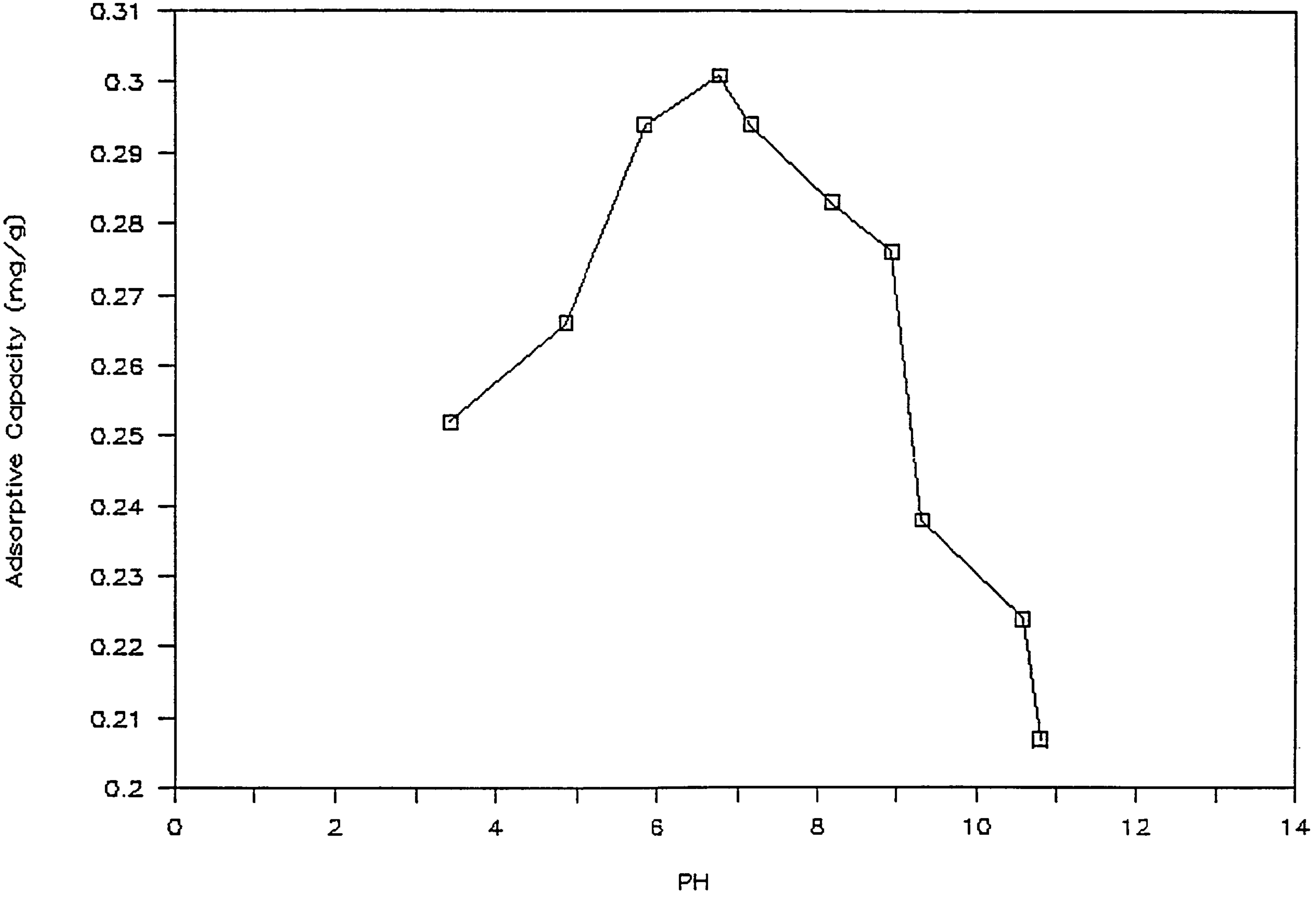


Fig A13, PH effect on Adsorption

Flyash, Phenol, NaCl, 7.06mM

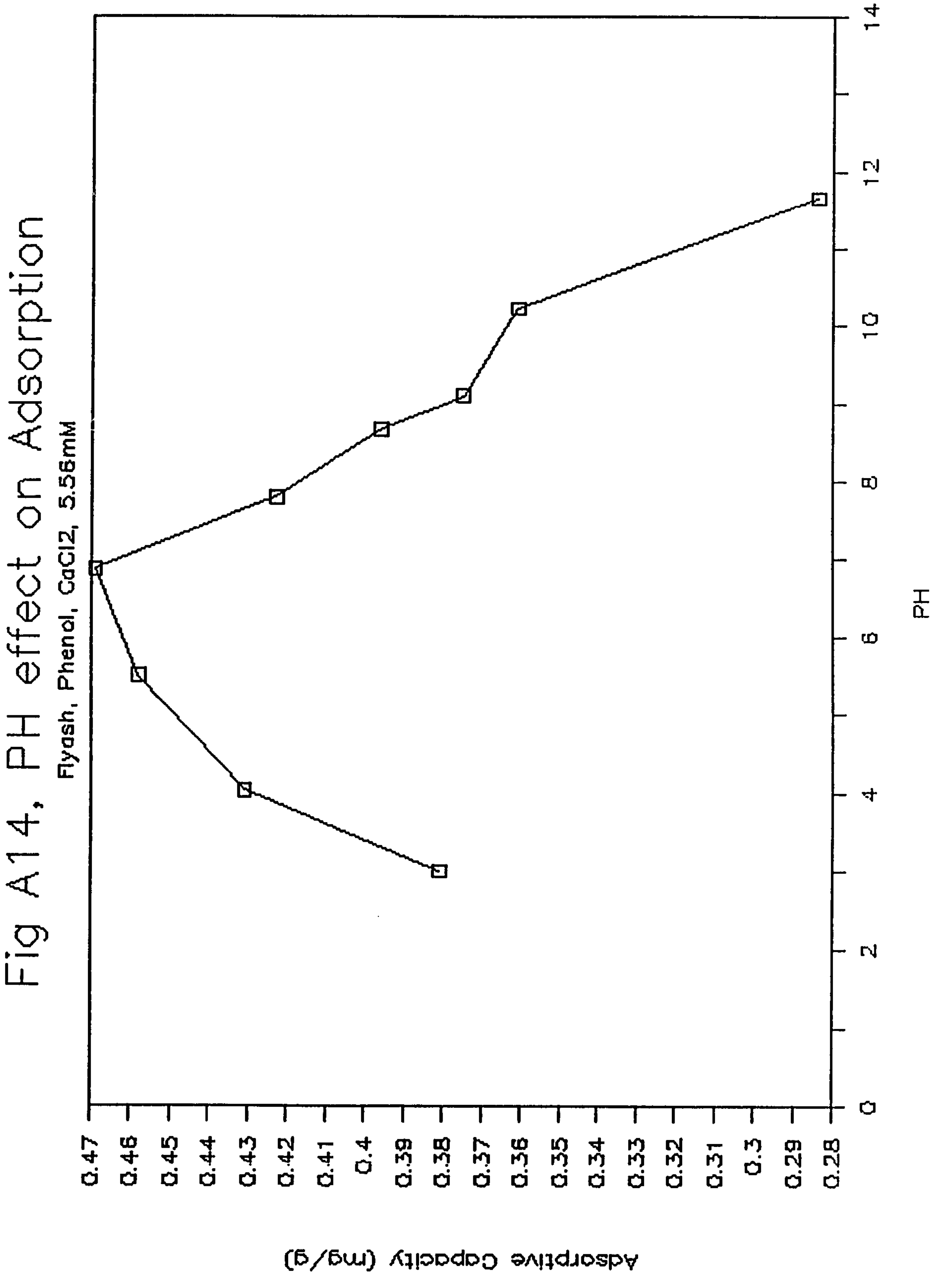
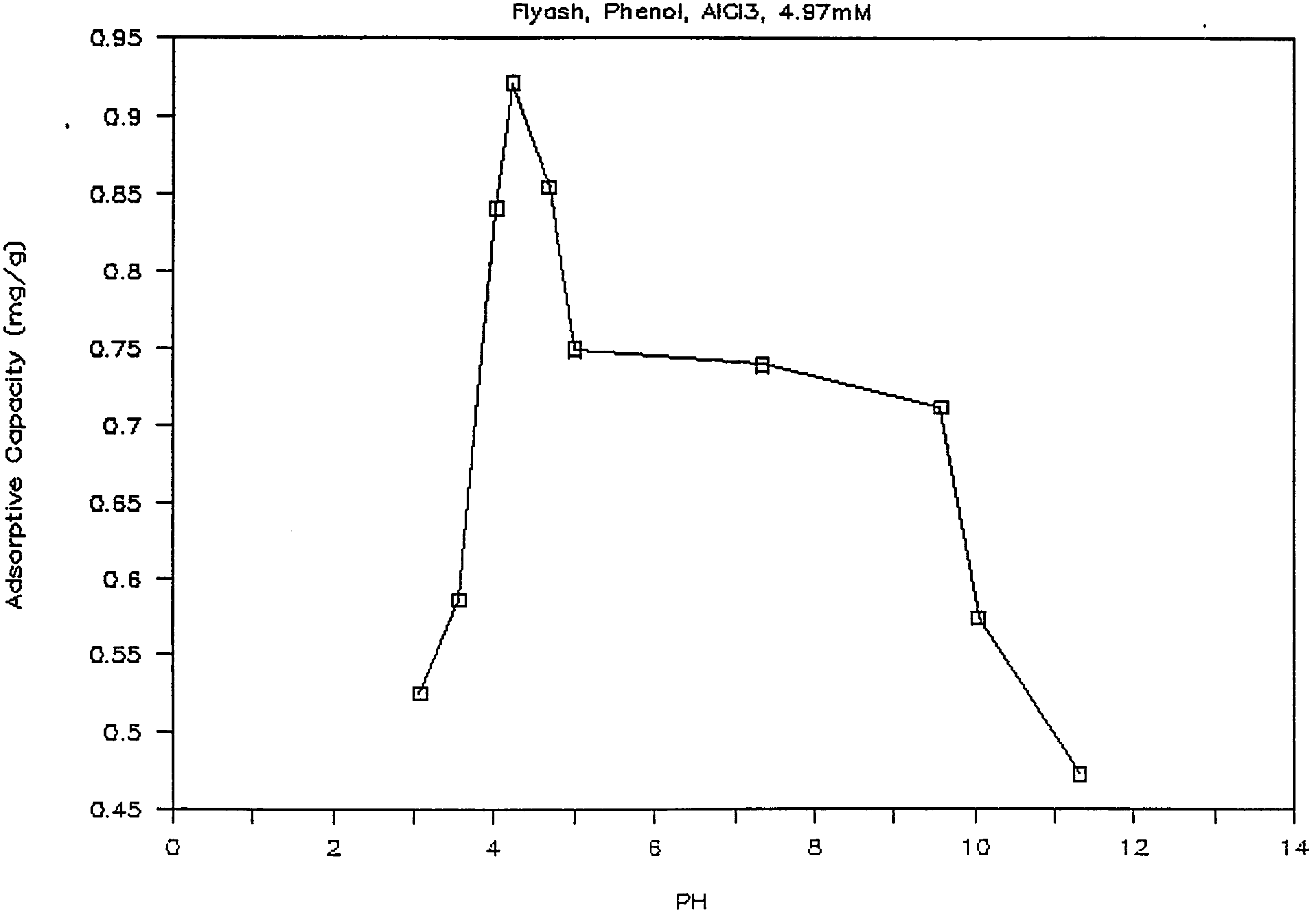


Fig A14, PH effect on Adsorption

Flyash, Phenol, CaCl2, 5.56mM

Fig A15, PH effect on Adsorption



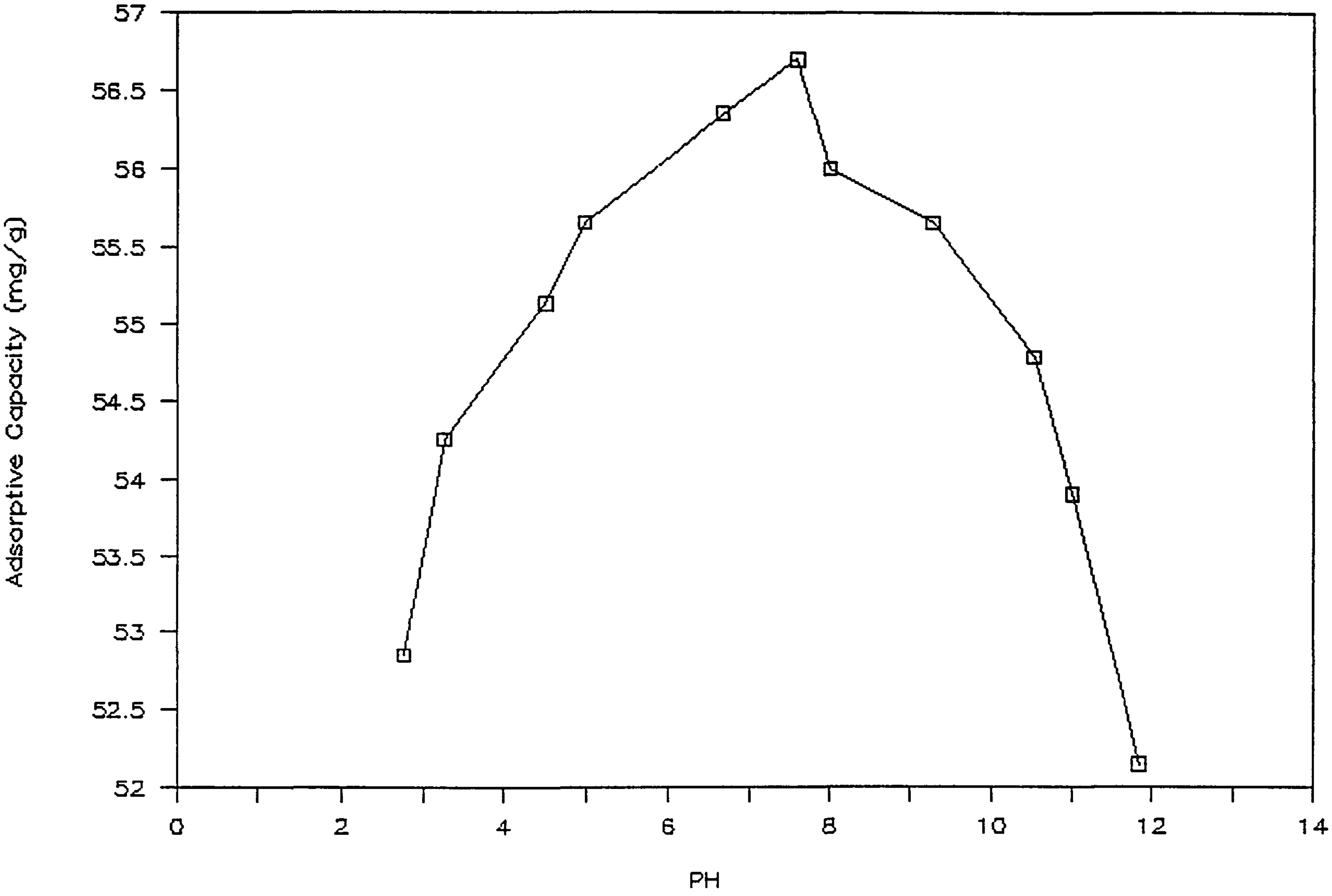
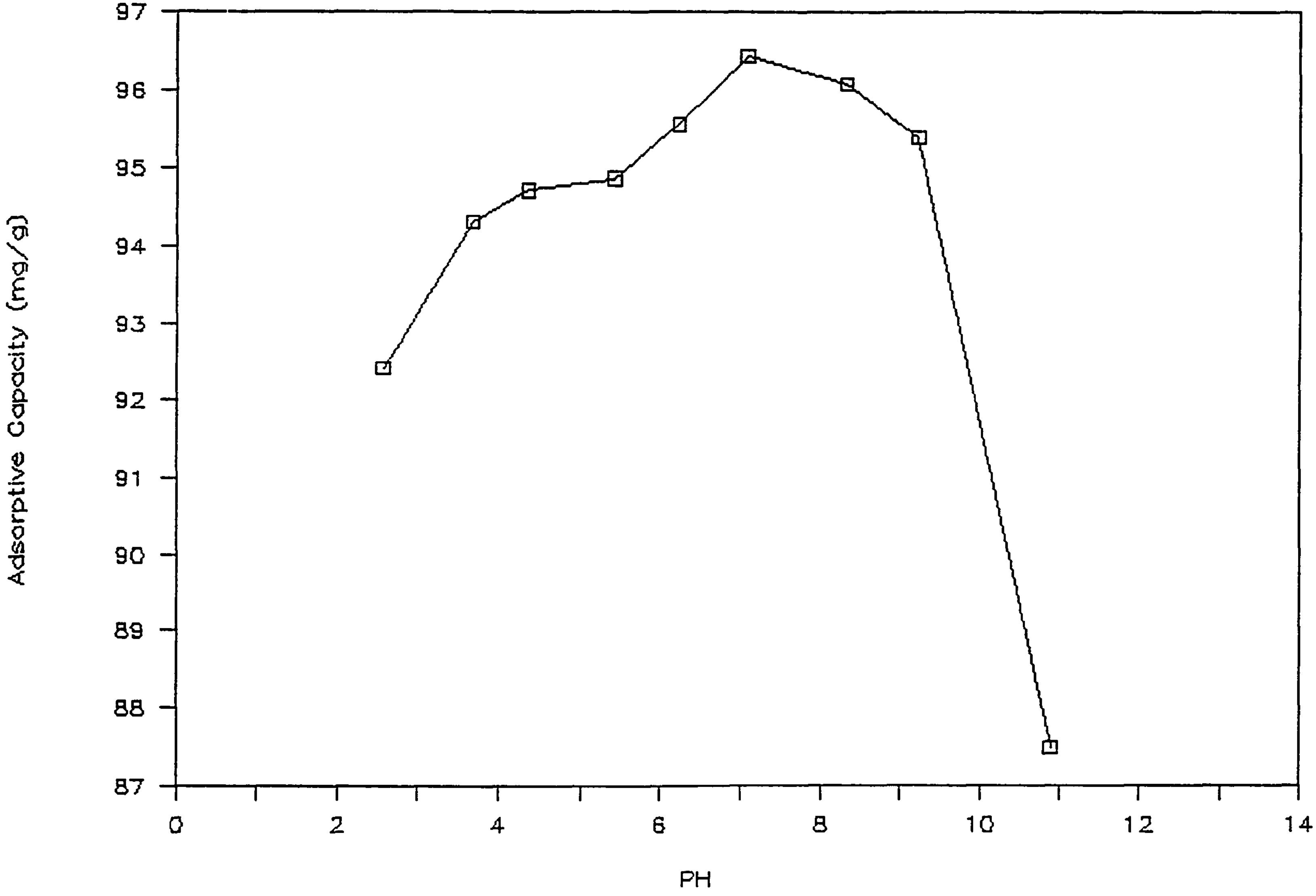


Fig A16, PH effect on Adsorption

Activated Carbon, Phenol, NaCl, 6.8mM

Fig A17, PH effect on Adsorption

Activated Carbon, Phenol, CaCl2, 5.36mM



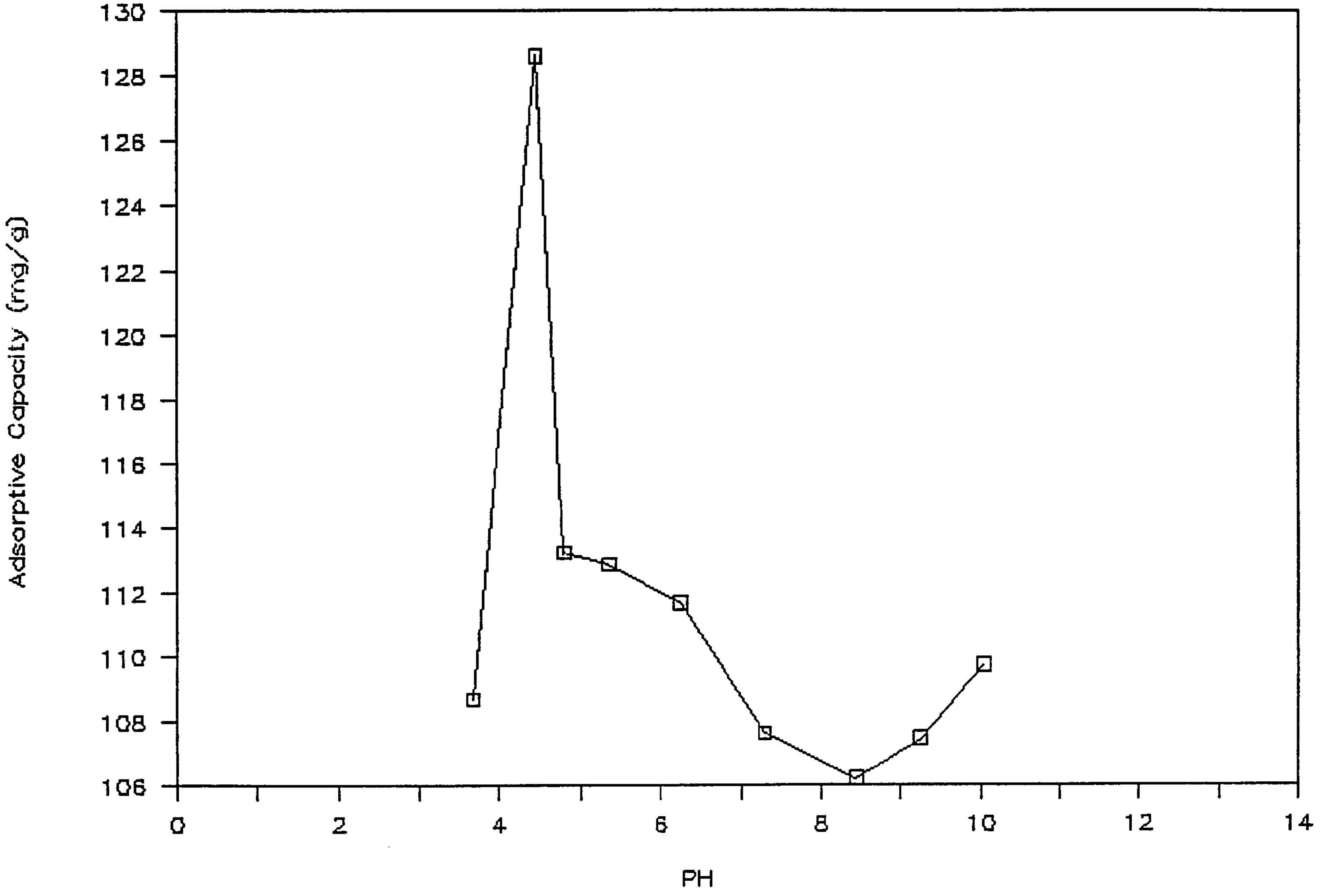


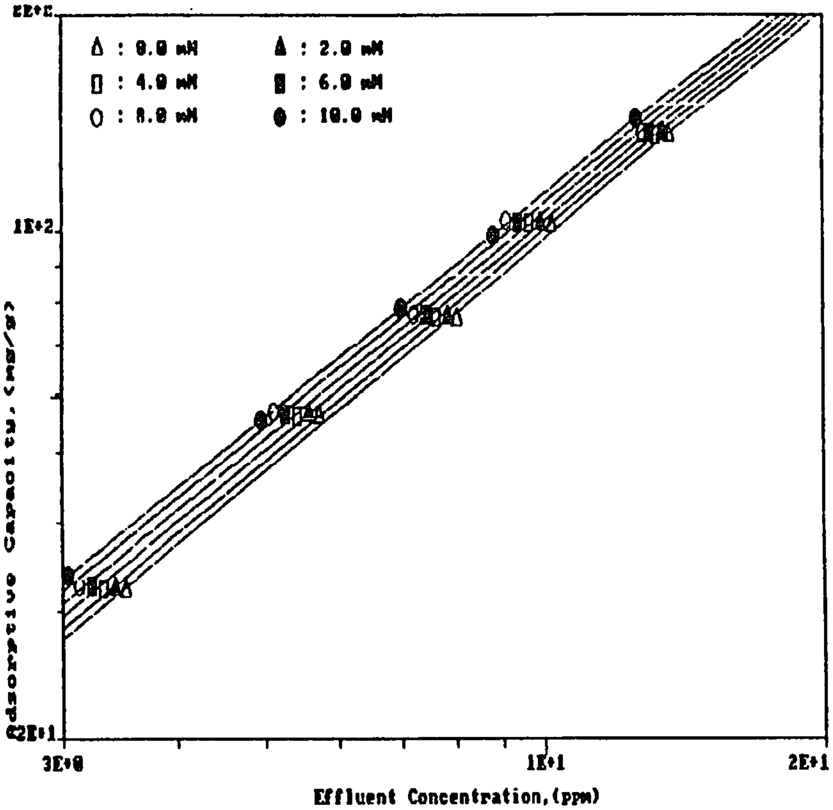
Fig A18, PH effect on Adsorption

Activated Carbon, Phenol, AlCl3, 5.11mM

APPENDIX - 'B'

ADSORPTION ISOTHERMS

Figure B1: Activated Carbon, Toluene, NaCl



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THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 9.362E-01) + ( 1.053E+00)*X
     THE VARIANCE -  7.758E-05

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 9.540E-01) + ( 1.048E+00)*X
     THE VARIANCE -  9.273E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 9.773E-01) + ( 1.036E+00)*X
     THE VARIANCE -  1.170E-04

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 9.974E-01) + ( 1.028E+00)*X
     THE VARIANCE -  1.497E-04

THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.020E+00) + ( 1.018E+00)*X
     THE VARIANCE -  1.837E-04

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.037E+00) + ( 1.014E+00)*X
     THE VARIANCE -  3.199E-08
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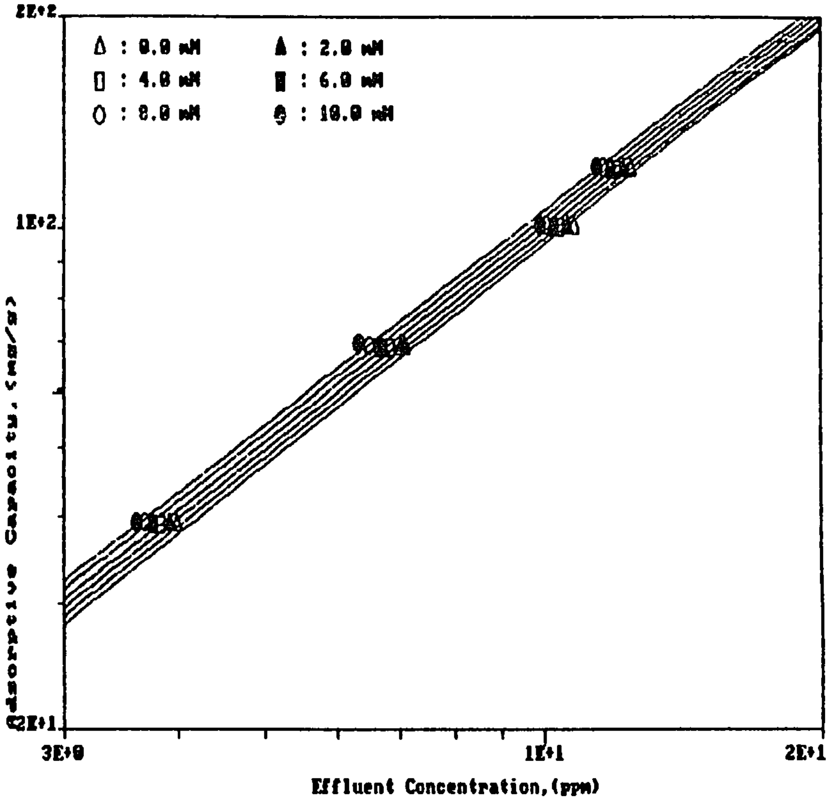
Figure B2: Activated Carbon, Toluene, CaCl2



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THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 9.639E-01) + ( 1.014E+00)*X
     THE VARIANCE -  8.472E-05

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 9.789E-01) + ( 1.007E+00)*X
     THE VARIANCE -  7.280E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 9.922E-01) + ( 1.004E+00)*X
     THE VARIANCE -  7.656E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.008E+00) + ( 9.977E-01)*X
     THE VARIANCE -  7.463E-05

THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.024E+00) + ( 9.915E-01)*X
     THE VARIANCE -  7.648E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.038E+00) + ( 9.873E-01)*X
     THE VARIANCE -  8.833E-05
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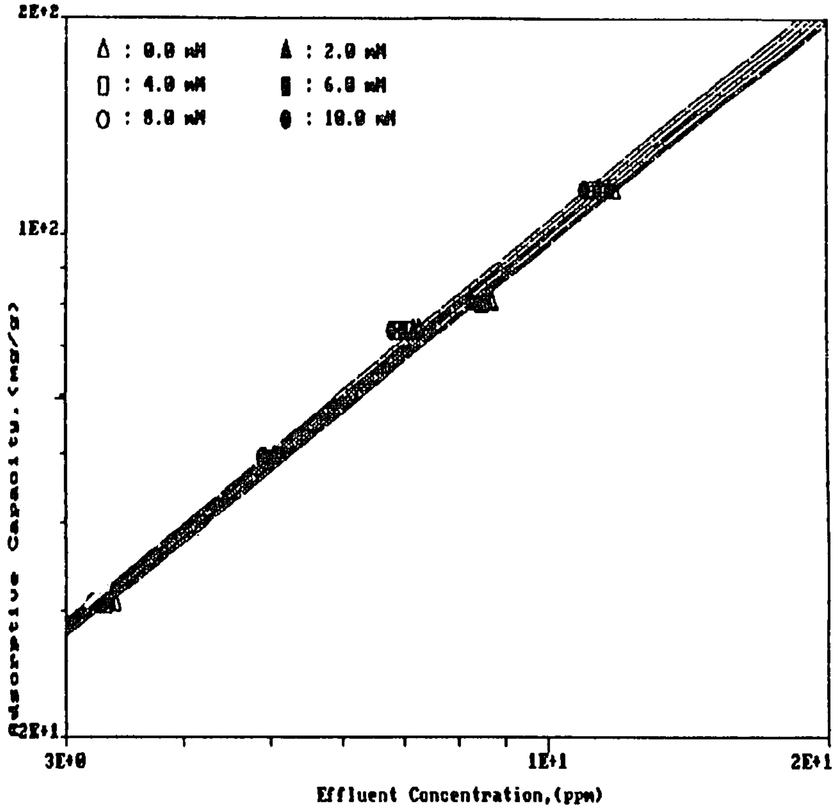

Figure B3: Activated Carbon, Toluene, AlCl3

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THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 9.487E-01) + ( 1.034E+00)*X
     THE VARIANCE -   2.379E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 9.517E-01) + ( 1.037E+00)*X
     THE VARIANCE -   2.384E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 9.531E-01) + ( 1.043E+00)*X
     THE VARIANCE -   2.491E-04

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 9.562E-01) + ( 1.046E+00)*X
     THE VARIANCE -   2.531E-04

THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 9.571E-01) + ( 1.053E+00)*X
     THE VARIANCE -   2.763E-04

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 9.609E-01) + ( 1.056E+00)*X
     THE VARIANCE -   2.877E-04
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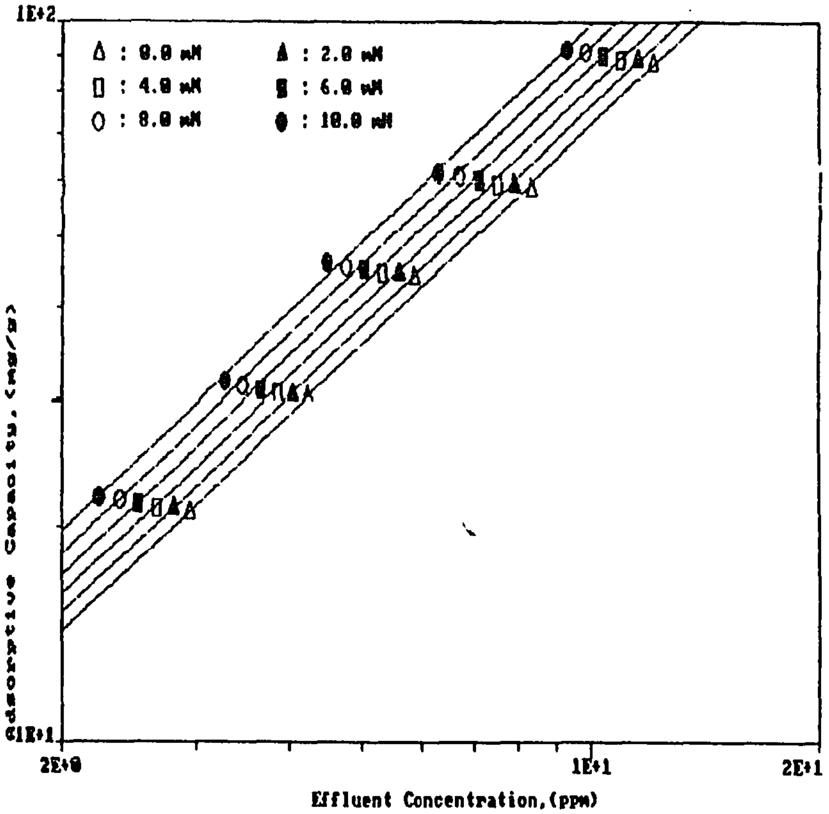
Figure B4: Activated Carbon, Benzene, NaCl



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THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 8.511E-01) + ( 1.003E+00)*X
     THE VARIANCE -  1.028E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 8.764E-01) + ( 1.004E+00)*X
     THE VARIANCE -  1.028E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 9.031E-01) + ( 1.004E+00)*X
     THE VARIANCE -  9.869E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 9.305E-01) + ( 1.005E+00)*X
     THE VARIANCE -  9.993E-05

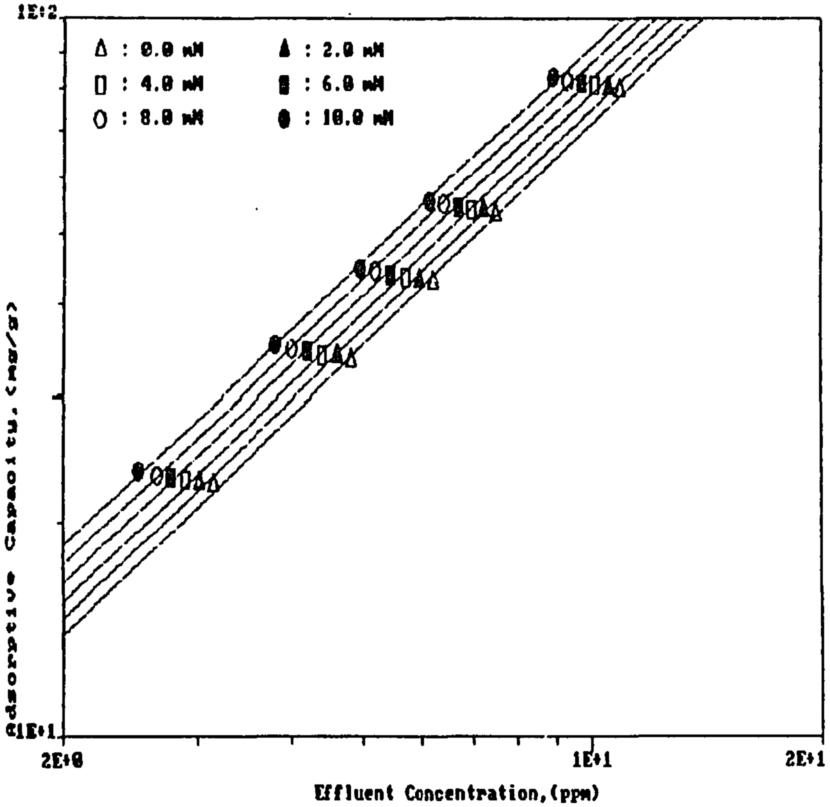
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 9.603E-01) + ( 1.004E+00)*X
     THE VARIANCE -  9.233E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 9.900E-01) + ( 1.006E+00)*X
     THE VARIANCE -  9.998E-05
```

Figure B5: Activated Carbon, Benzene, CaCl2



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 8.348E-01) + ( 1.018E+00)*X
     THE VARIANCE -   5.400E-05

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 8.613E-01) + ( 1.011E+00)*X
     THE VARIANCE -   4.631E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 8.860E-01) + ( 1.008E+00)*X
     THE VARIANCE -   3.705E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 9.142E-01) + ( 1.001E+00)*X
     THE VARIANCE -   3.235E-05

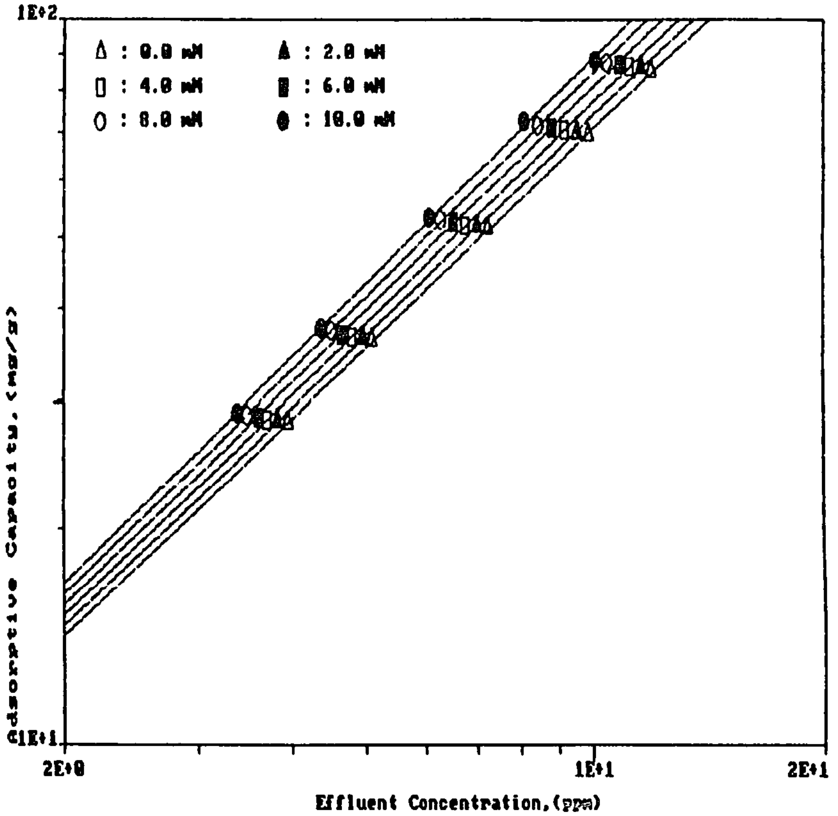
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 9.399E-01) + ( 9.976E-01)*X
     THE VARIANCE -   2.250E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 9.706E-01) + ( 9.886E-01)*X
     THE VARIANCE -   2.889E-05
```

Figure B6: Activated Carbon, Benzene, AlCl3



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THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 8.503E-01) + ( 9.955E-01)*X
     THE VARIANCE -  7.247E-06

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 8.620E-01) + ( 1.002E+00)*X
     THE VARIANCE -  3.700E-06

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 8.756E-01) + ( 1.008E+00)*X
     THE VARIANCE -  1.225E-06

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 8.870E-01) + ( 1.016E+00)*X
     THE VARIANCE -  2.246E-06

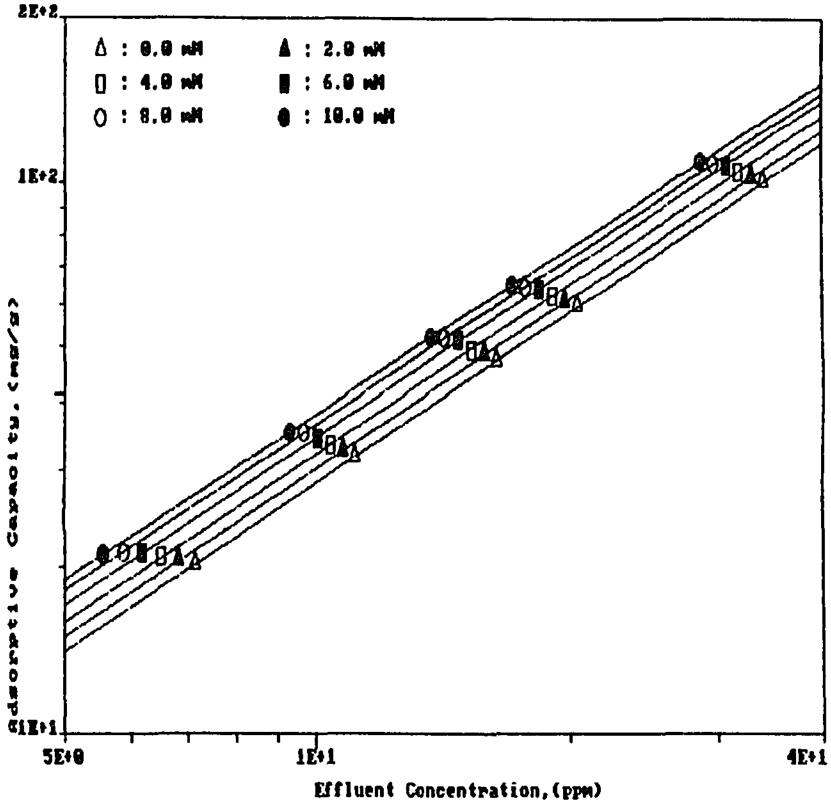
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 9.007E-01) + ( 1.023E+00)*X
     THE VARIANCE -  6.565E-06

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 9.140E-01) + ( 1.031E+00)*X
     THE VARIANCE -  1.452E-05
```

Figure B7: Activated Carbon, Phenol, NaCl



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 4.394E-01) + ( 1.017E+00)*X
     THE VARIANCE -   2.034E-06

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 4.695E-01) + ( 1.012E+00)*X
     THE VARIANCE -   1.926E-06

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 4.970E-01) + ( 1.010E+00)*X
     THE VARIANCE -   1.725E-06

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 5.313E-01) + ( 1.006E+00)*X
     THE VARIANCE -   1.520E-06

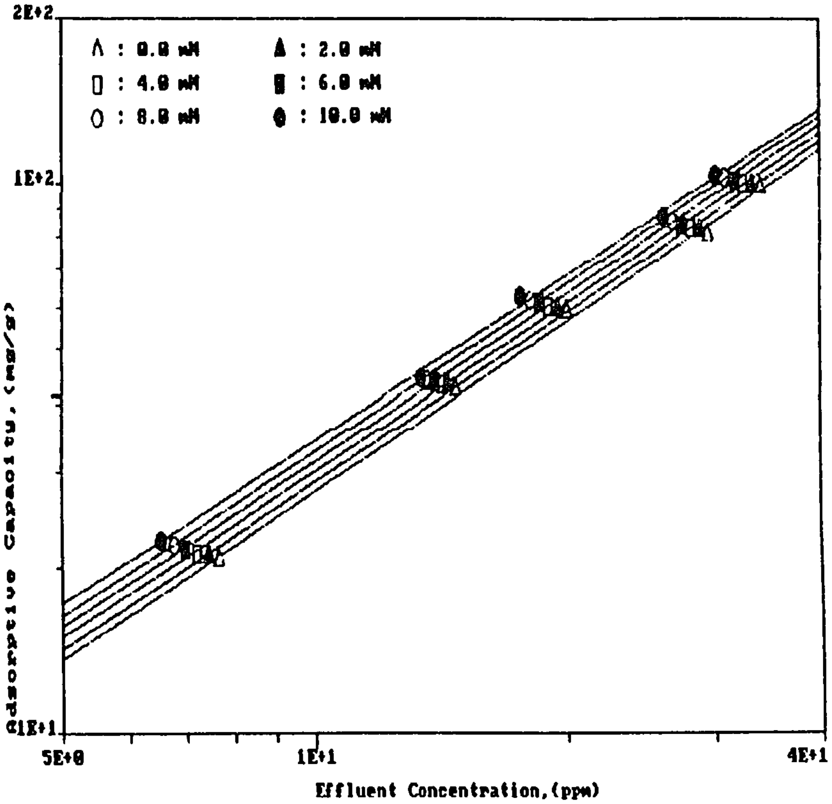
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 5.633E-01) + ( 9.972E-01)*X
     THE VARIANCE -   7.520E-07

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 5.829E-01) + ( 9.964E-01)*X
     THE VARIANCE -   4.307E-07
```

Figure 88: Activated Carbon, Phenol, CaCl2



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 4.215E-01) + ( 1.020E+00)*X
     THE VARIANCE -   1.500E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 4.463E-01) + ( 1.014E+00)*X
     THE VARIANCE -   1.182E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 4.692E-01) + ( 1.009E+00)*X
     THE VARIANCE -   9.789E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 4.930E-01) + ( 1.003E+00)*X
     THE VARIANCE -   8.869E-05

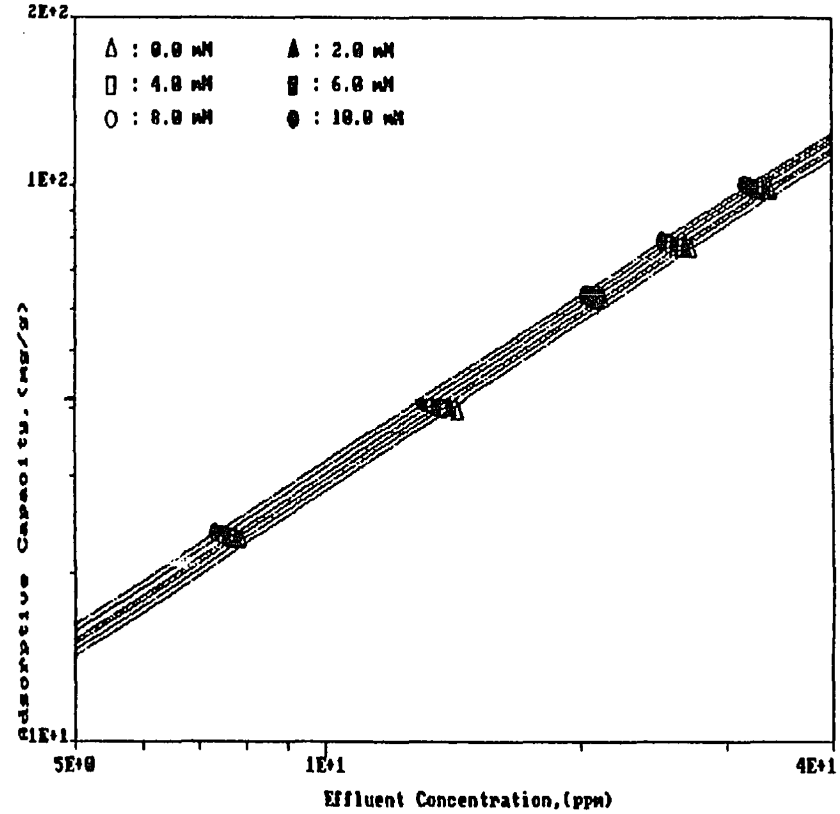
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 5.163E-01) + ( 9.984E-01)*X
     THE VARIANCE -   8.925E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 5.426E-01) + ( 9.912E-01)*X
     THE VARIANCE -   1.032E-04
```

Figure B9: Activated Carbon, Phenol, AlCl3



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 4.656E-01) + ( 9.862E-01)*X
     THE VARIANCE -  1.036E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 4.777E-01) + ( 9.844E-01)*X
     THE VARIANCE -  7.003E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 4.897E-01) + ( 9.827E-01)*X
     THE VARIANCE -  4.320E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 4.978E-01) + ( 9.839E-01)*X
     THE VARIANCE -  2.045E-05

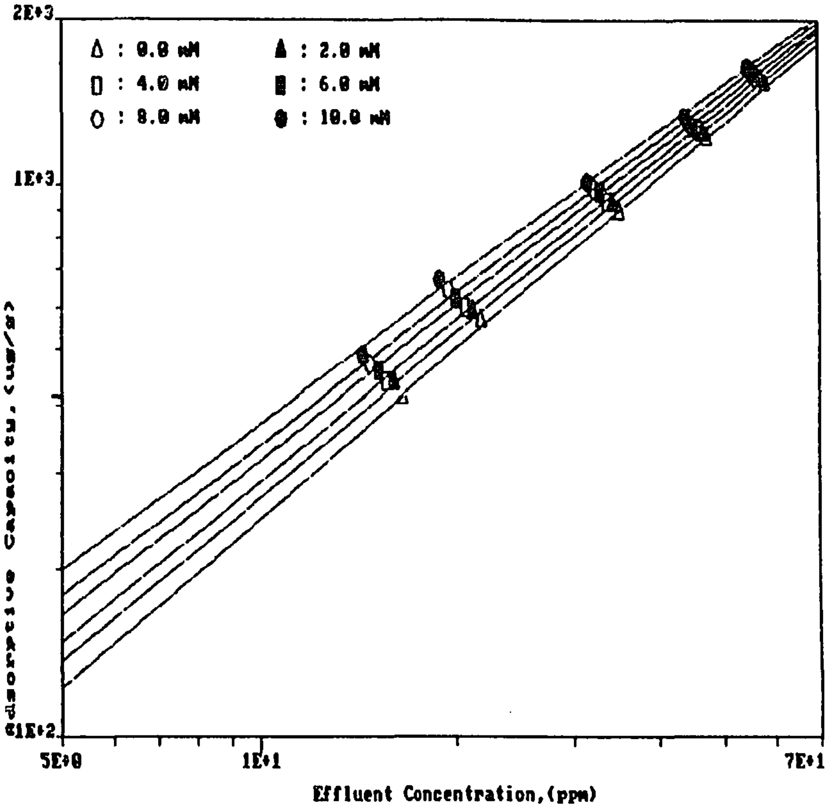
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 5.131E-01) + ( 9.799E-01)*X
     THE VARIANCE -  1.218E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 5.262E-01) + ( 9.775E-01)*X
     THE VARIANCE -  8.432E-06
```

Figure B10: Hudson Flyash, Toluene, NaCl



```
THF RFGRESSION POLYNOMIAL OF LINF  1 -

     ( 1.374E+00) + ( 1.020F+00)*X
     THF VARIANCE -  2.236E-05

THF REGRESSION POLYNOMIAL OF LINF  2 -

     ( 1.449E+00) + ( 9.852E-01)*X
     THE VARIANCE -  2.269E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.500E+00) + ( 9.636E-01)*X
     THE VARIANCE -  3.749E-05

THF REGRESSION POLYNOMIAL OF LINF  4 -

     ( 1.569E+00) + ( 9.312E-01)*X
     THE VARIANCE -  4.123E-05

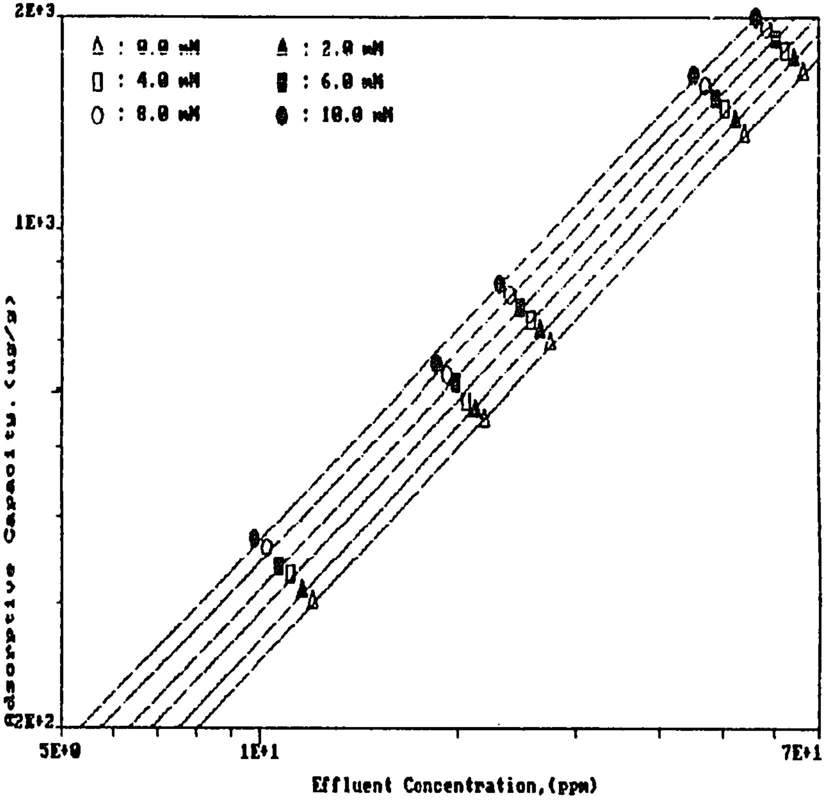
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.621F+00) + ( 9.081E-01)*X
     THE VARIANCE -  7.574E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.691F+00) + ( 8.752E-01)*X
     THF VARIANCE -  1.128E-04
```

Figure B11: Hudson Flyash, Toluene,CaCl2



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 1.394E+00) + ( 1.002E+00)*X
     THE VARIANCE -  7.138E-06

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.420E+00) + ( 1.006E+00)*X
     THE VARIANCE -  1.111E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.473E+00) + ( 9.926E-01)*X
     THE VARIANCE -  4.470E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.507E+00) + ( 9.911E-01)*X
     THE VARIANCE -  2.416E-05

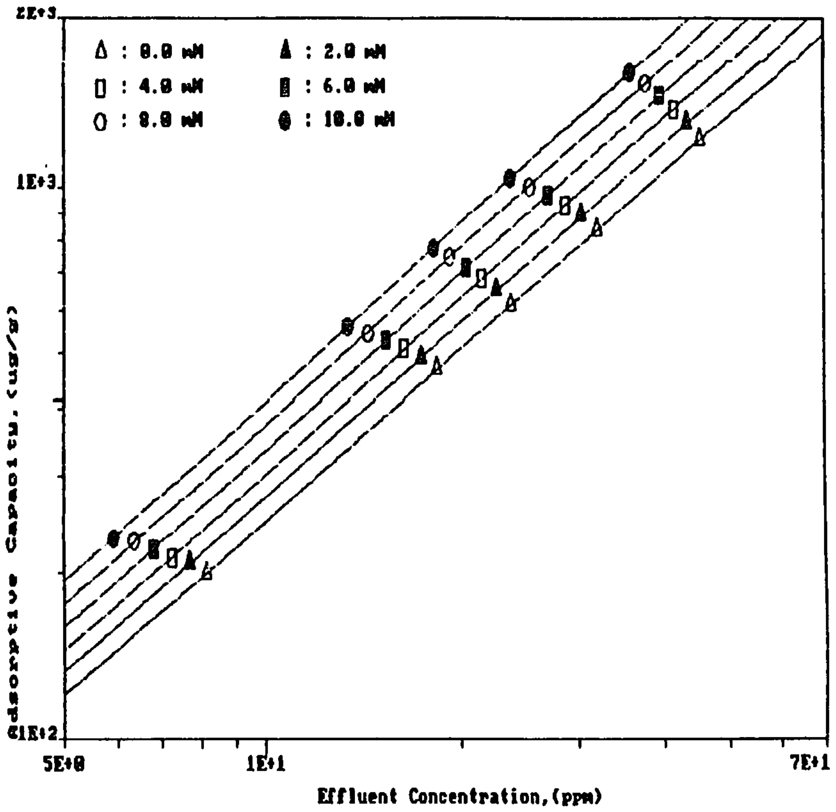
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.561E+00) + ( 9.764E-01)*X
     THE VARIANCE -  7.262E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.589E+00) + ( 9.777E-01)*X
     THE VARIANCE -  8.988E-05
```

Figure B12: Hudson Flyash, Toluene, AlCl3



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 1.350E+00) + ( 1.043E+00)*X
     THE VARIANCE -   2.920E-07

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.388E+00) + ( 1.051E+00)*X
     THE VARIANCE -   2.382E-08

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.418E+00) + ( 1.061E+00)*X
     THE VARIANCE -   1.054E-07

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.458E+00) + ( 1.066E+00)*X
     THE VARIANCE -   1.040E-07

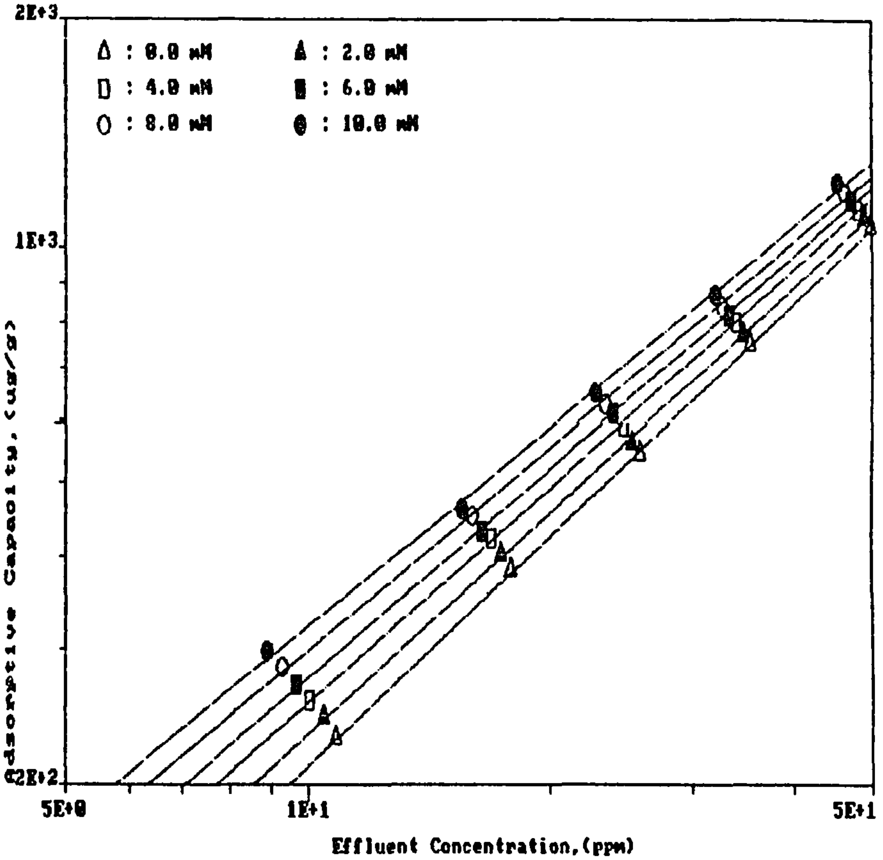
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.499E+00) + ( 1.069E+00)*X
     THE VARIANCE -   5.195E-08

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.533E+00) + ( 1.076E+00)*X
     THE VARIANCE -   1.173E-08
```

Figure B13: Hudson Flyash, Benzene, NaCl



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

      ( 1.323E+00) + ( 1.002E+00)*X
      THE VARIANCE -   1.561E-05

THE REGRESSION POLYNOMIAL OF LINE  2 -

      ( 1.392E+00) + ( 9.665E-01)*X
      THE VARIANCE -   2.577E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

      ( 1.469E+00) + ( 9.377E-01)*X
      THE VARIANCE -   1.042E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

      ( 1.527E+00) + ( 9.129E-01)*X
      THE VARIANCE -   2.230E-05

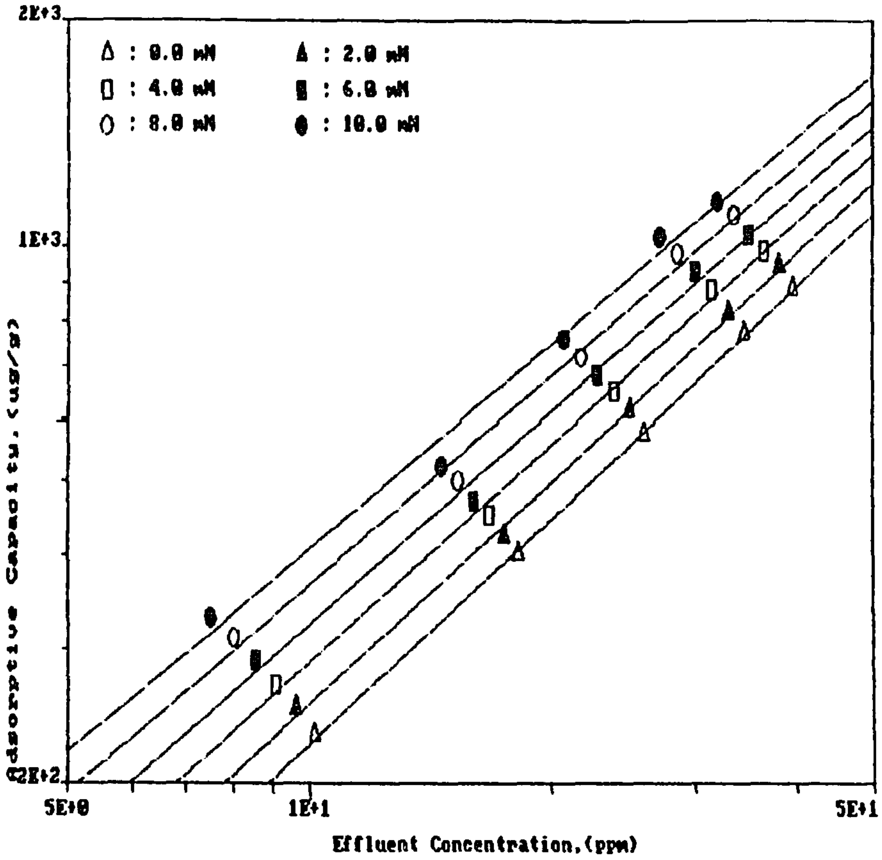
THE REGRESSION POLYNOMIAL OF LINE  5 -

      ( 1.594E+00) + ( 8.823E-01)*X
      THE VARIANCE -   3.633E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

      ( 1.648E+00) + ( 8.605E-01)*X
      THE VARIANCE -   6.910E-05
```

Figure B14: Hudson Flyash, Benzene, CaCl2



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 1.363E+00) + ( 9.879E-01)*X
     THE VARIANCE  -   1.621E-05

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.435E+00) + ( 9.696E-01)*X
     THE VARIANCE  -   8.057E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.512E+00) + ( 9.476E-01)*X
     THE VARIANCE  -   1.212E-04

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.584E+00) + ( 9.251E-01)*X
     THE VARIANCE  -   2.548E-04

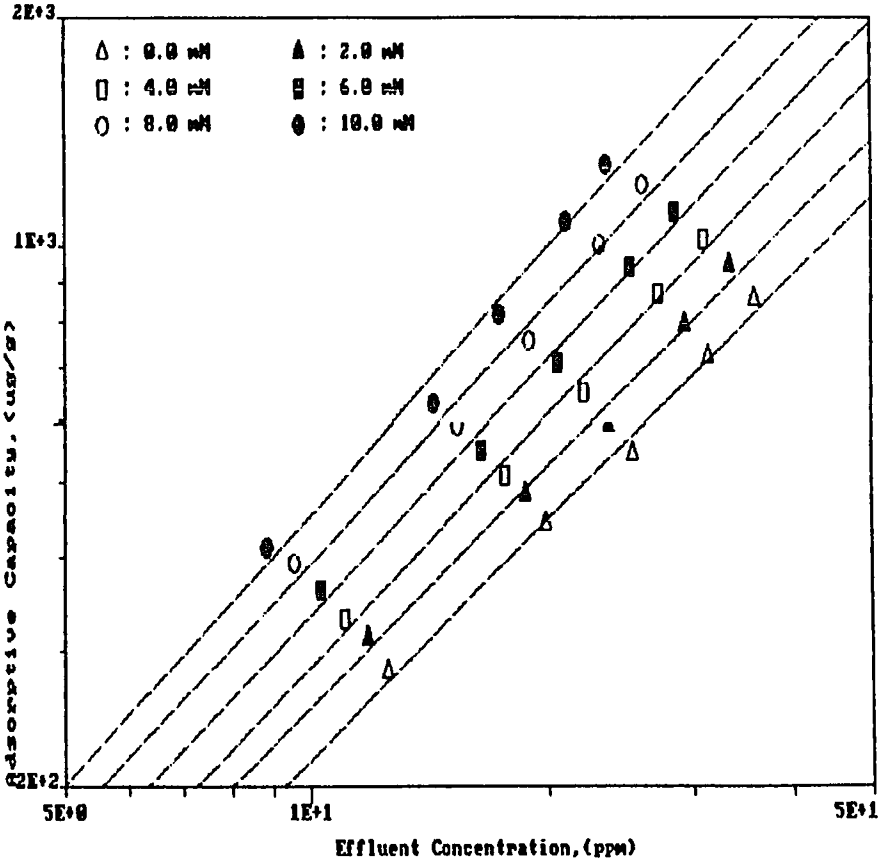
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.657E+00) + ( 9.044E-01)*X
     THE VARIANCE  -   3.036E-04

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.725E+00) + ( 8.839E-01)*X
     THE VARIANCE  -   4.672E-04
```

Figure B15: Hudson Flyash, Benzene, AlCl3



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 1.292E+00) + ( 1.043E+00)*X
     THE VARIANCE -   1.967E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.351E+00) + ( 1.051E+00)*X
     THE VARIANCE -   2.852E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.361E+00) + ( 1.094E+00)*X
     THE VARIANCE -   2.708E-04

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.415E+00) + ( 1.106E+00)*X
     THE VARIANCE -   3.428E-04

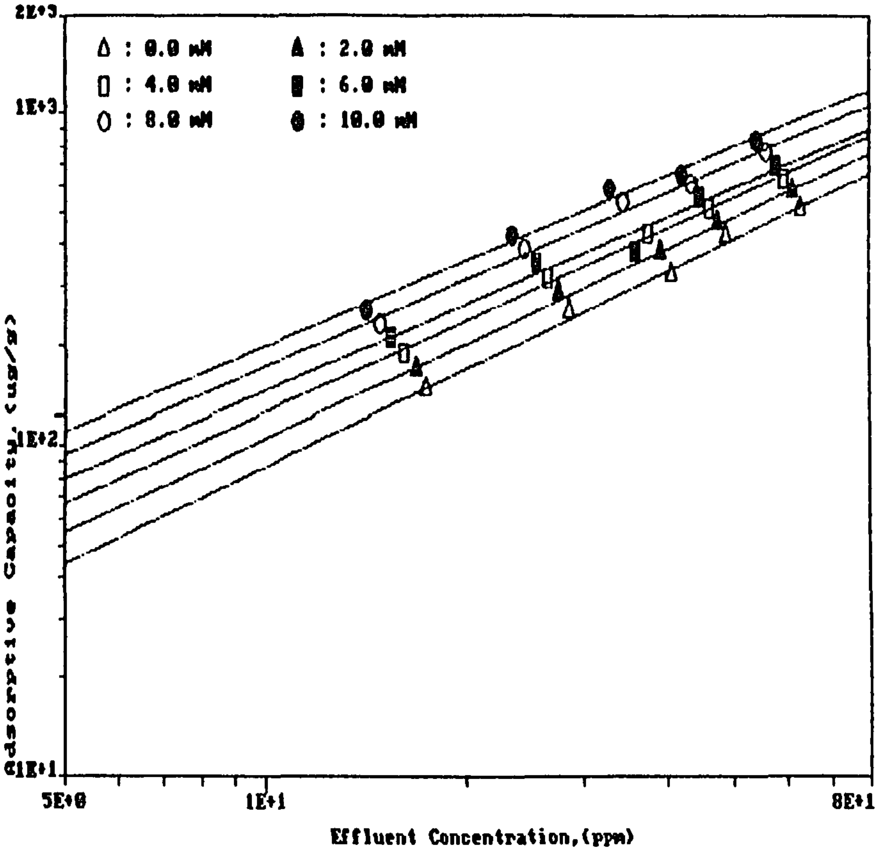
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.470E+00) + ( 1.119E+00)*X
     THE VARIANCE -   4.960E-04

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.495E+00) + ( 1.156E+00)*X
     THE VARIANCE -   5.158E-04
```

Figure B16: Hudson Flyash, Phenol, NaCl



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 9.665E-01) + ( 9.714E-01)*X
     THE VARIANCE -   1.915E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.079E+00) + ( 9.437E-01)*X
     THE VARIANCE -   1.236E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.183E+00) + ( 9.175E-01)*X
     THE VARIANCE -   1.364E-04

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.292E+00) + ( 8.714E-01)*X
     THE VARIANCE -   1.088E-03

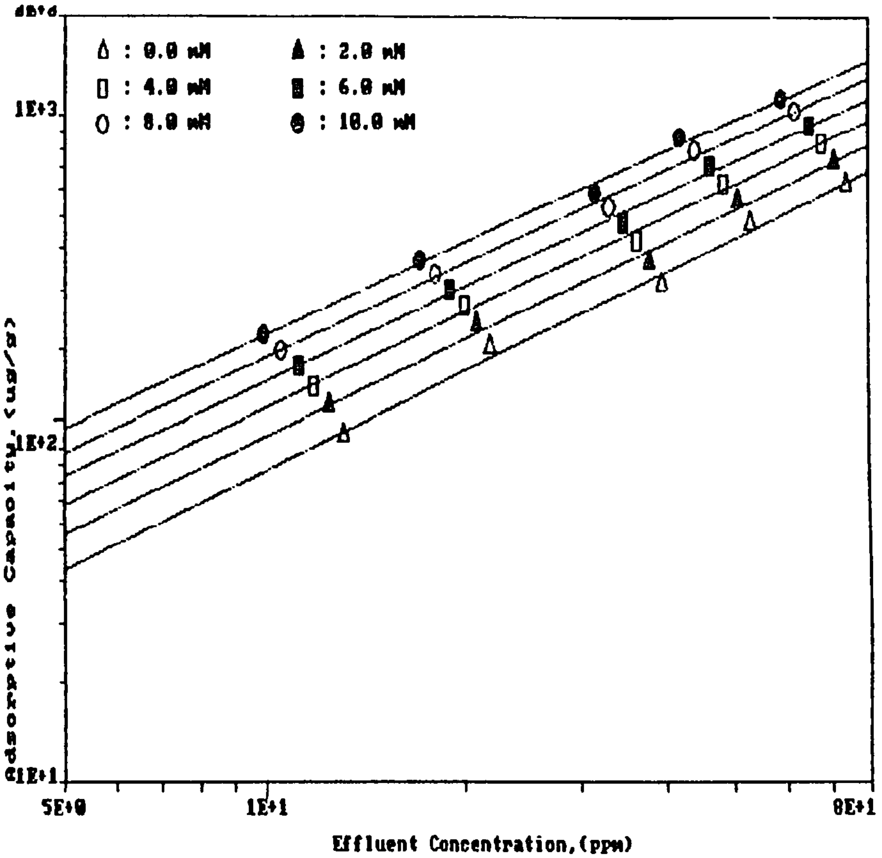
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.364E+00) + ( 8.731E-01)*X
     THE VARIANCE -   2.875E-04

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.444E+00) + ( 8.543E-01)*X
     THE VARIANCE -   4.242E-04
```

Figure B17: Hudson Flyash, Phenol, CaCl2



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 9.497E-01) + ( 9.852E-01)*X
     THE VARIANCE -  4.721E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.070E+00) + ( 9.655E-01)*X
     THE VARIANCE -  3.707E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.170E+00) + ( 9.524E-01)*X
     THE VARIANCE -  3.401E-04

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.259E+00) + ( 9.412E-01)*X
     THE VARIANCE -  3.022E-04

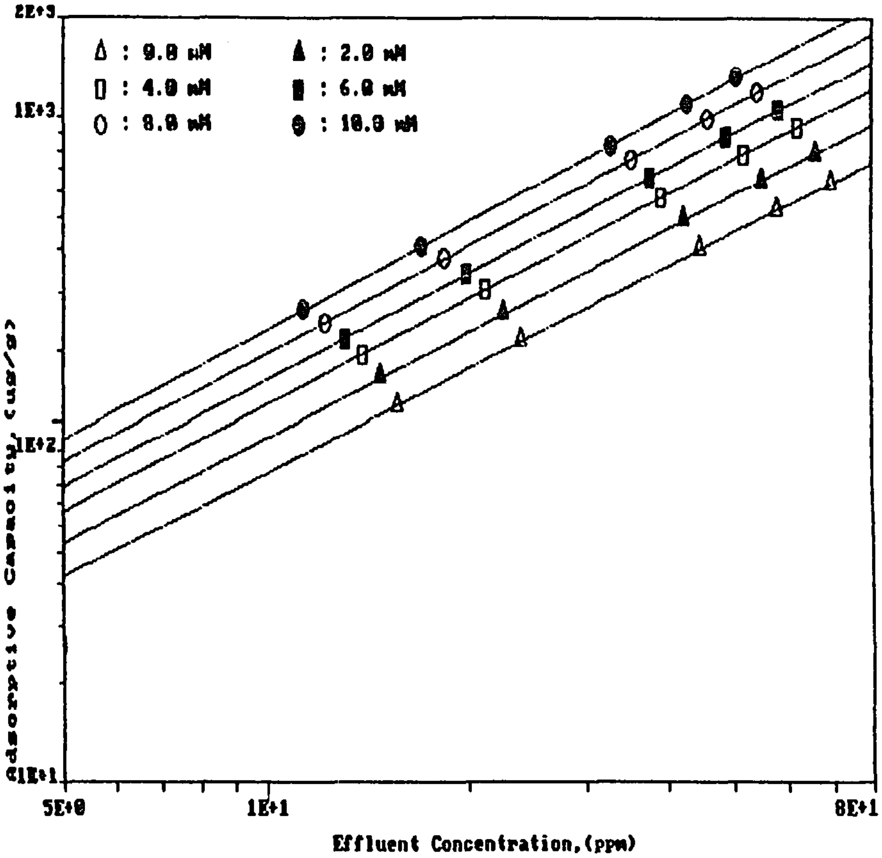
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.338E+00) + ( 9.340E-01)*X
     THE VARIANCE -  3.050E-04

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.416E+00) + ( 9.242E-01)*X
     THE VARIANCE -  3.082E-04
```

Figure B18: Hudson Flyash, Phenol, AlCl3



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 9.023E-01) + ( 1.030E+00)*X
     THE VARIANCE -   1.110E-06

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 9.993E-01) + ( 1.037E+00)*X
     THE VARIANCE -   3.743E-07

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.090E+00) + ( 1.046E+00)*X
     THE VARIANCE -   4.214E-07

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.150E+00) + ( 1.059E+00)*X
     THE VARIANCE -   5.350E-07

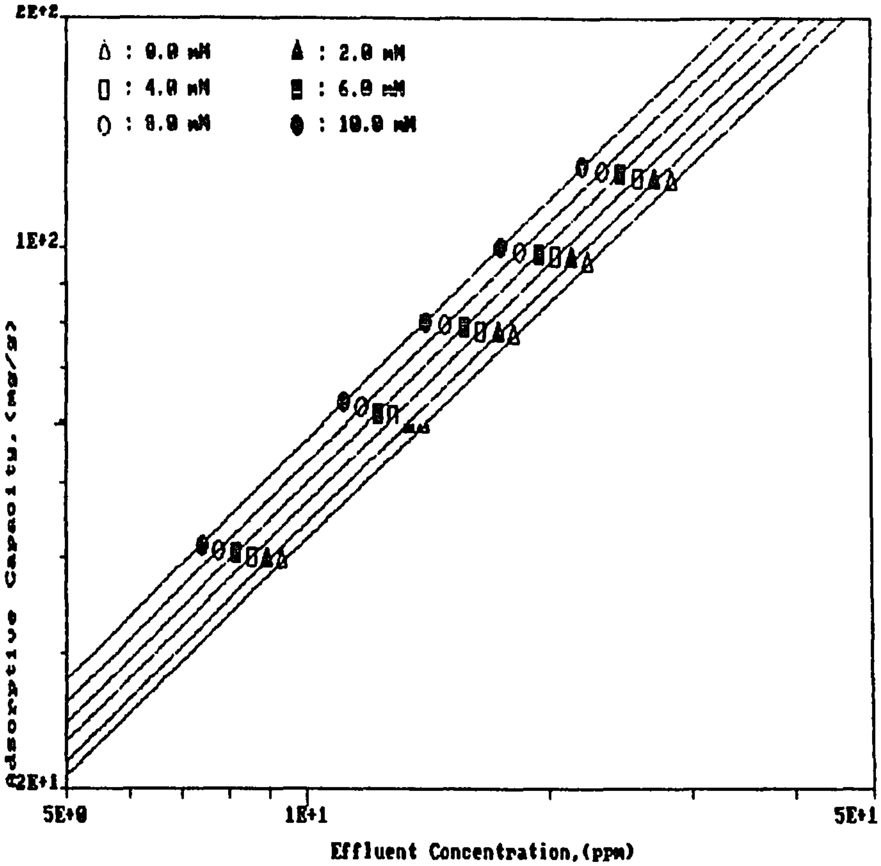
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.217E+00) + ( 1.070E+00)*X
     THE VARIANCE -   4.479E-07

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.279E+00) + ( 1.079E+00)*X
     THE VARIANCE -   3.235E-07
```

Figure B19: Activated Carbon, MIBK, NaCl



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 6.105E-01) + ( 1.013E+00)*X
     THE VARIANCE -  4.460E-07

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 6.234E-01) + ( 1.021E+00)*X
     THE VARIANCE -  3.021E-06

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 6.474E-01) + ( 1.023E+00)*X
     THE VARIANCE -  1.244E-08

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 6.694E-01) + ( 1.026E+00)*X
     THE VARIANCE -  2.056E-07

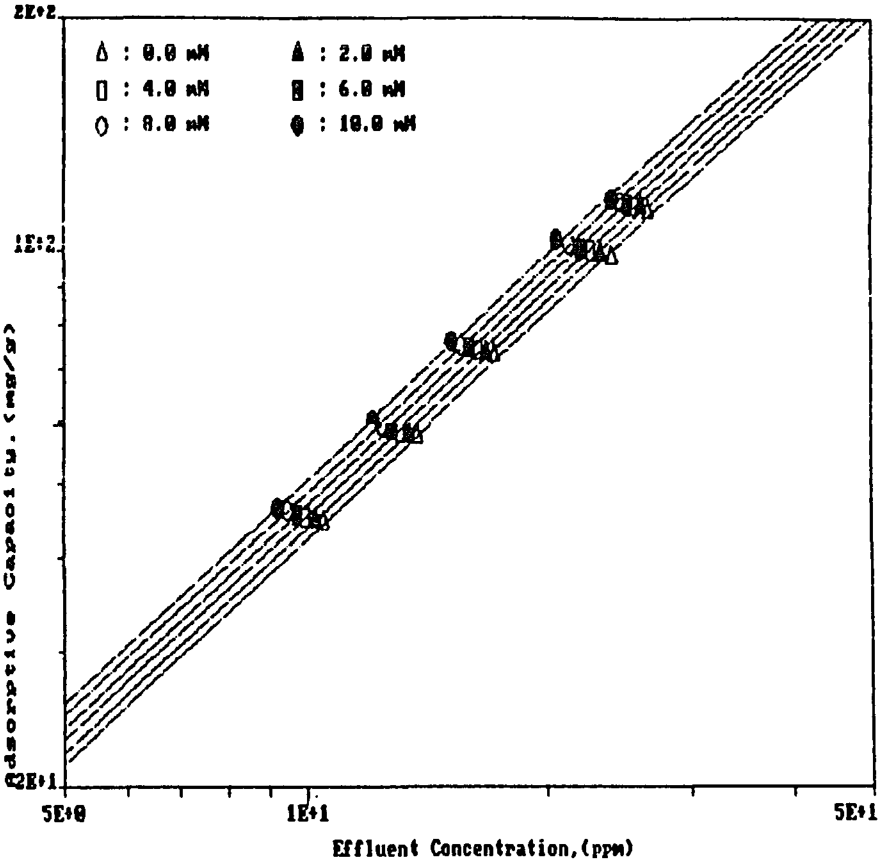
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 6.949E-01) + ( 1.028E+00)*X
     THE VARIANCE -  3.841E-07

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 7.205E-01) + ( 1.031E+00)*X
     THE VARIANCE -  3.415E-07
```

Figure B20: Activated Carbon, MIBK, CaCl2



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 6.520E-01) + ( 9.725E-01)*X
     THE VARIANCE -   3.360E-05

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 6.669E-01) + ( 9.723E-01)*X
     THE VARIANCE -   1.803E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 6.843E-01) + ( 9.701E-01)*X
     THE VARIANCE -   8.871E-06

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 6.999E-01) + ( 9.696E-01)*X
     THE VARIANCE -   7.472E-06

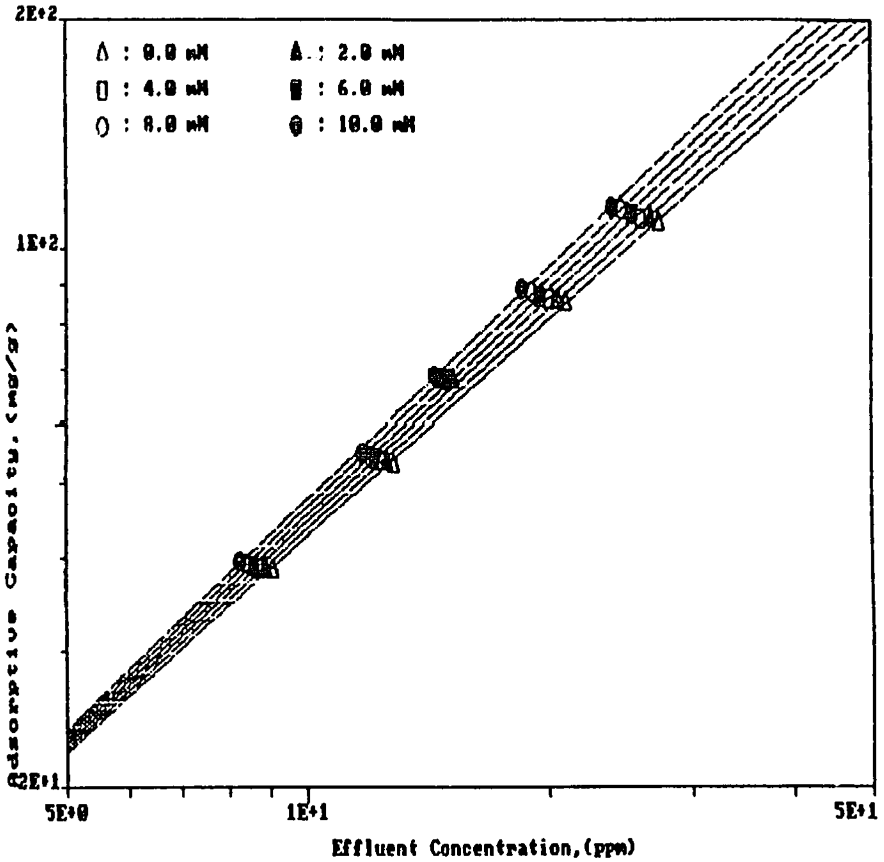
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 7.180E-01) + ( 9.672E-01)*X
     THE VARIANCE -   1.233E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 7.357E-01) + ( 9.653E-01)*X
     THE VARIANCE -   2.684E-05
```

Figure B21: Activated Carbon, MIBK, AlCl3



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 6.911E-01) + ( 9.362E-01)*X
     THE VARIANCE -  1.979E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 6.876E-01) + ( 9.486E-01)*X
     THE VARIANCE -  1.363E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 6.846E-01) + ( 9.607E-01)*X
     THE VARIANCE -  8.688E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 6.824E-01) + ( 9.725E-01)*X
     THE VARIANCE -  5.201E-05

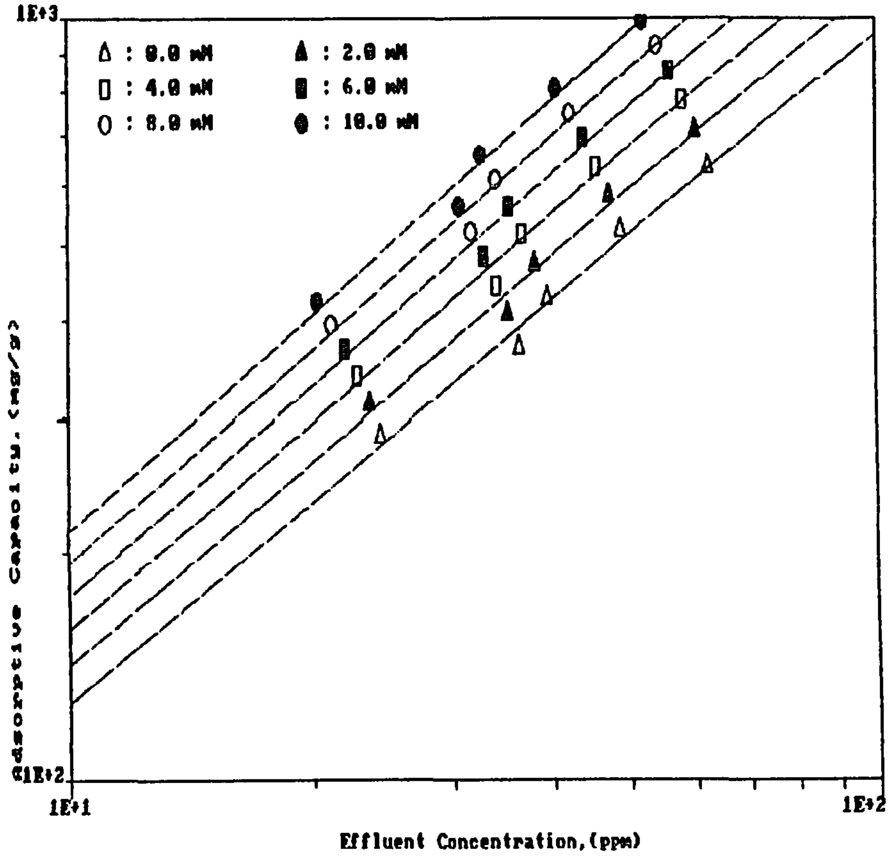
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 6.795E-01) + ( 9.853E-01)*X
     THE VARIANCE -  2.882E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 6.762E-01) + ( 9.986E-01)*X
     THE VARIANCE -  2.206E-05
```

Figure B22: Hudson Flyash, MIBK, NaCl



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 1.220E+00) + ( 8.799E-01)*X
     THE VARIANCE -   2.289E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.255E+00) + ( 8.941E-01)*X
     THE VARIANCE -   2.278E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.290E+00) + ( 9.057E-01)*X
     THE VARIANCE -   2.351E-04

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.323E+00) + ( 9.170E-01)*X
     THE VARIANCE -   2.359E-04

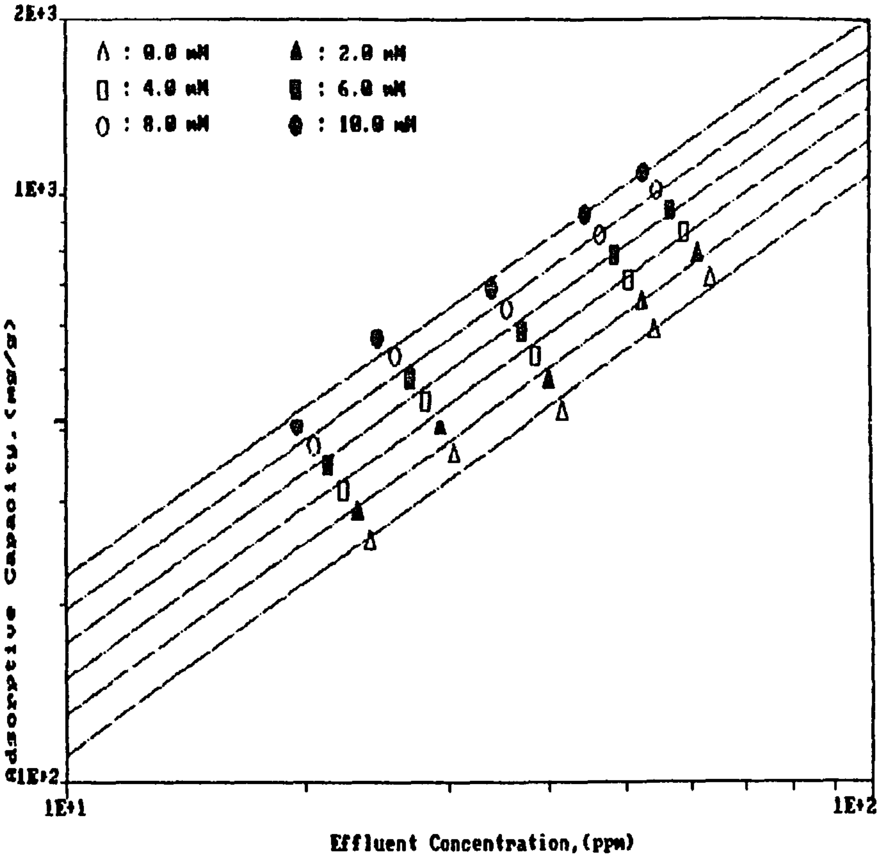
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.359E+00) + ( 9.253E-01)*X
     THE VARIANCE -   2.479E-04

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.395E+00) + ( 9.329E-01)*X
     THE VARIANCE -   2.574E-04
```

Figure B23: Hudson Flyash, MIBK, CaCl2



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 1.040E+00) + ( 9.847E-01)*X
     THE VARIANCE -  4.833E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.137E+00) + ( 9.769E-01)*X
     THE VARIANCE -  4.360E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.208E+00) + ( 9.698E-01)*X
     THE VARIANCE -  4.038E-04

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.277E+00) + ( 9.620E-01)*X
     THE VARIANCE -  3.844E-04

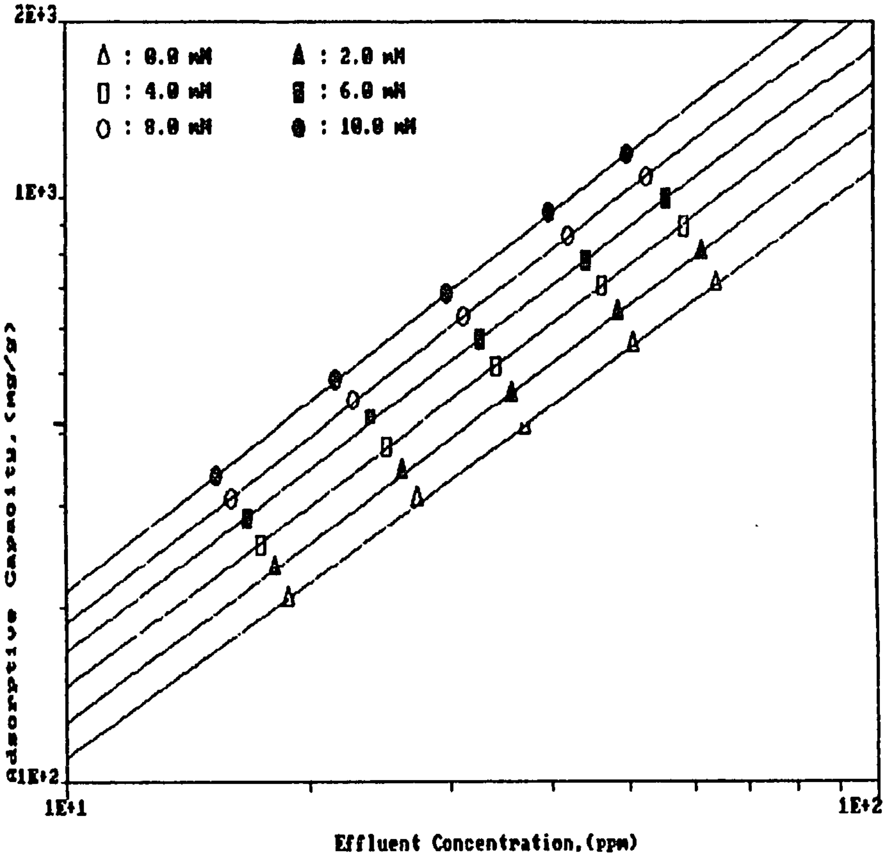
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.340E+00) + ( 9.557E-01)*X
     THE VARIANCE -  3.756E-04

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.401E+00) + ( 9.498E-01)*X
     THE VARIANCE -  3.786E-04
```

Figure B24: Hudson Flyash, MIBK, AlCl3



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THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 1.046E+00) + ( 9.970E-01)*X
     THE VARIANCE -   1.700E-05

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 1.090E+00) + ( 1.014E+00)*X
     THE VARIANCE -   4.263E-06

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 1.140E+00) + ( 1.025E+00)*X
     THE VARIANCE -   6.574E-06

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 1.199E+00) + ( 1.028E+00)*X
     THE VARIANCE -   1.512E-06

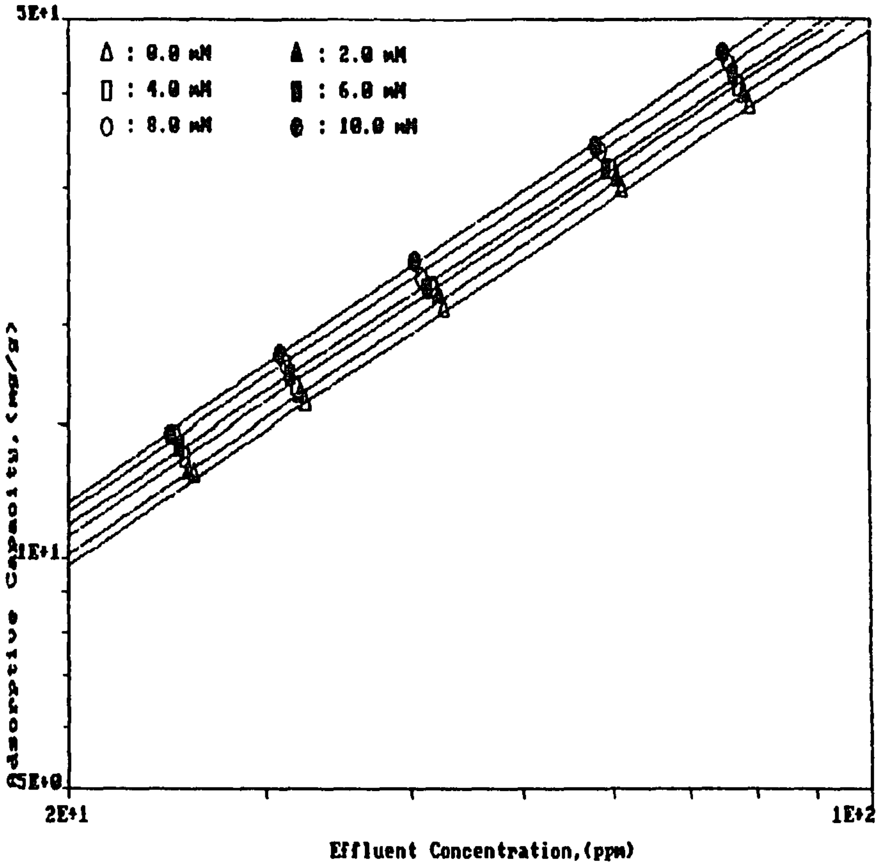
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.223E+00) + ( 1.052E+00)*X
     THE VARIANCE -   4.694E-06

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.270E+00) + ( 1.061E+00)*X
     THE VARIANCE -   [illegible]
```

Figure B25: Activated Carbon, IPA, NaCl



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THE REGRESSION POLYNOMIAL OF LINE  1 -

     (-3.023E-01) + ( 9.942E-01)*X
     THE VARIANCE -  5.076E-06

THE REGRESSION POLYNOMIAL OF LINE  2 -

     (-3.104E-01) + ( 1.010E+00)*X
     THE VARIANCE -  1.067E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     (-2.752E-01) + ( 1.001E+00)*X
     THE VARIANCE -  1.597E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     (-2.501E-01) + ( 9.935E-01)*X
     THE VARIANCE -  2.806E-05

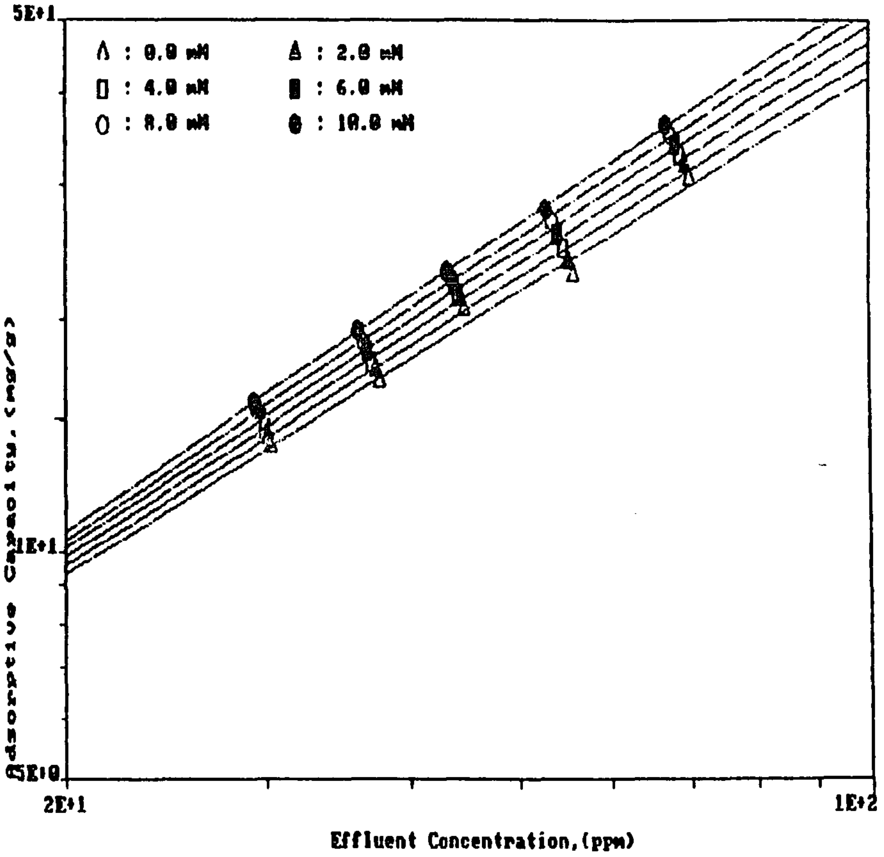
THE REGRESSION POLYNOMIAL OF LINE  5 -

     (-2.411E-01) + ( 1.000E+00)*X
     THE VARIANCE -  1.588E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     (-2.435E-01) + ( 1.012E+00)*X
     THE VARIANCE -  9.199E-06
```

Figure B26: Activated Carbon, IPA, CaCl2



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THE REGRESSION POLYNOMIAL OF LINE  1 -

      (-2.370E-01) + ( 9.276E-01)*X
      THE VARIANCE -  2.318E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

      (-2.507E-01) + ( 9.466E-01)*X
      THE VARIANCE -  1.512E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

      (-2.622E-01) + ( 9.641E-01)*X
      THE VARIANCE -  9.100E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

      (-2.712E-01) + ( 9.800E-01)*X
      THE VARIANCE -  4.536E-05

THE REGRESSION POLYNOMIAL OF LINE  5 -

      (-2.805E-01) + ( 9.958E-01)*X
      THE VARIANCE -  1.832E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

      (-2.880E-01) + ( 1.010E+00)*X
      THE VARIANCE -  5.429E-06
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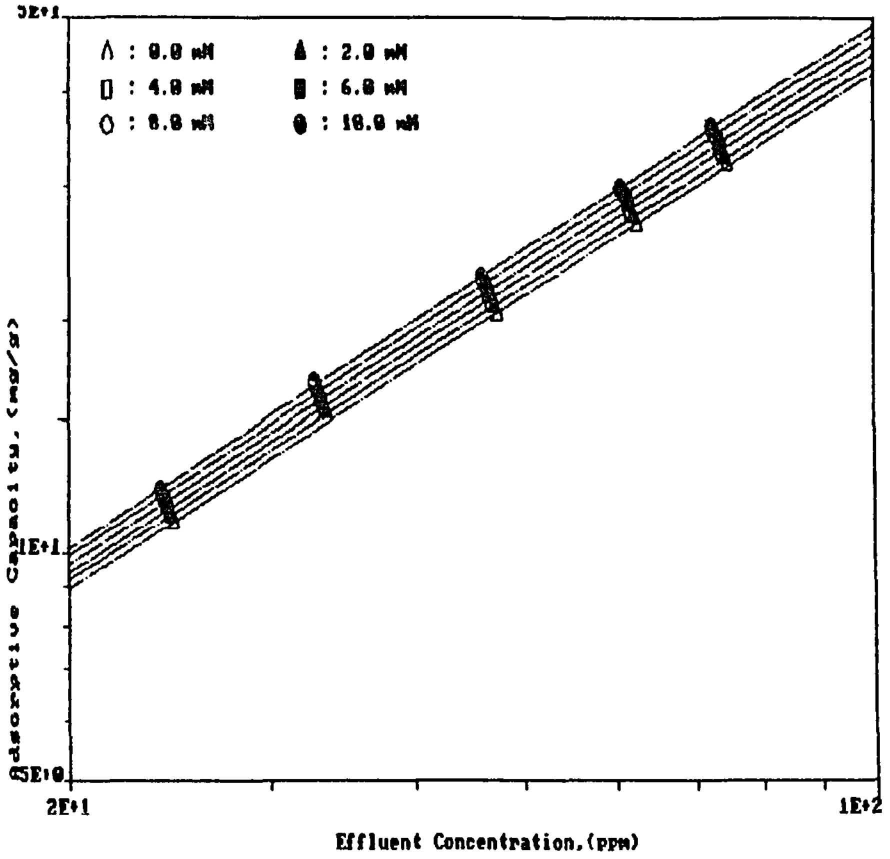

Figure B27: Activated Carbon, IPA, AlCl3

```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     (-3.014E-01) + ( 9.628E-01)*X
     THE VARIANCE -   4.381E-06

THE REGRESSION POLYNOMIAL OF LINE  2 -

     (-2.959E-01) + ( 9.670E-01)*X
     THE VARIANCE -   4.256E-06

THE REGRESSION POLYNOMIAL OF LINE  3 -

     (-2.900E-01) + ( 9.708E-01)*X
     THE VARIANCE -   4.051E-06

THE REGRESSION POLYNOMIAL OF LINE  4 -

     (-2.825E-01) + ( 9.736E-01)*X
     THE VARIANCE -   3.352E-06

THE REGRESSION POLYNOMIAL OF LINE  5 -

     (-2.768E-01) + ( 9.773E-01)*X
     THE VARIANCE -   3.260E-06

THE REGRESSION POLYNOMIAL OF LINE  6 -

     (-2.709E-01) + ( 9.808E-01)*X
     THE VARIANCE -   3.246E-06
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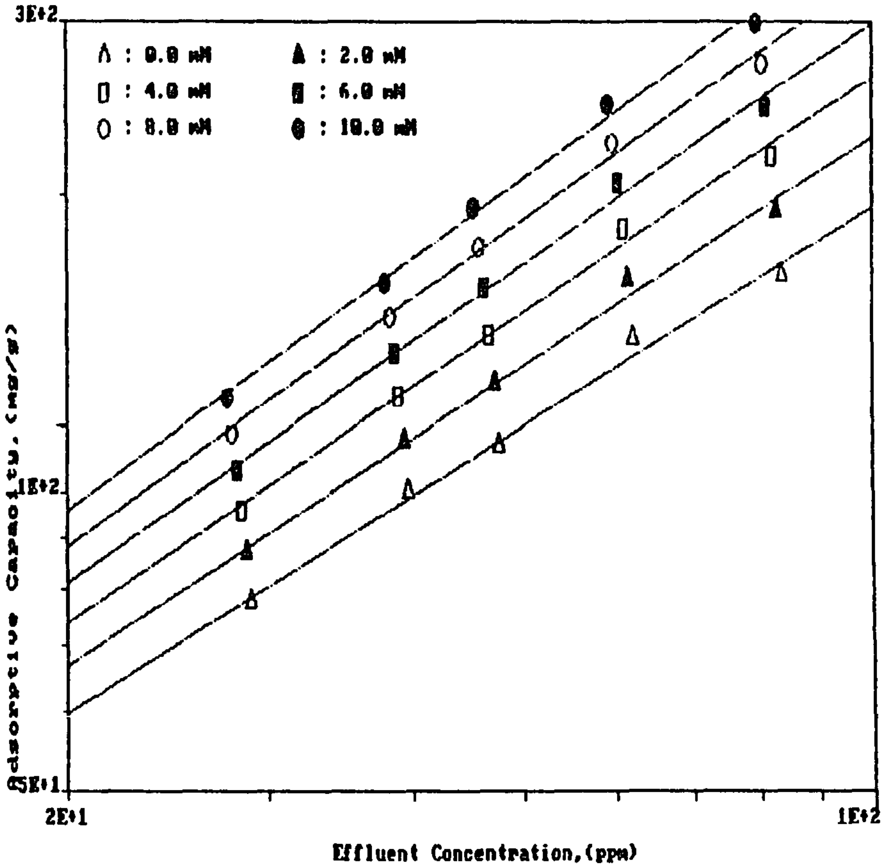
Figure B28: Hudson Flyash, IPA, NaCl



```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 8.267E-01) + ( 7.305E-01)*X
     THE VARIANCE -  1.104E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 8.336E-01) + ( 7.620E-01)*X
     THE VARIANCE -  8.862E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 8.433E-01) + ( 7.880E-01)*X
     THE VARIANCE -  8.469E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 8.576E-01) + ( 8.082E-01)*X
     THE VARIANCE -  8.135E-05

THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 8.736E-01) + ( 8.252E-01)*X
     THE VARIANCE -  8.517E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 8.919E-01) + ( 8.386E-01)*X
     THE VARIANCE -  8.625E-05
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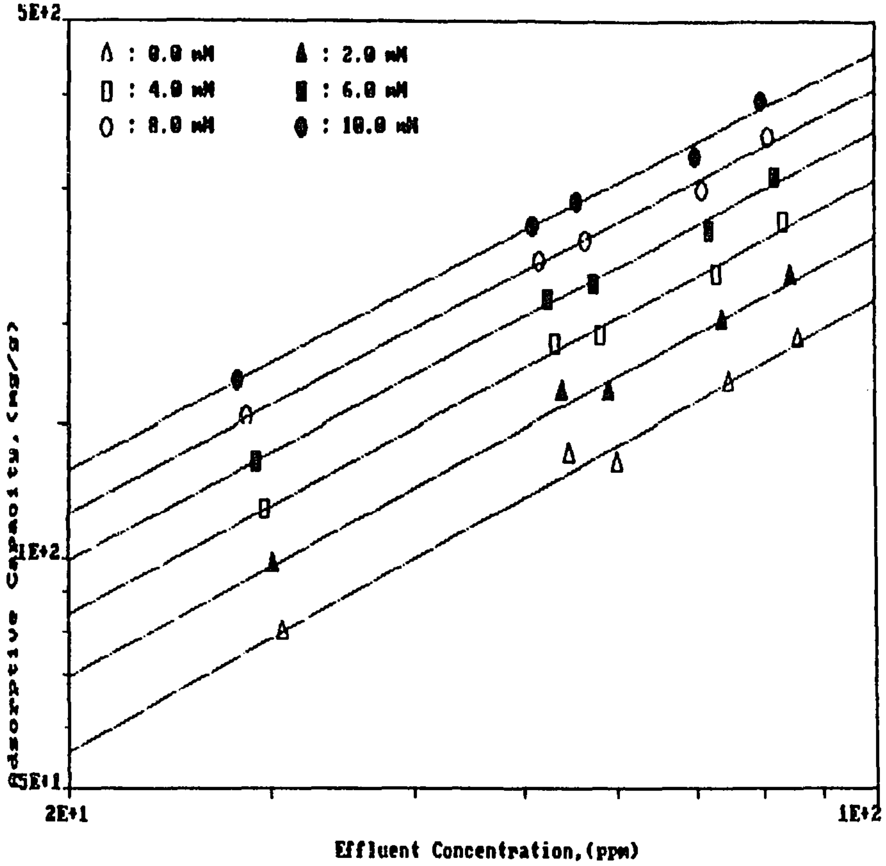


Figure B29: Hudson Flyash, IPA, CaCl2

```
THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 6.578E-01) + ( 8.362E-01)*X
     THE VARIANCE -  2.329E-04

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 7.817E-01) + ( 8.164E-01)*X
     THE VARIANCE -  1.063E-04

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 8.802E-01) + ( 8.036E-01)*X
     THE VARIANCE -  7.255E-05

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 9.626E-01) + ( 7.939E-01)*X
     THE VARIANCE -  6.564E-05

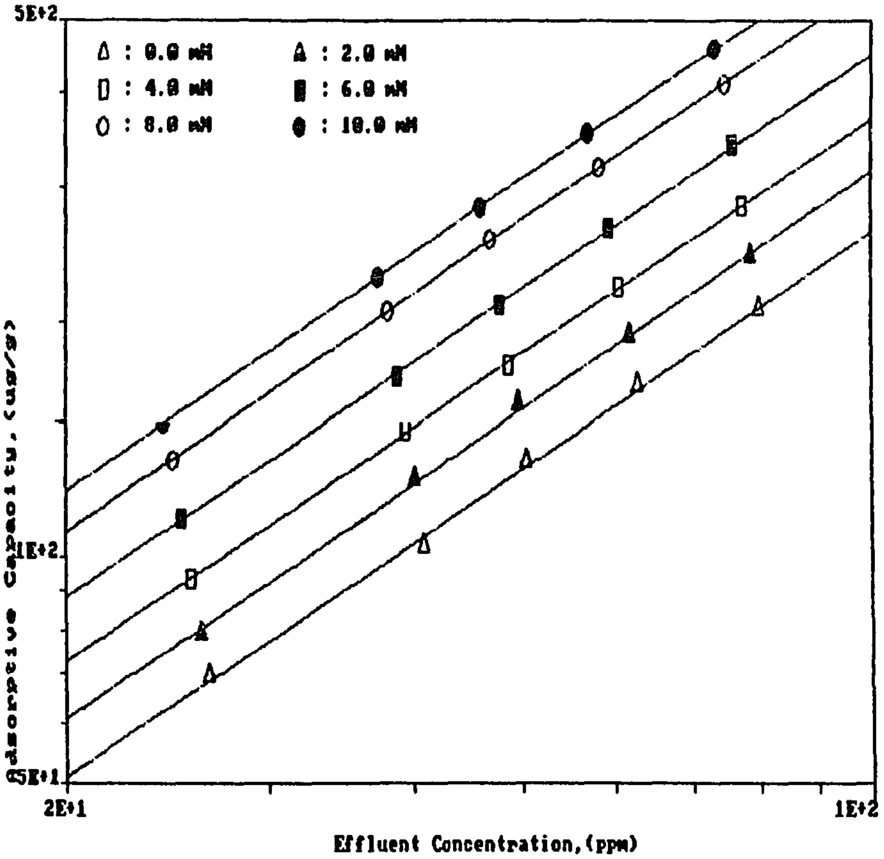
THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 1.038E+00) + ( 7.842E-01)*X
     THE VARIANCE -  7.126E-05

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 1.104E+00) + ( 7.766E-01)*X
     THE VARIANCE -  8.759E-05
```

Figure B30: Hudson Flyash, IPA, AlCl3



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THE REGRESSION POLYNOMIAL OF LINE  1 -

     ( 3.871E-01) + ( 1.016E+00)*X
     THE VARIANCE -  6.569E-05

THE REGRESSION POLYNOMIAL OF LINE  2 -

     ( 4.494E-01) + ( 1.025E+00)*X
     THE VARIANCE -  3.215E-05

THE REGRESSION POLYNOMIAL OF LINE  3 -

     ( 5.448E-01) + ( 1.012E+00)*X
     THE VARIANCE -  9.555E-06

THE REGRESSION POLYNOMIAL OF LINE  4 -

     ( 6.278E-01) + ( 1.012E+00)*X
     THE VARIANCE -  4.918E-06

THE REGRESSION POLYNOMIAL OF LINE  5 -

     ( 7.028E-01) + ( 1.021E+00)*X
     THE VARIANCE -  2.412E-06

THE REGRESSION POLYNOMIAL OF LINE  6 -

     ( 7.580E-01) + ( 1.020E+00)*X
     THE VARIANCE -  2.526E-06
```

APPENDIX - 'C'

EFFECT OF INORGANIC SALTS ON ADSORPTIVE CAPACITY

Fig. C1

Activated Carbon, Toluene, Eff., 10ppm

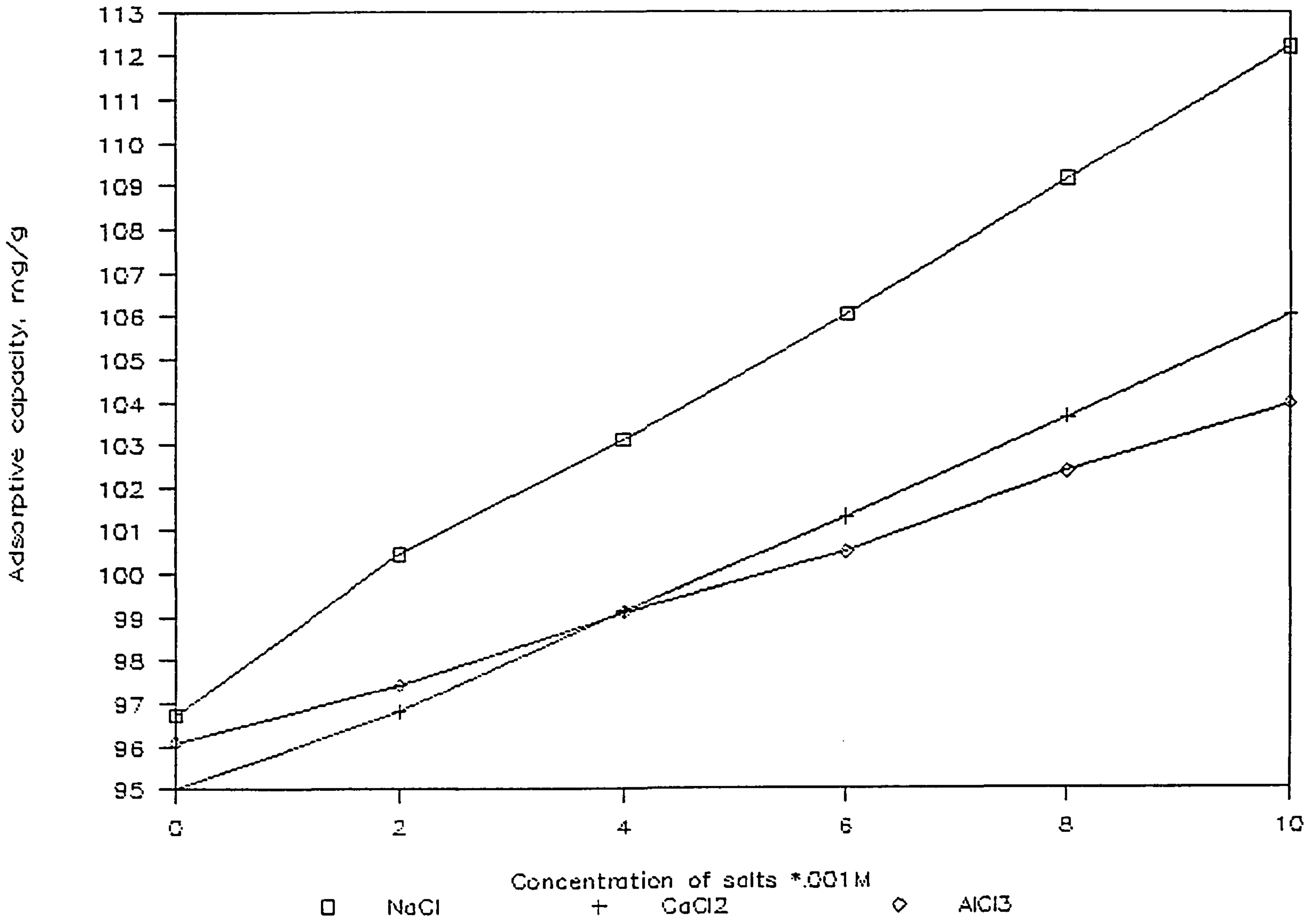


Fig. C2

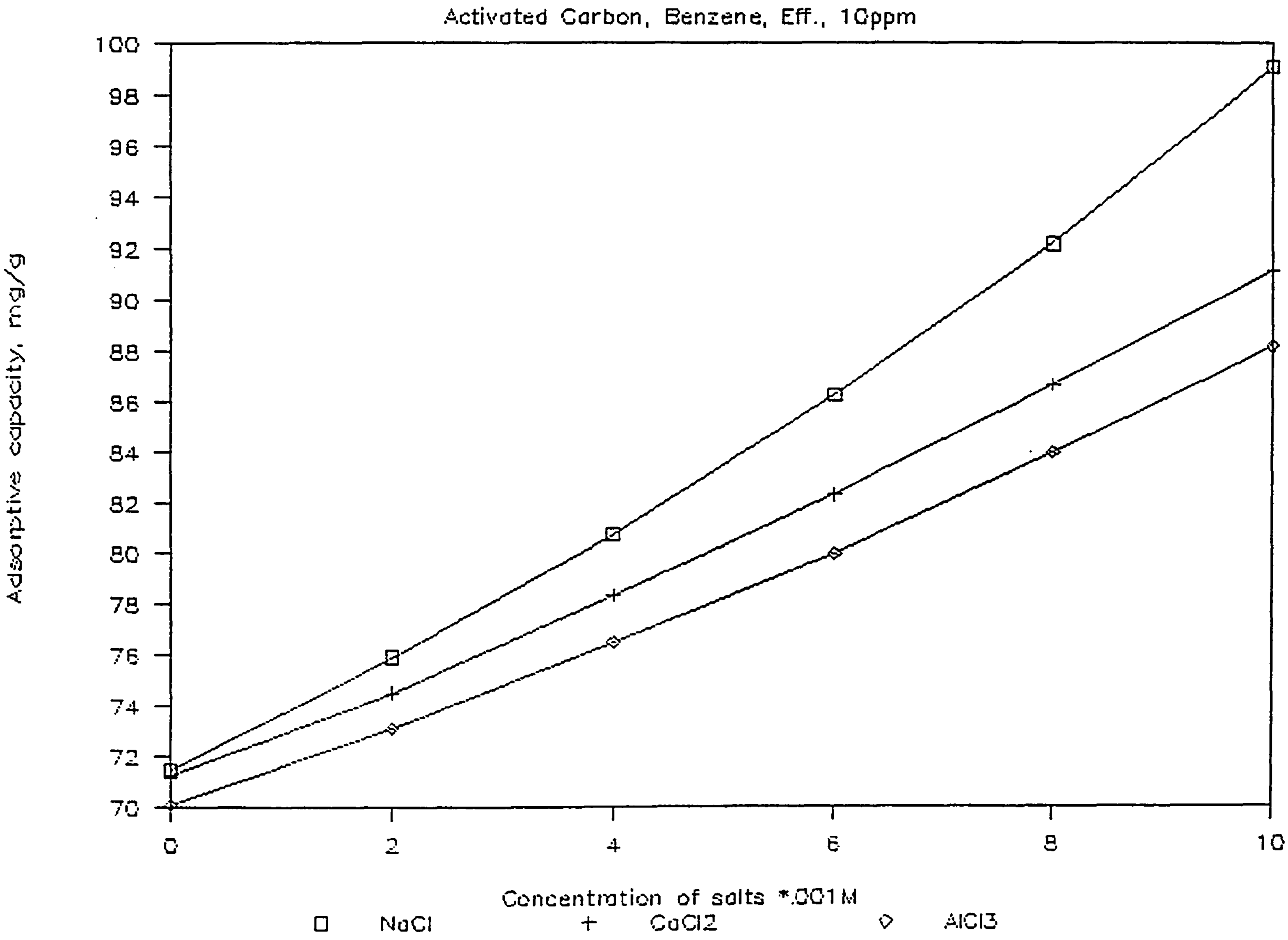

Activated Carbon, Benzene, Eff., 10ppm
Adsorptive capacity, mg/g
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
0
2
4
6
8
10
Concentration of salts *.001M
□ NaCl
+ CaCl2
◇ AlCl3

Fig. C3

Activated Carbon, Phenol, Eff., 10ppm

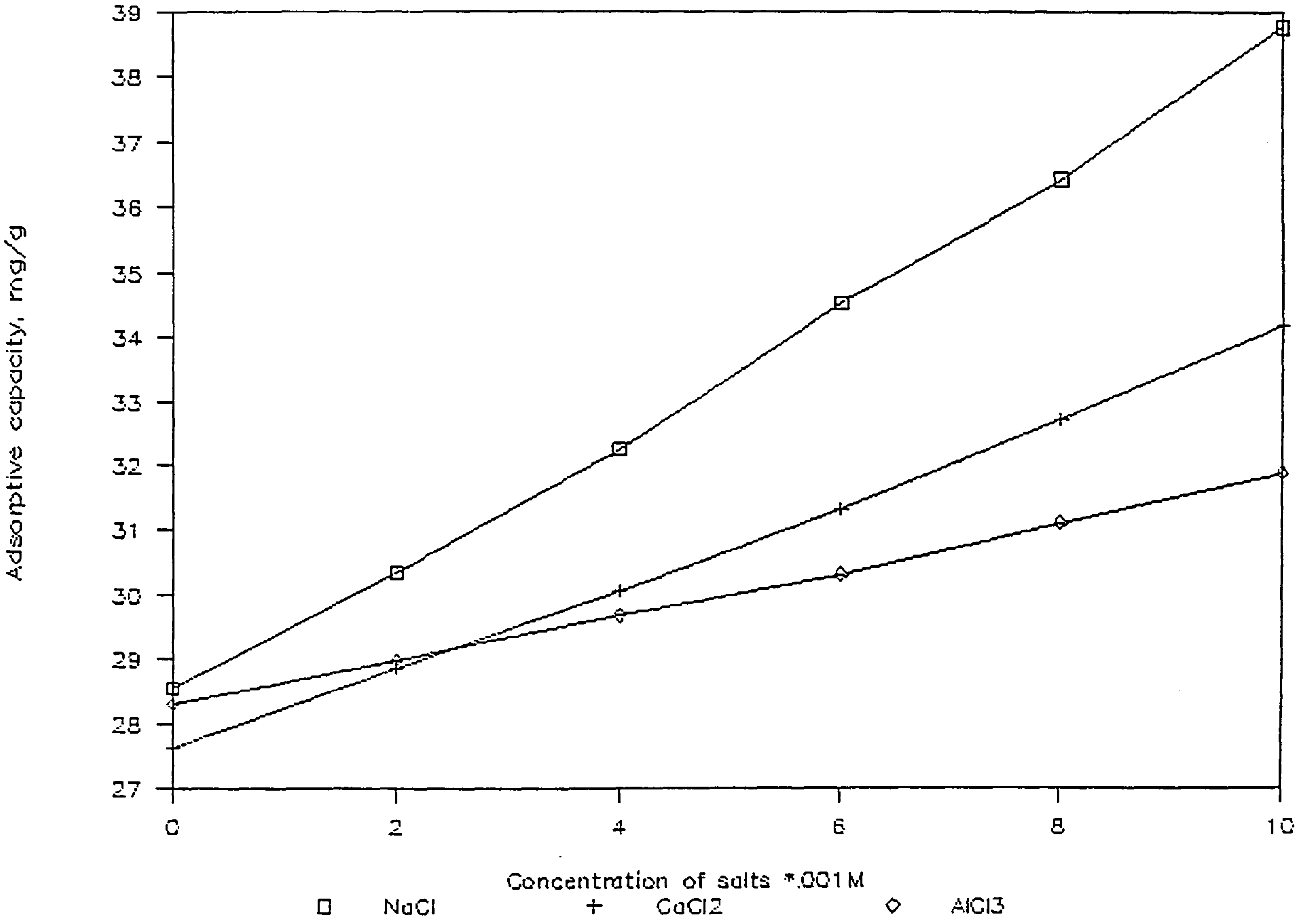


Fig. C4

Hudson Flyash, Toluene, Eff., 30ppm

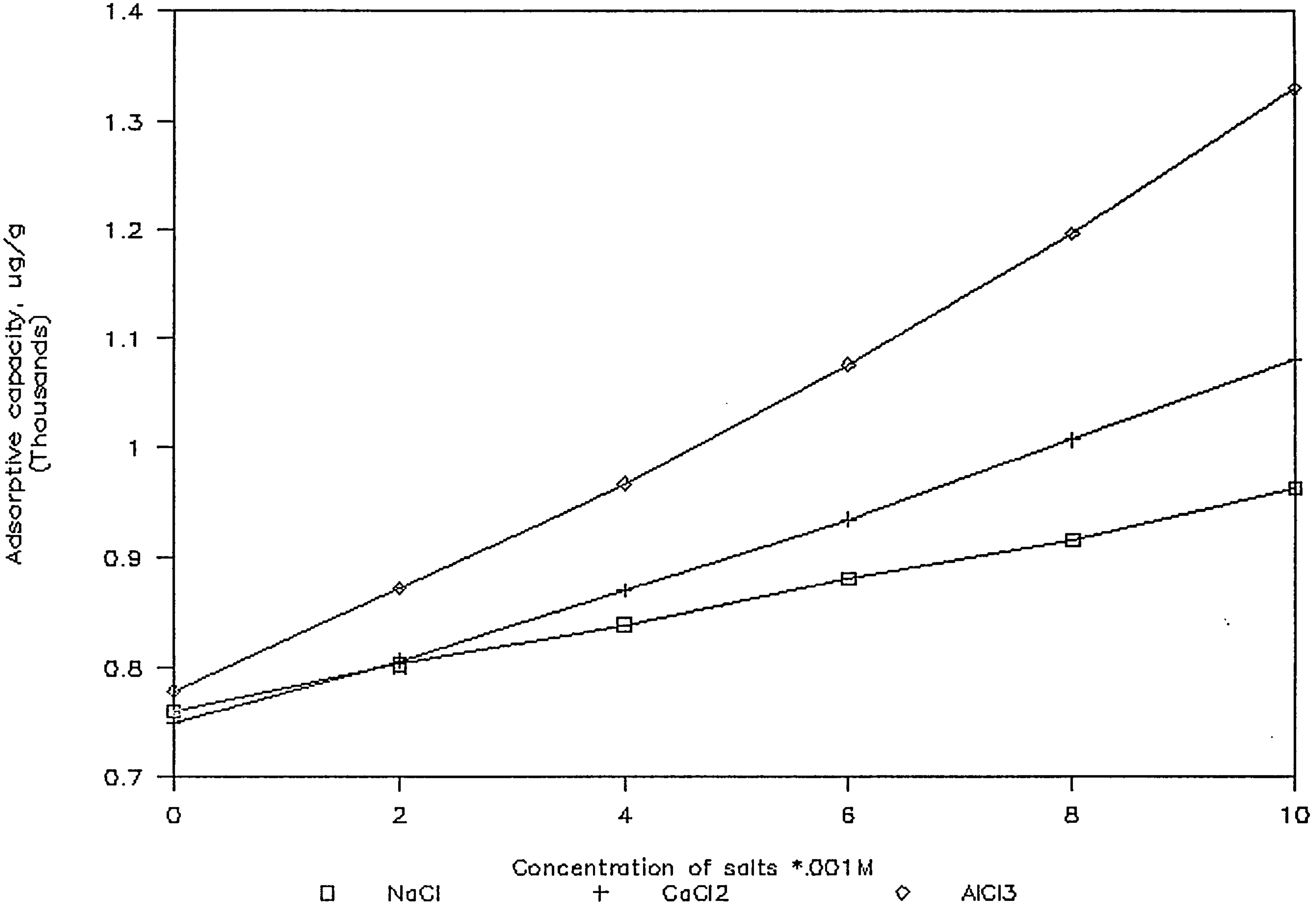


Fig. C5

Hudson Flyash, Benzene, Eff., 30ppm

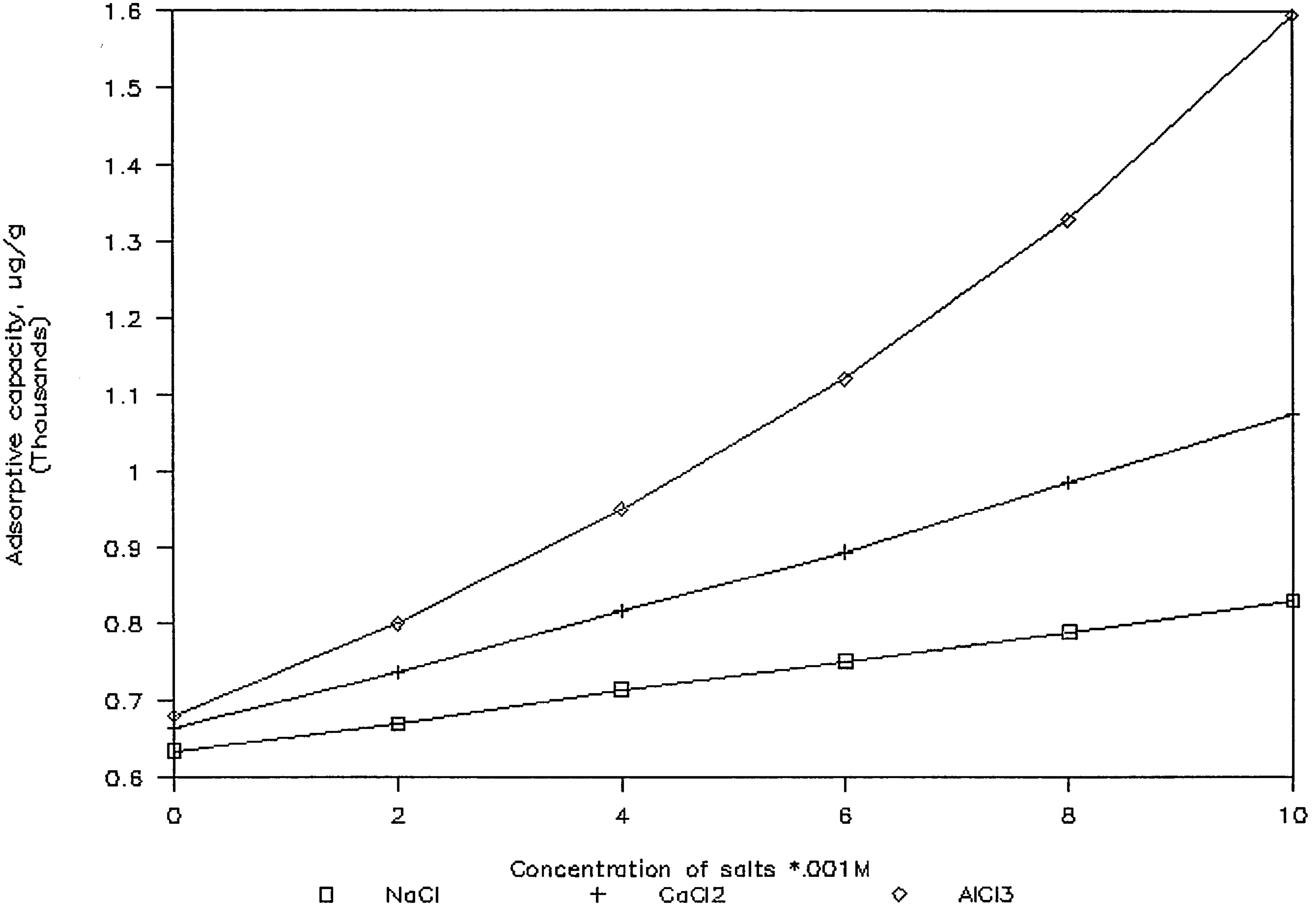


Fig. C6

Hudson Flyash, Phenol, Eff., 30ppm

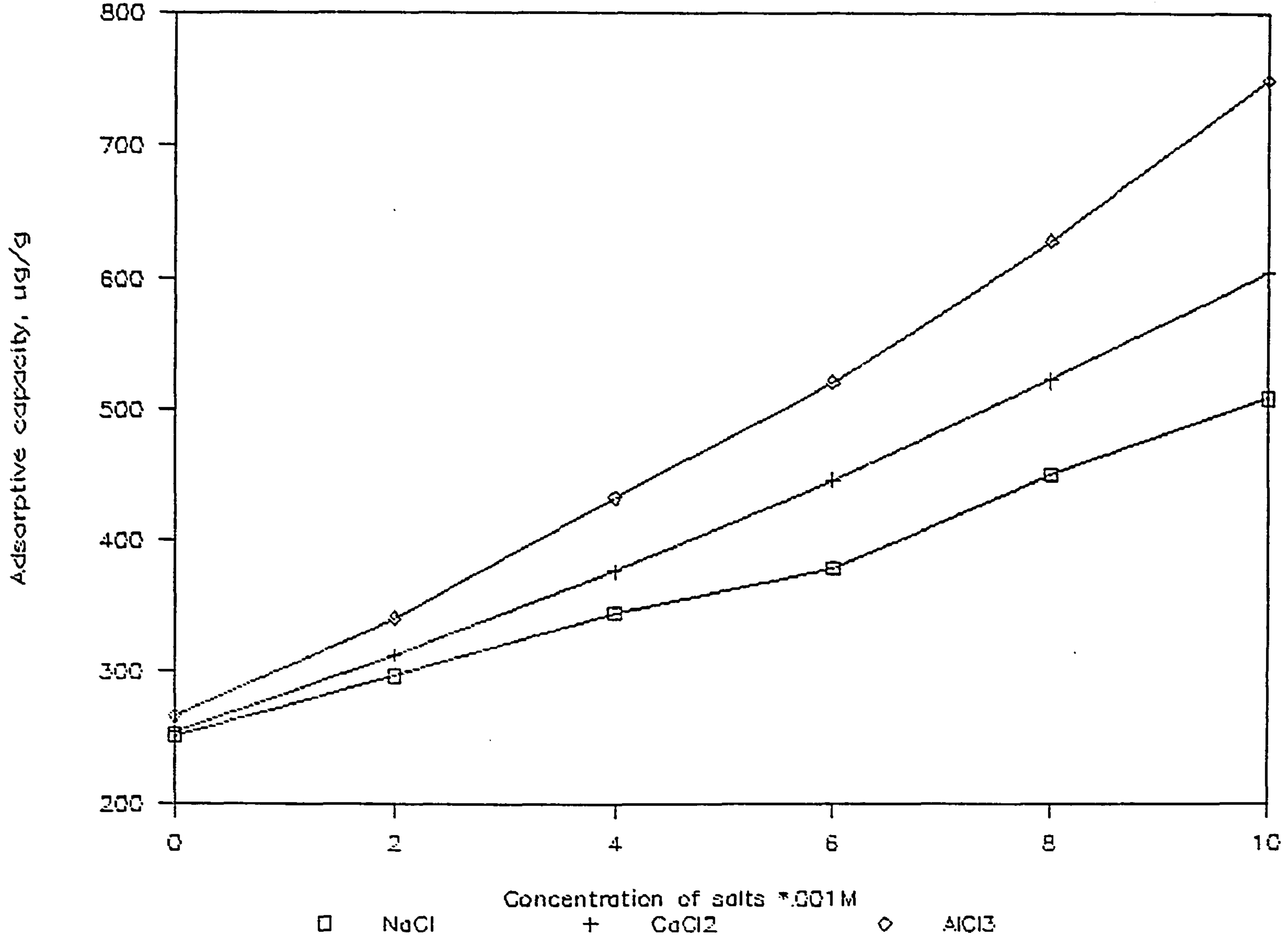


Fig. C7

Activated Carbon, MIBK, Eff., 10ppm

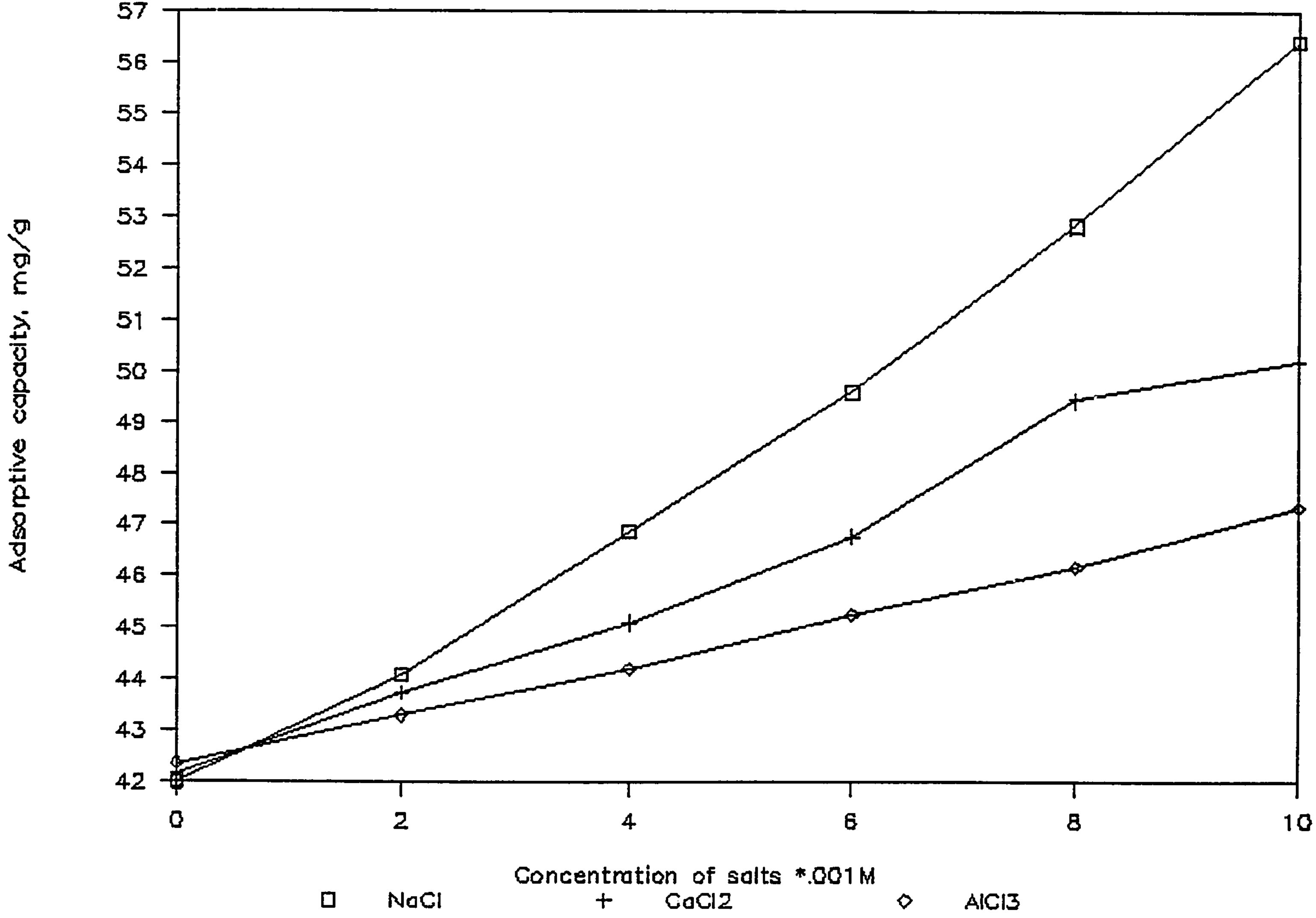


Fig. C8

Activated Carbon, IPA, Eff., 10ppm

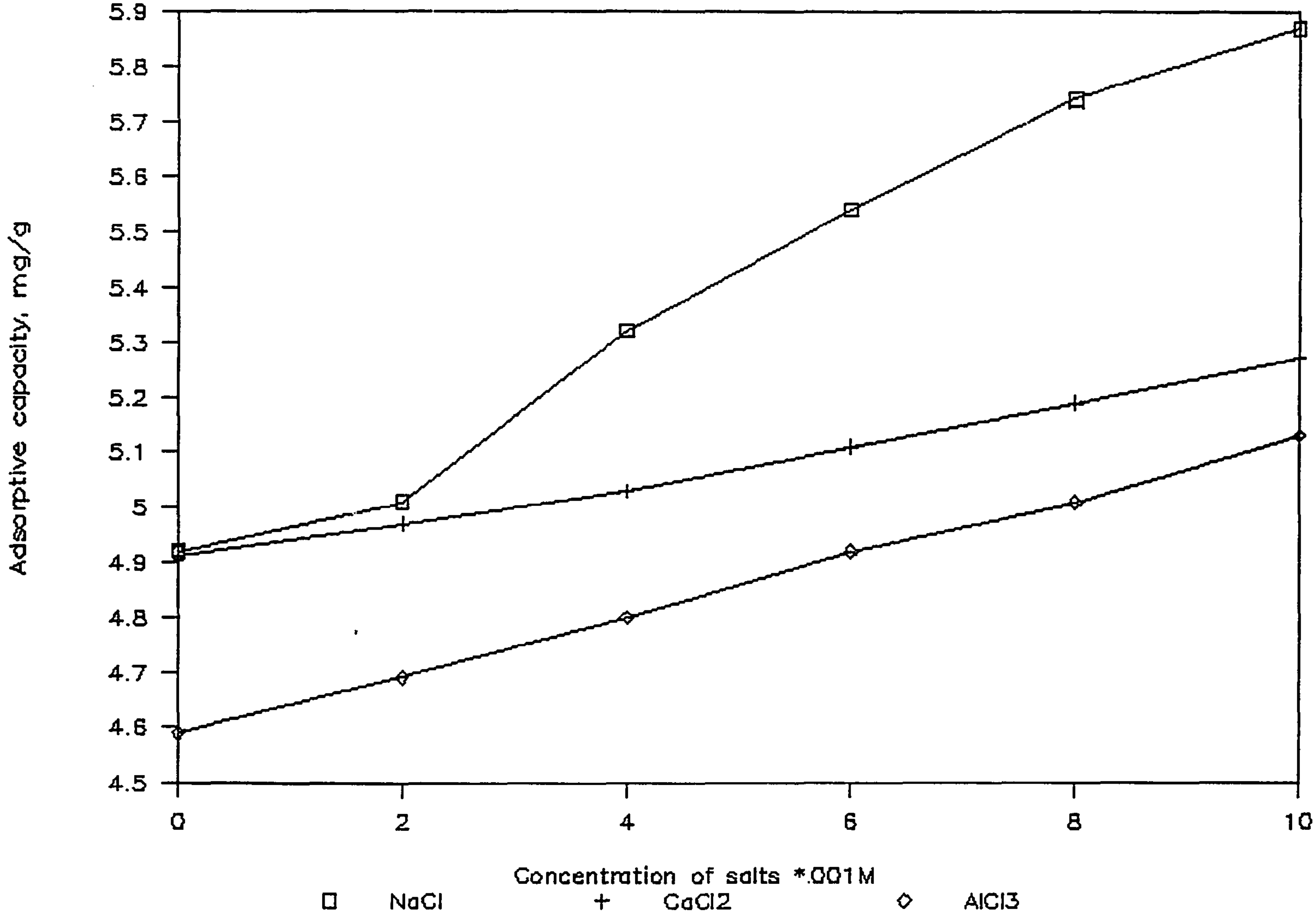


Fig. C9

Hudson Flyash, MIBK, Eff., 30ppm

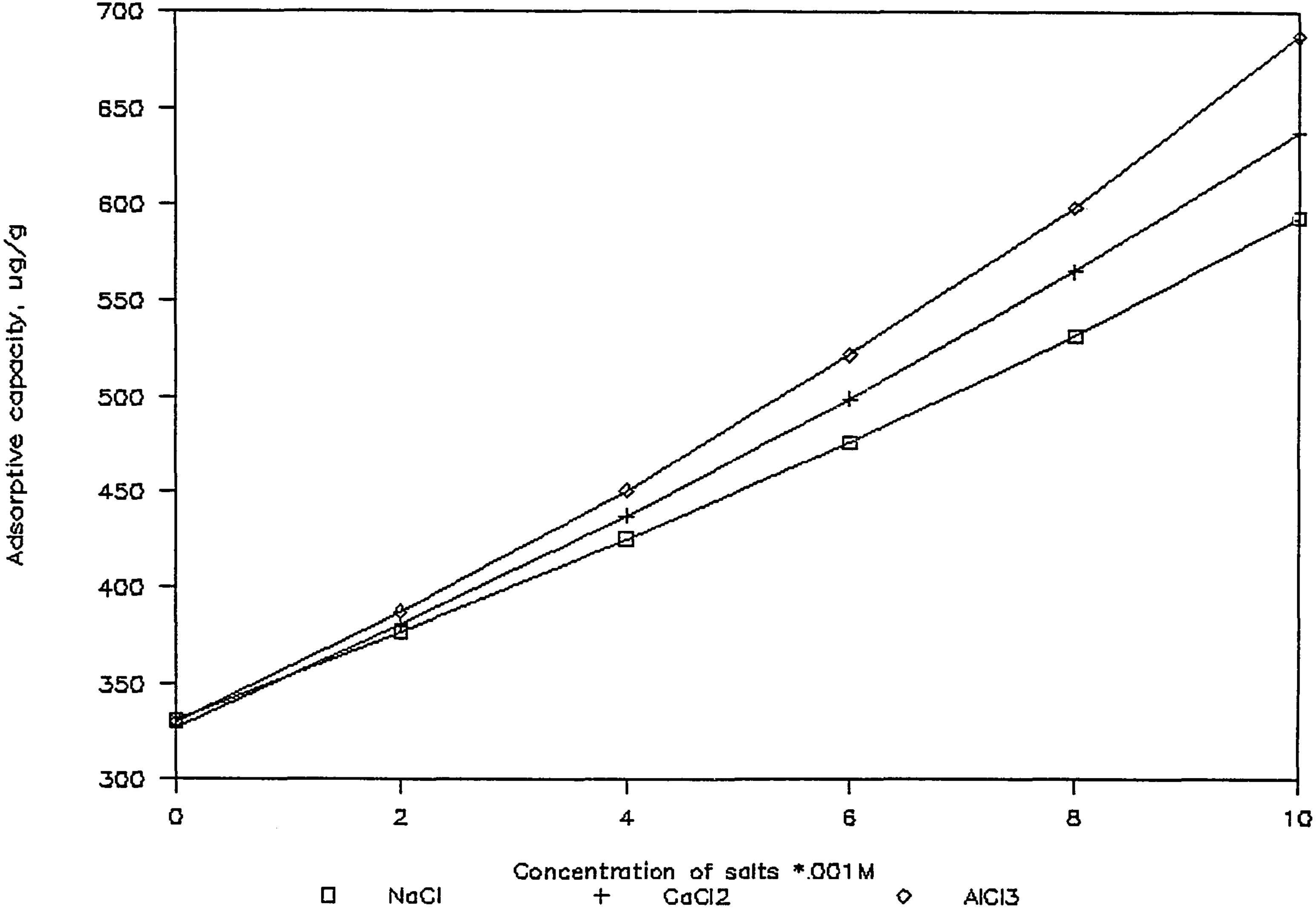
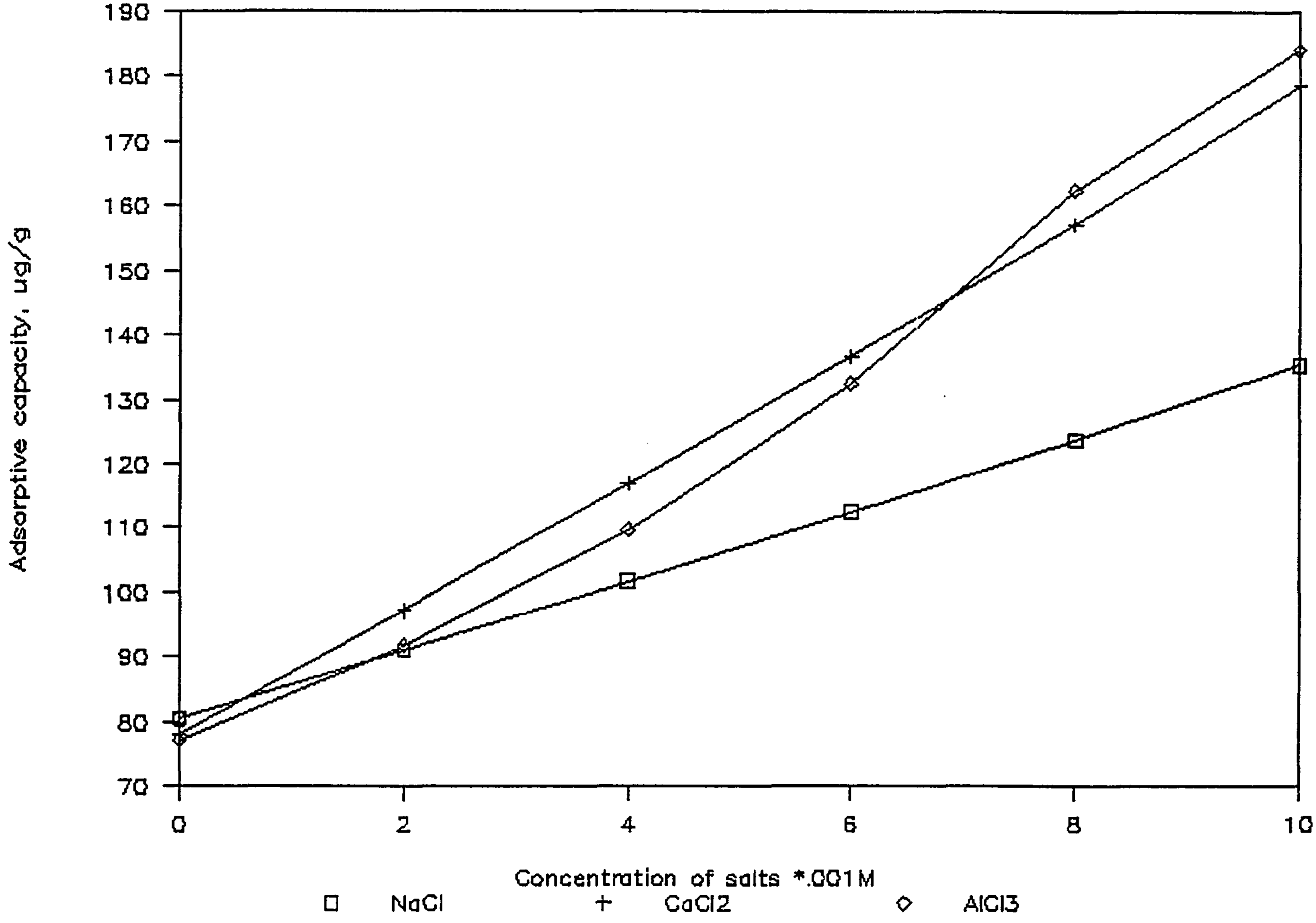


Fig. C10

Hudson Flyash, IPA, Eff., 30ppm



APPENDIX - 'E'

MULTI-COMPONENT ADSORPTION EQUILIBRIA

Figure E1. Multi-component Equilibria

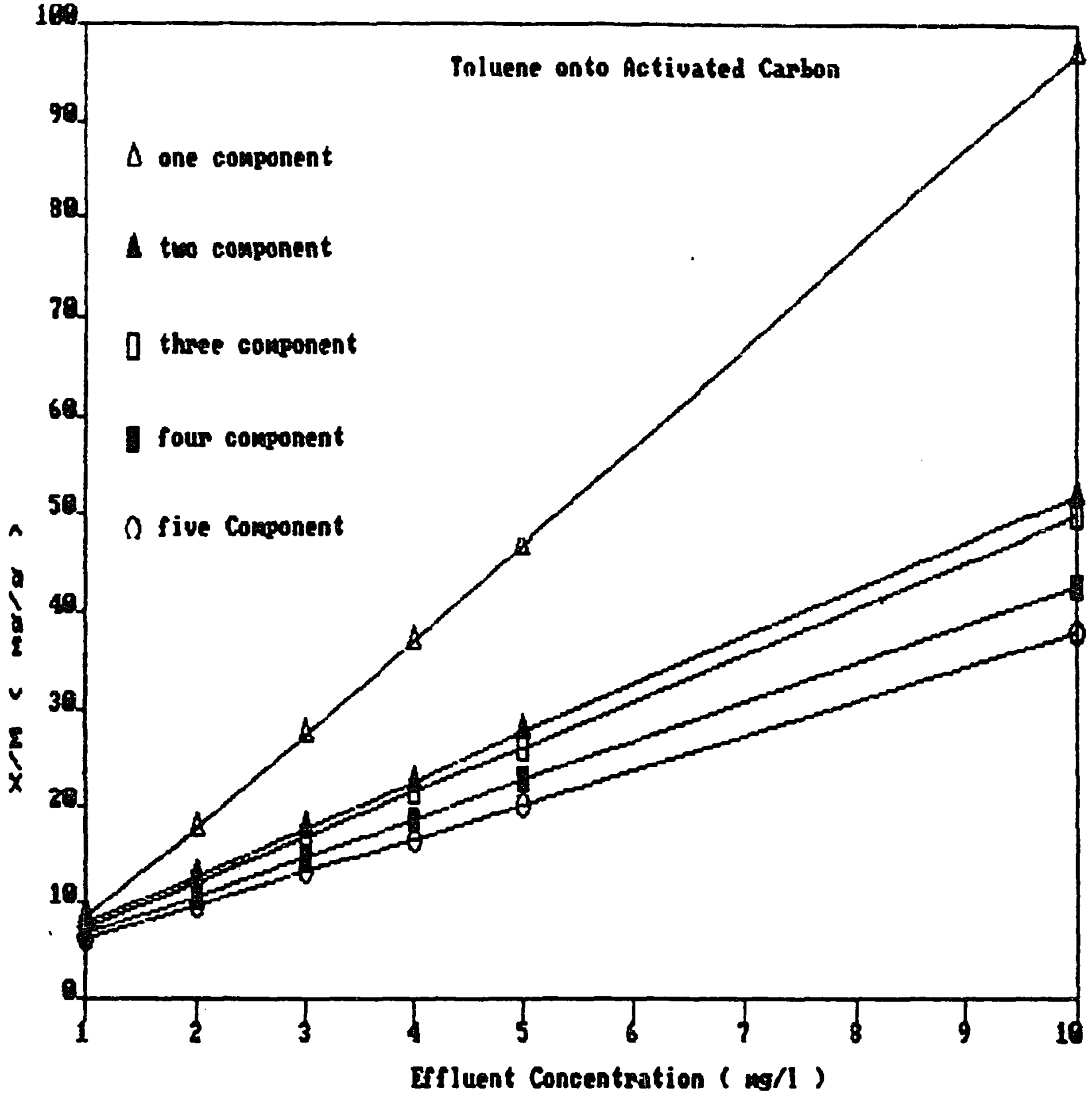
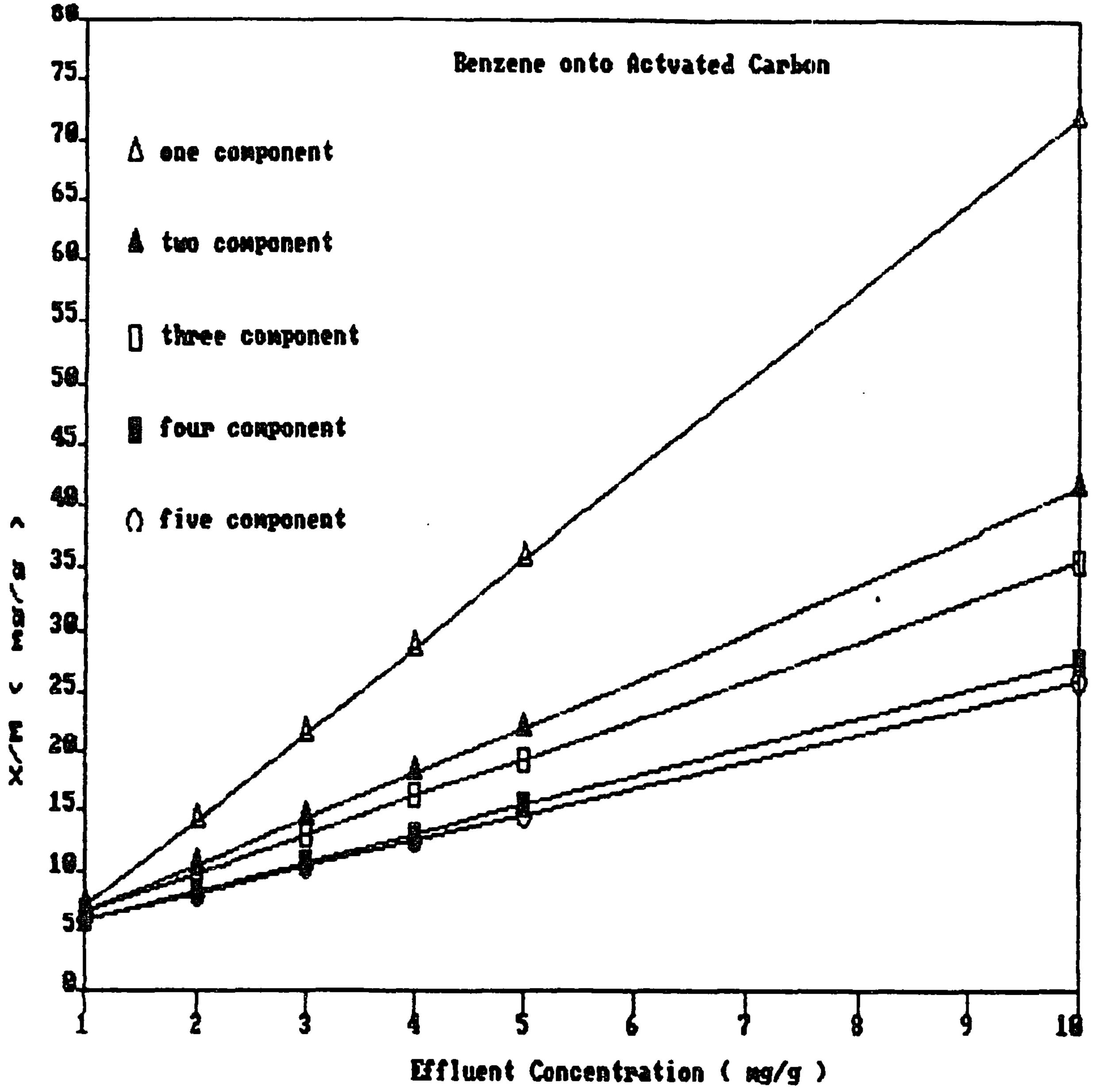


Figure E2. Multi-component Equilibria



Fgure E3. Multi-component Equilibria

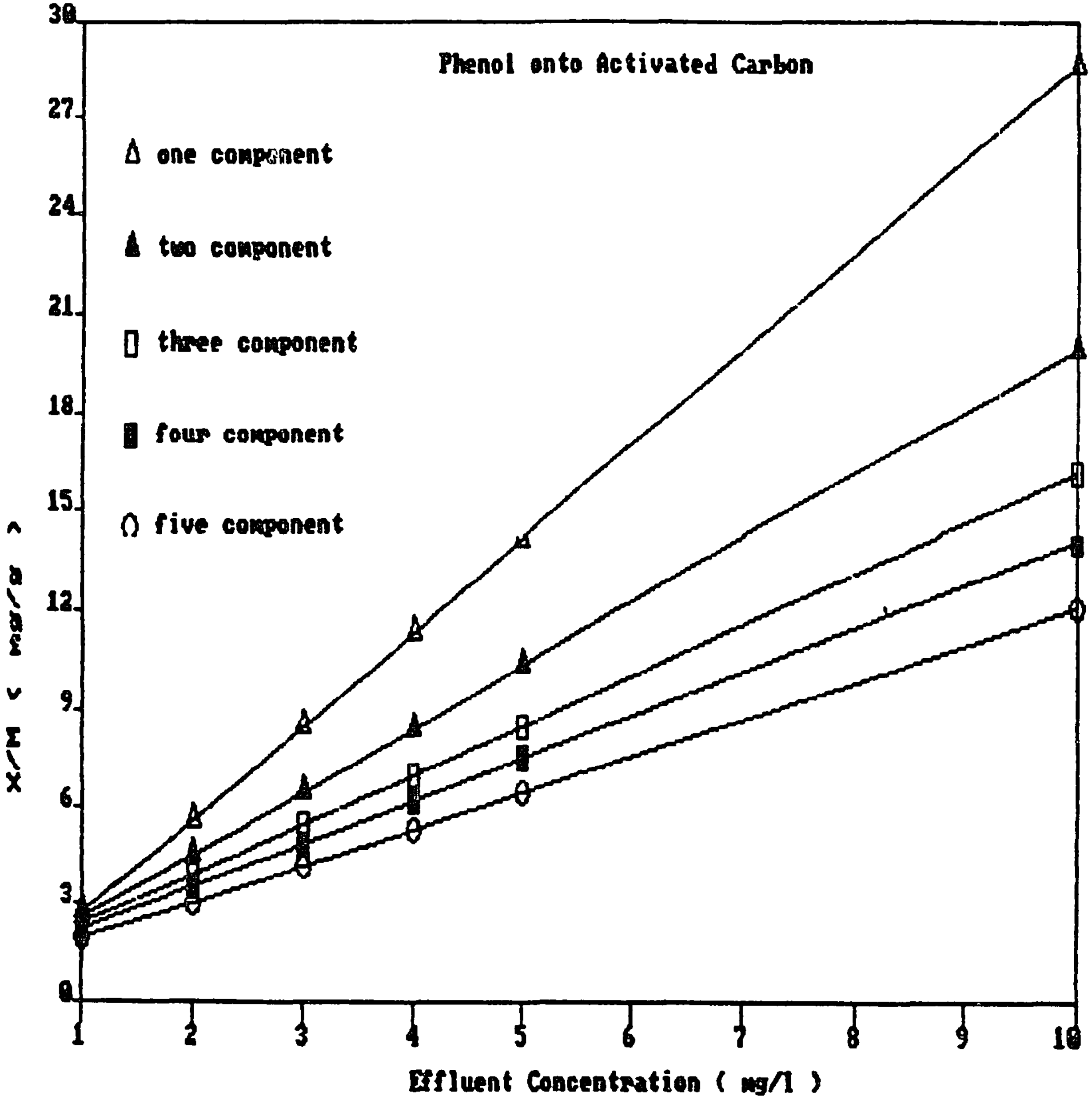


Figure E4.Multi-component Equilibria

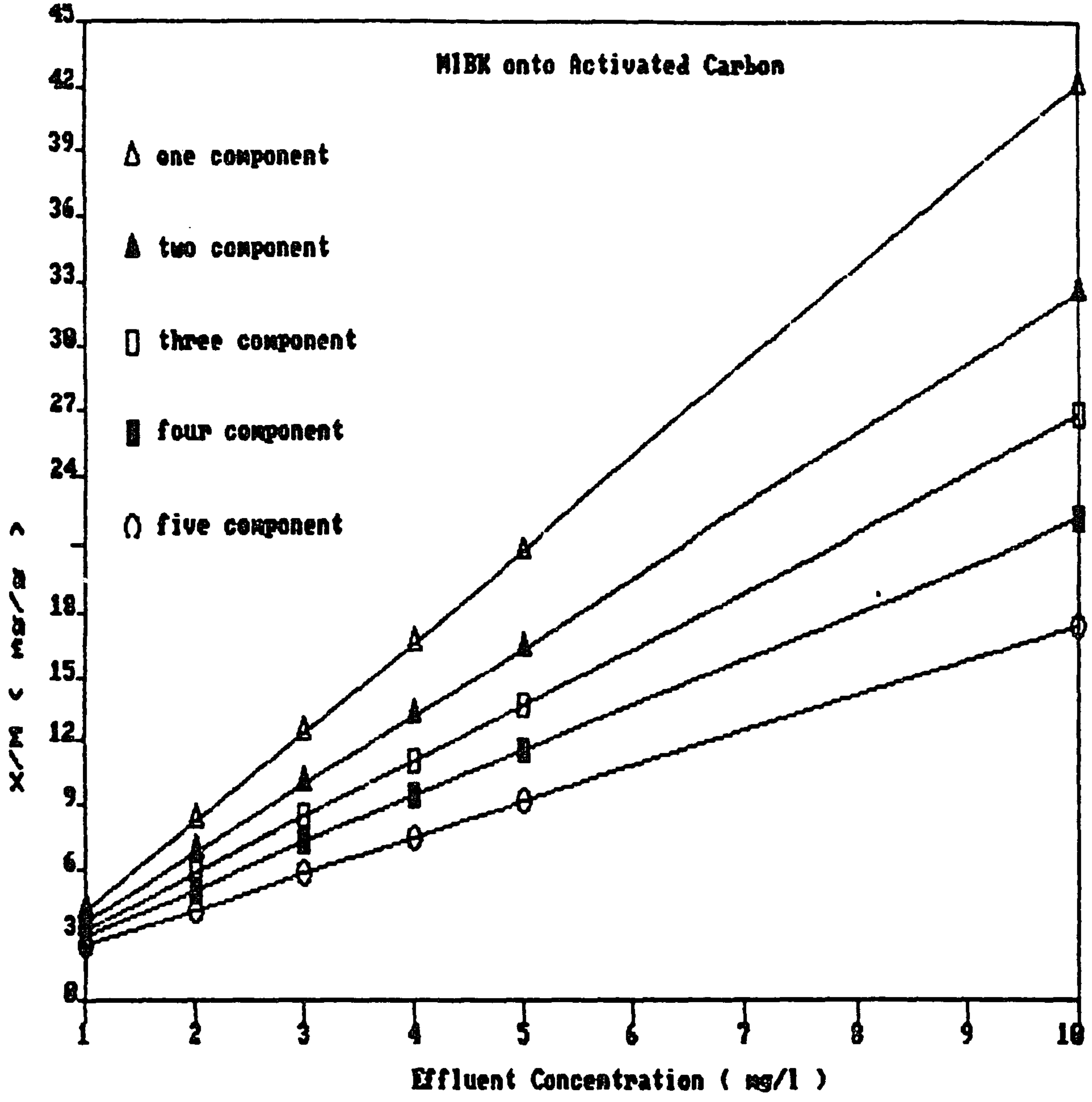


Figure E5. Multi-component Equilibria

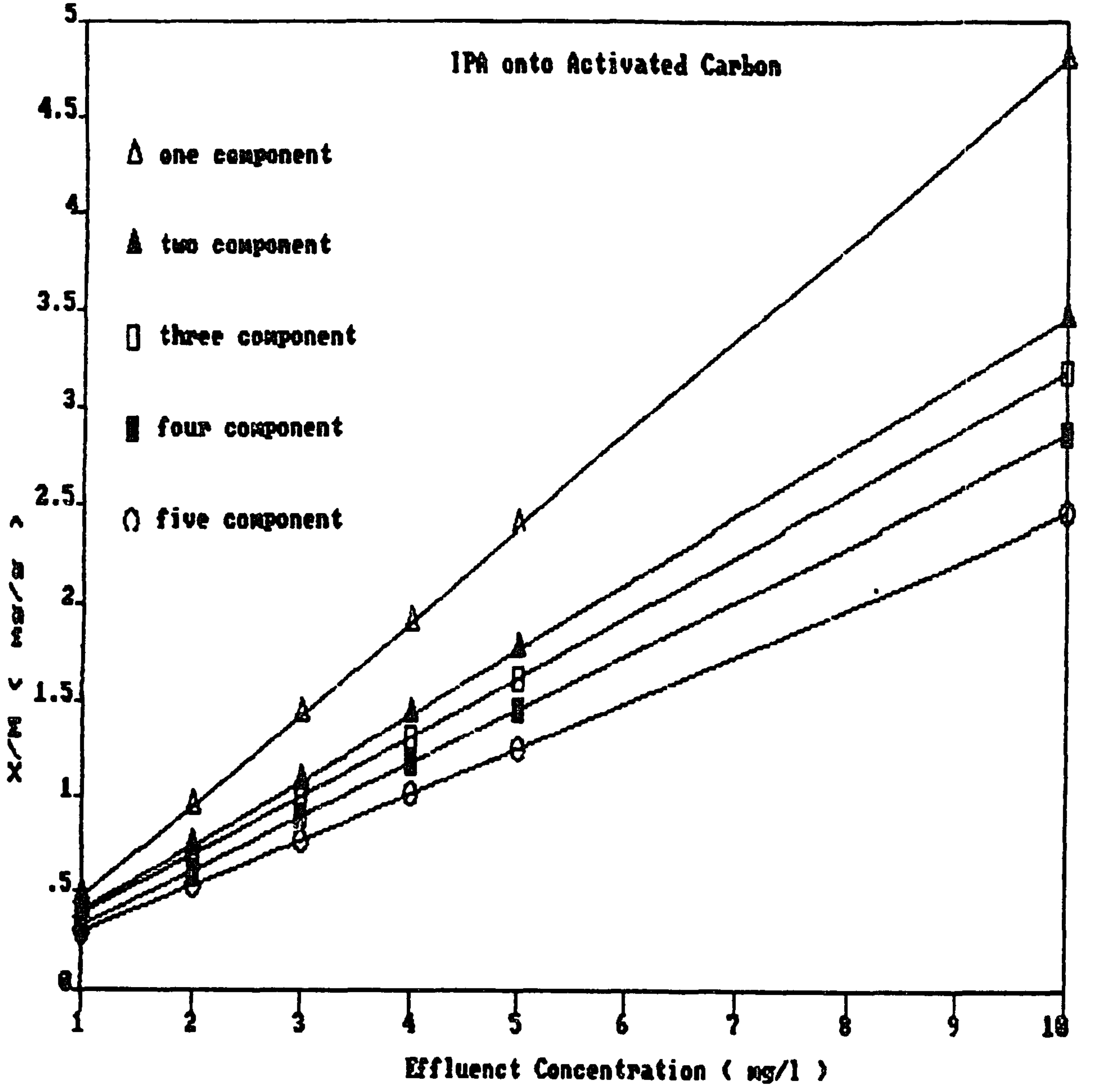


Figure E6. Multi-component Equilibria

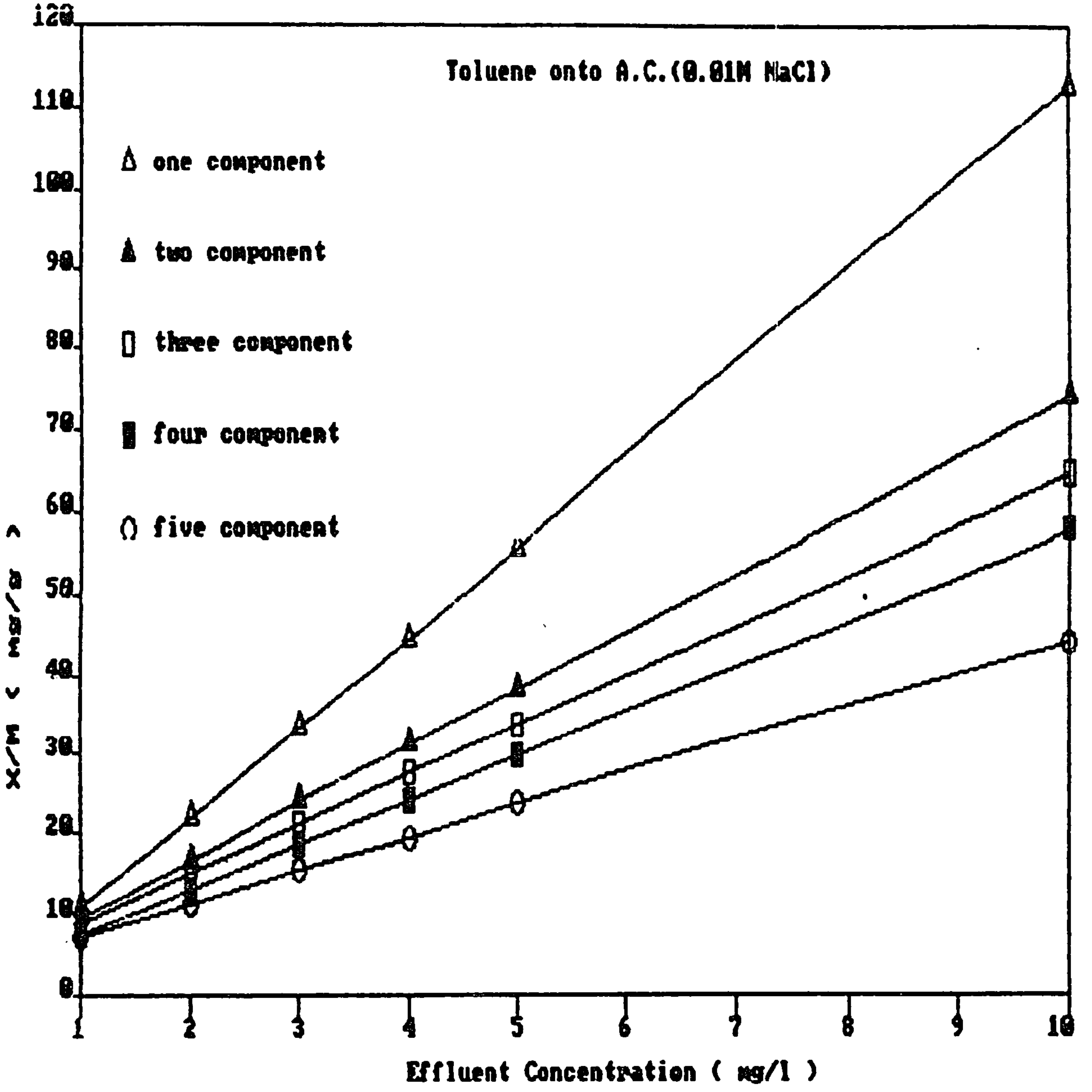
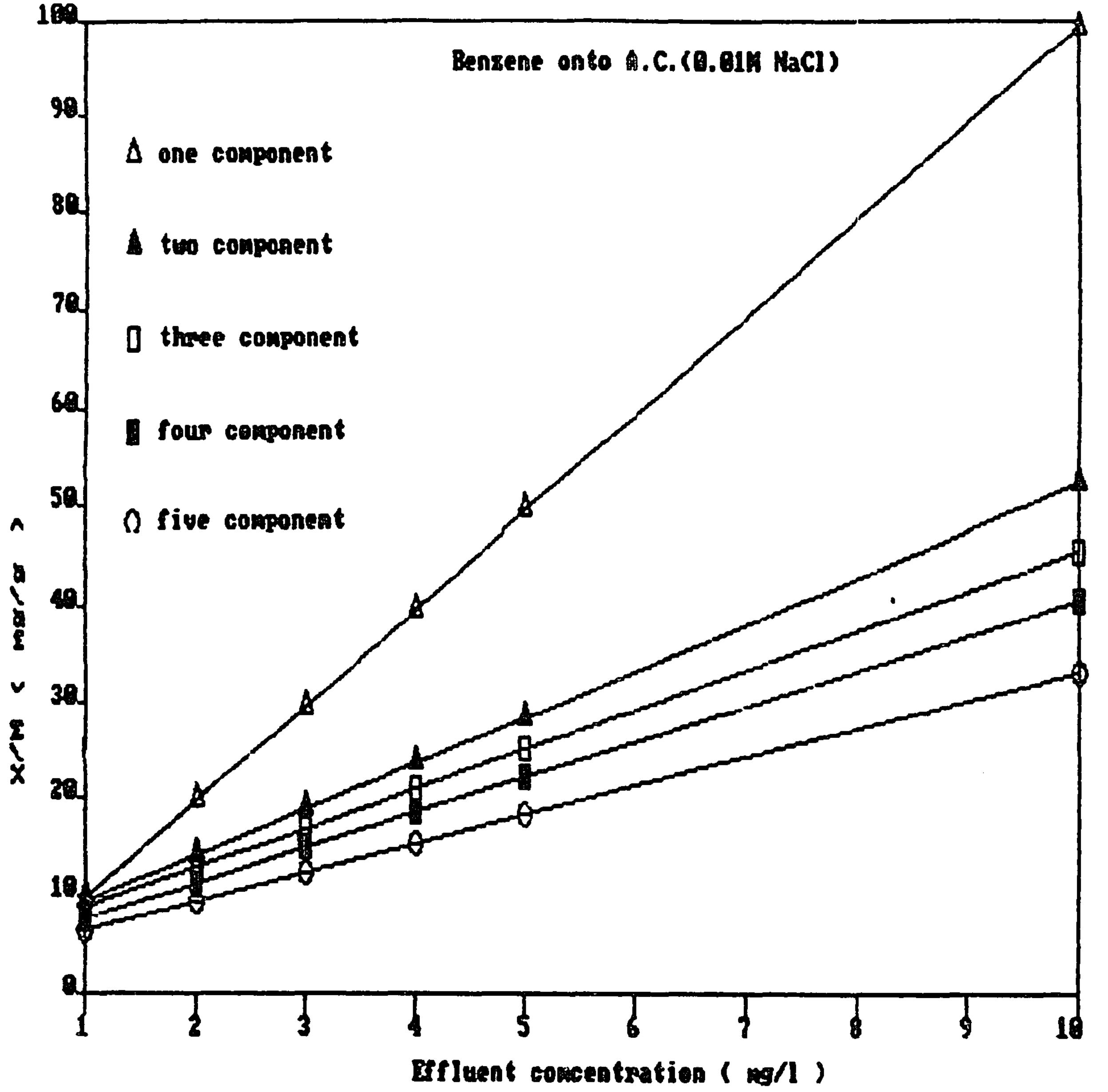


Figure E7. Multi-component Equilibria



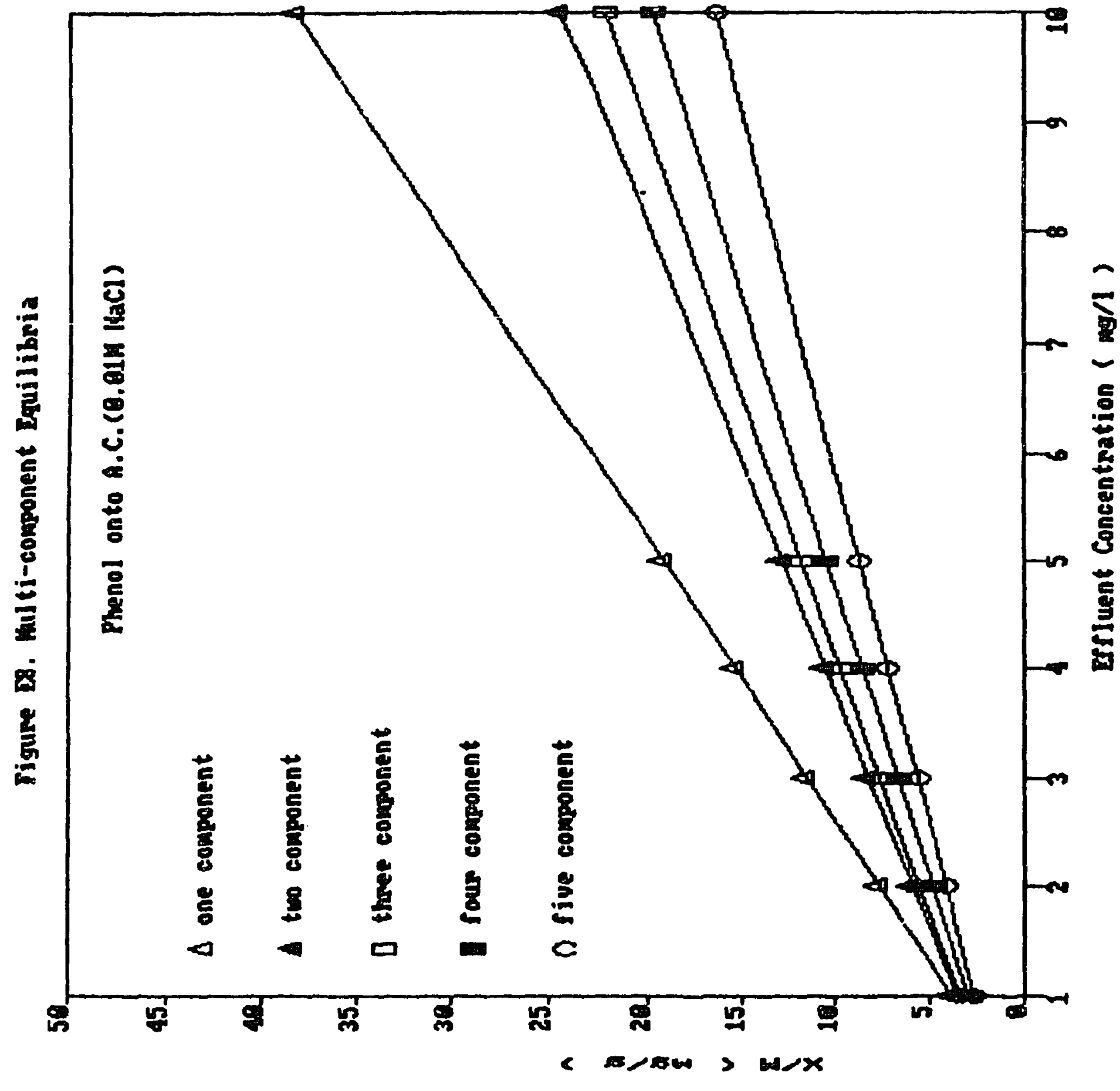


Figure E8. Multi-component Equilibria

Figure E9. Multi-component Equilibria

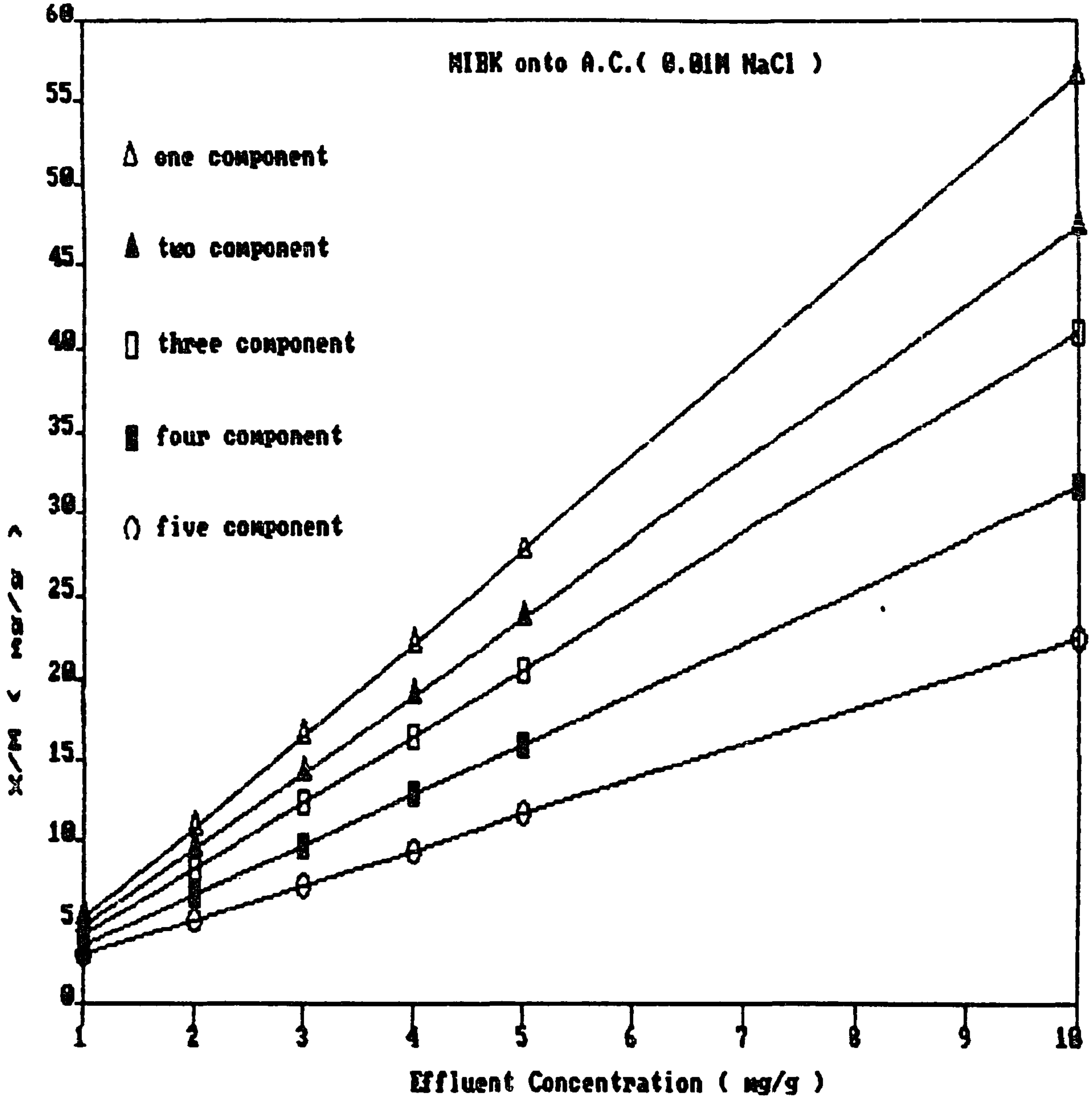


Figure E10. Multi-component Equilibria

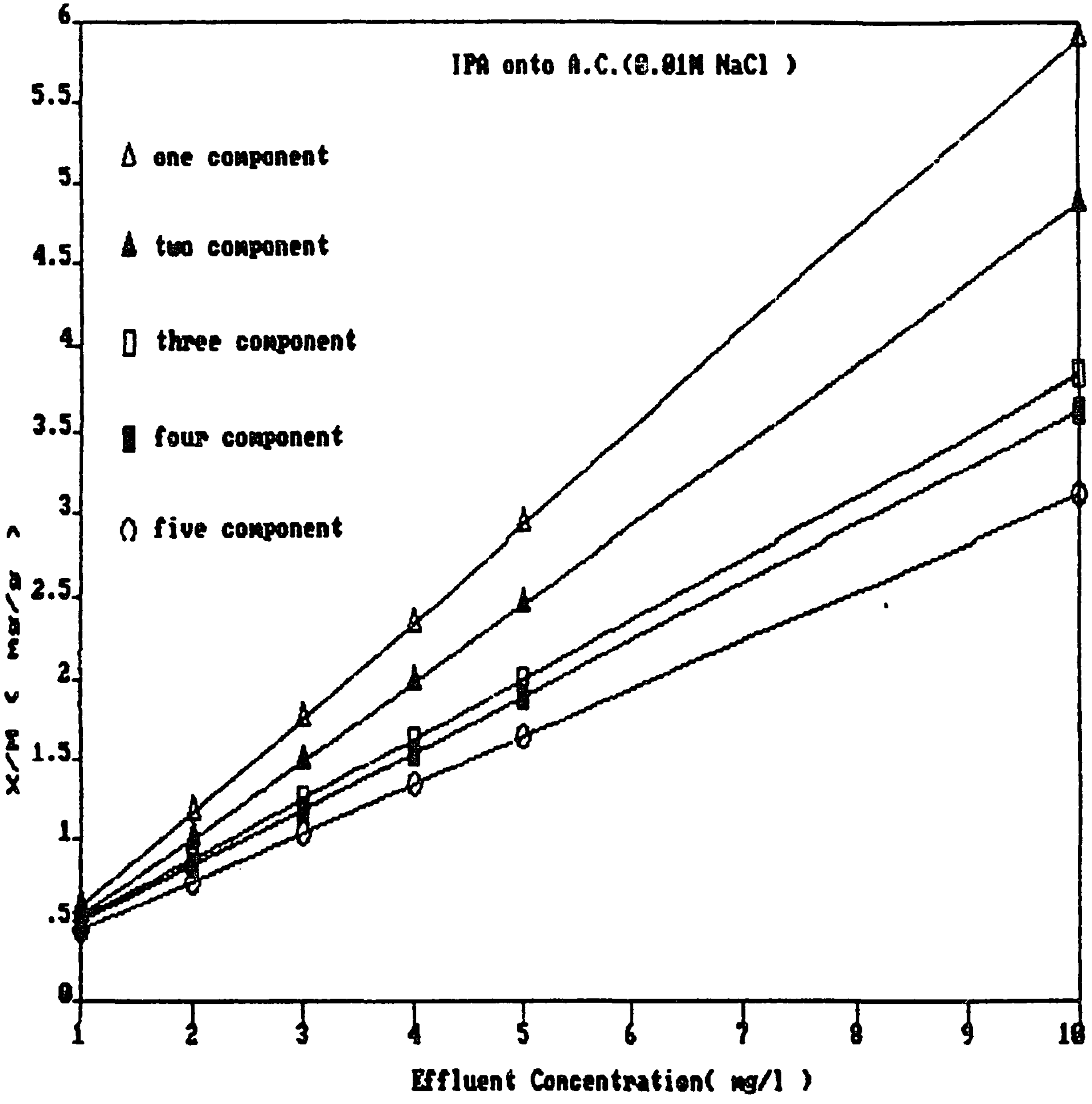
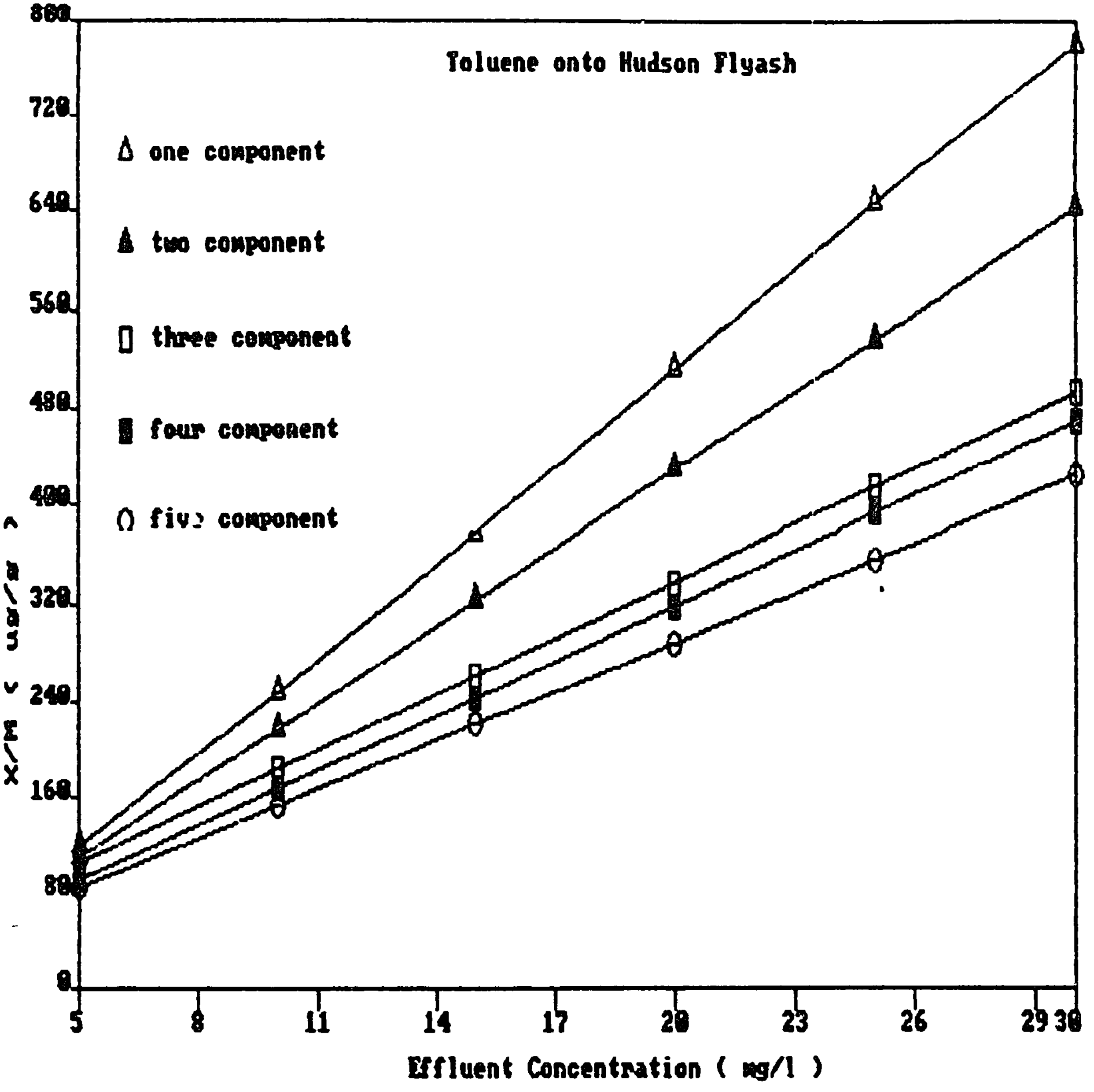


Figure E11.Multi-component Equilibria



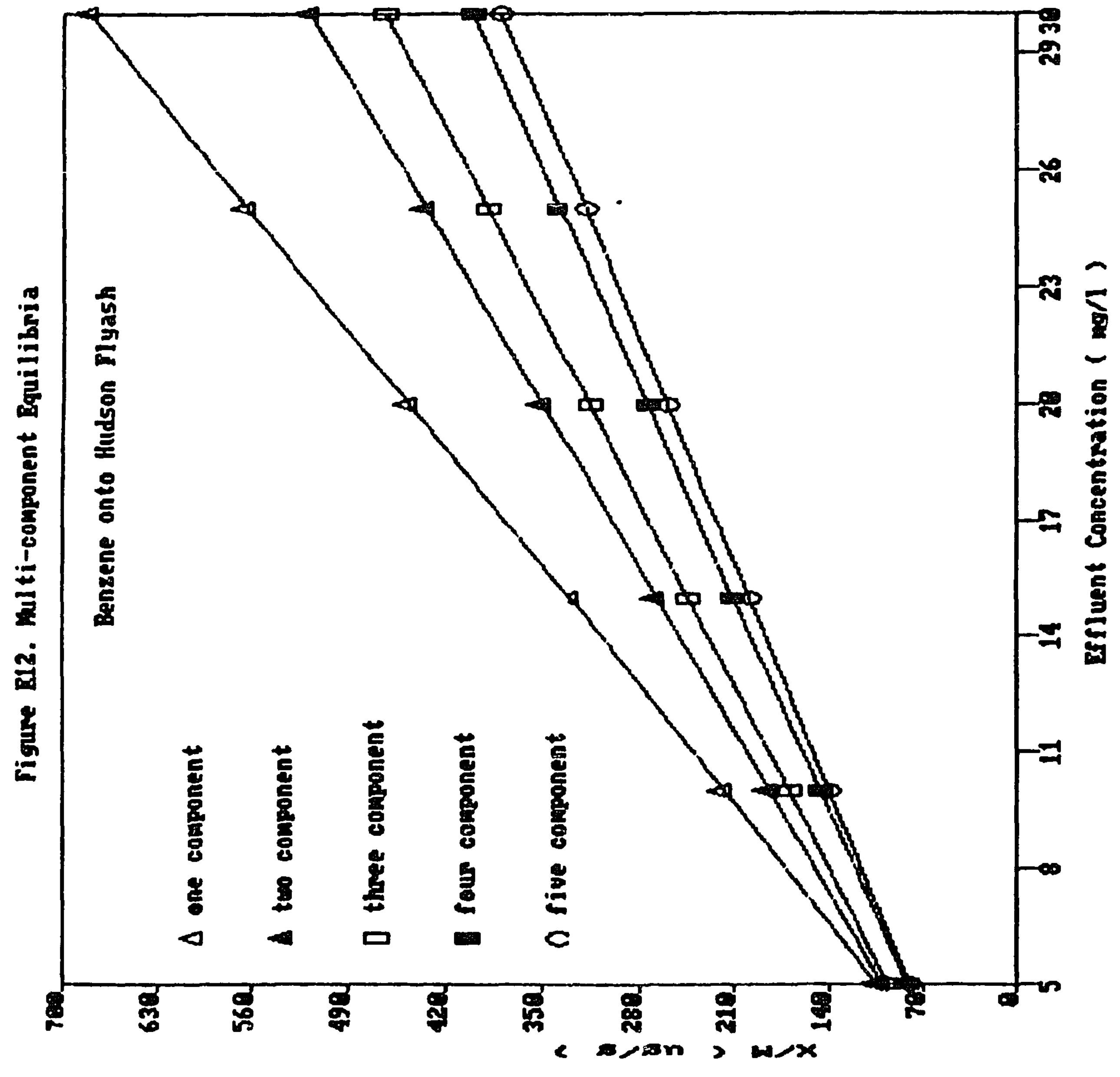


Figure E12. Multi-component Equilibria

Figure E13. Multi-component Equilibria

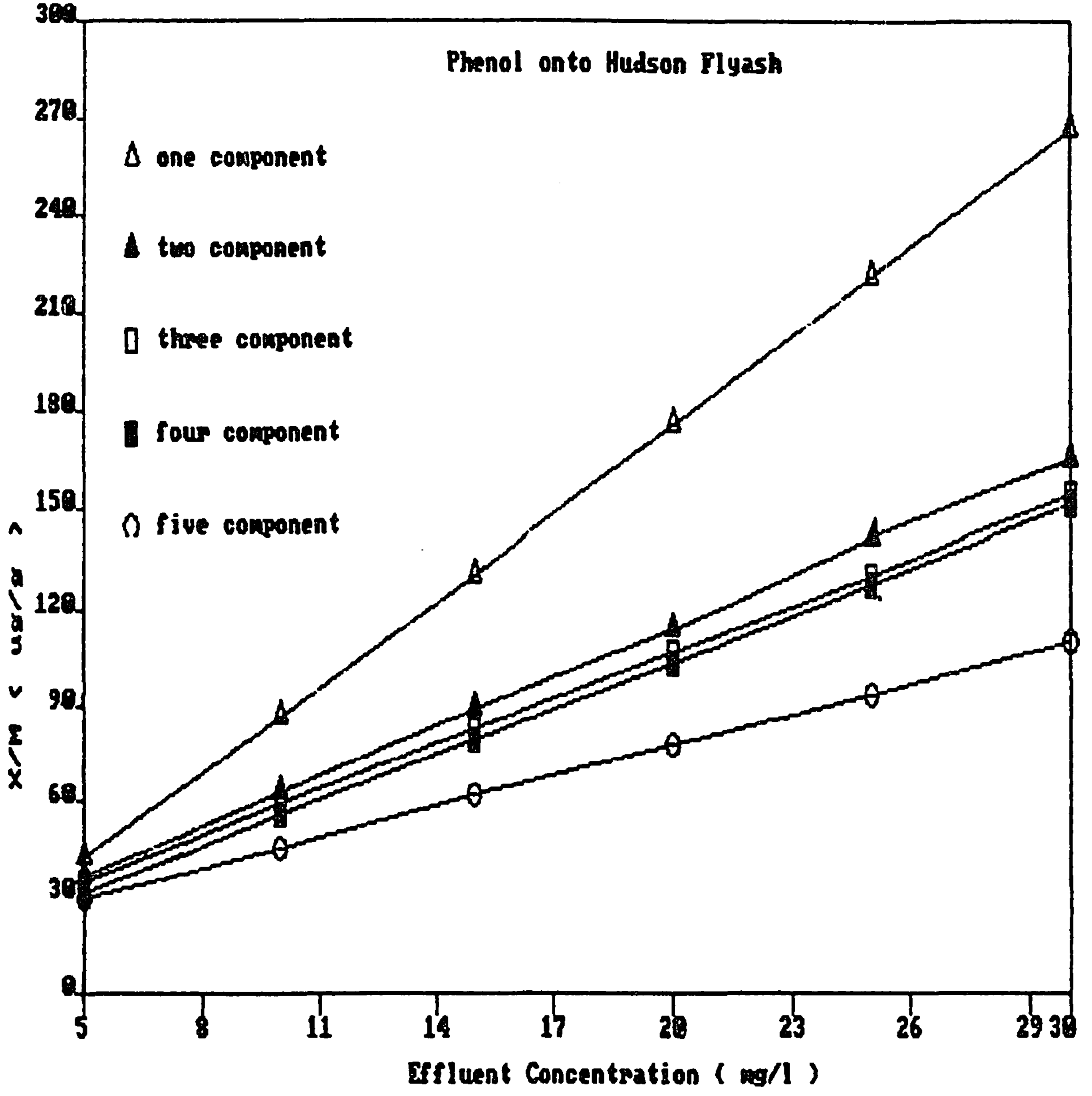


Figure E14. Multi-component Euilibria

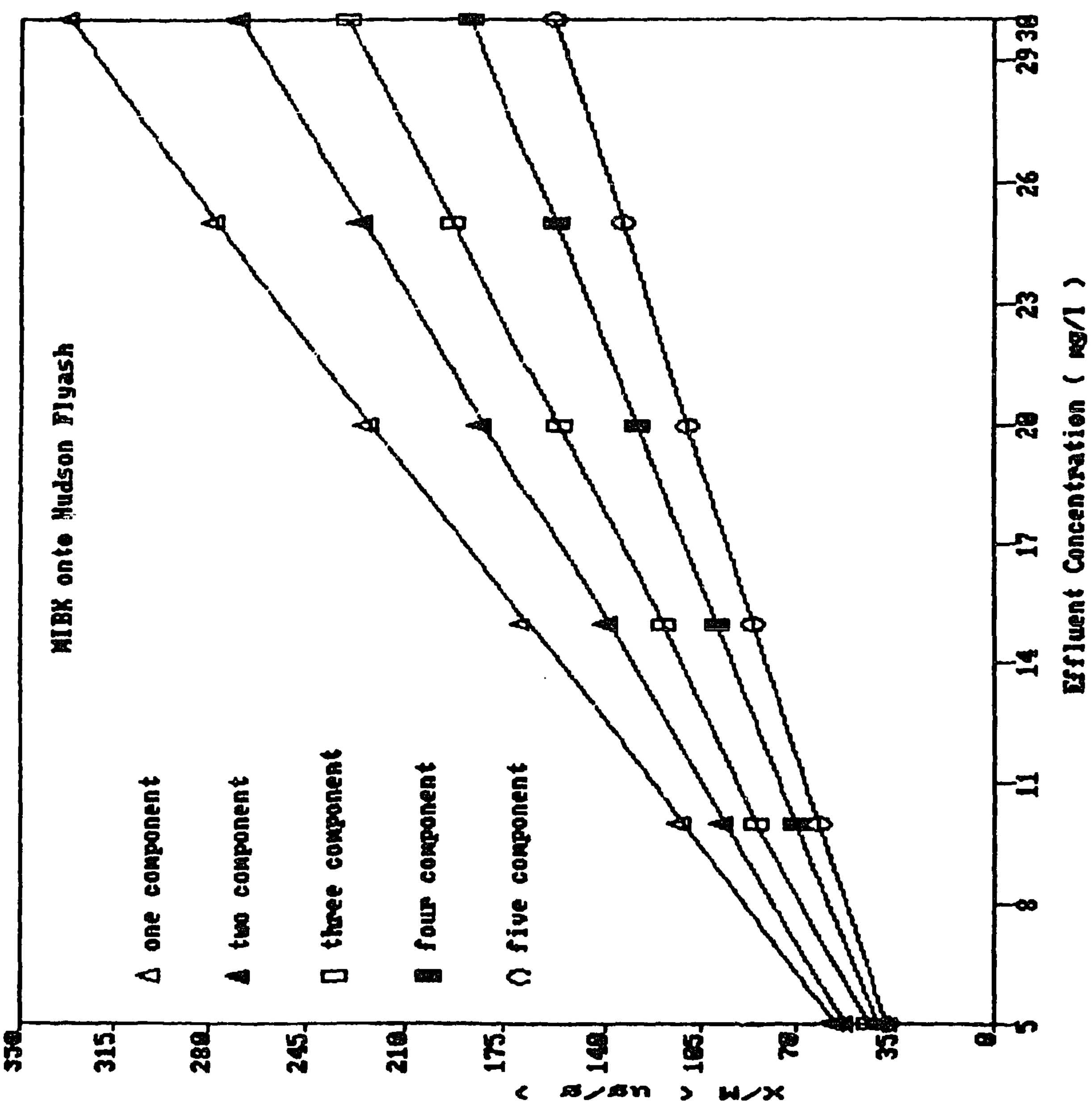


Figure E15. Multi-component Equilibria

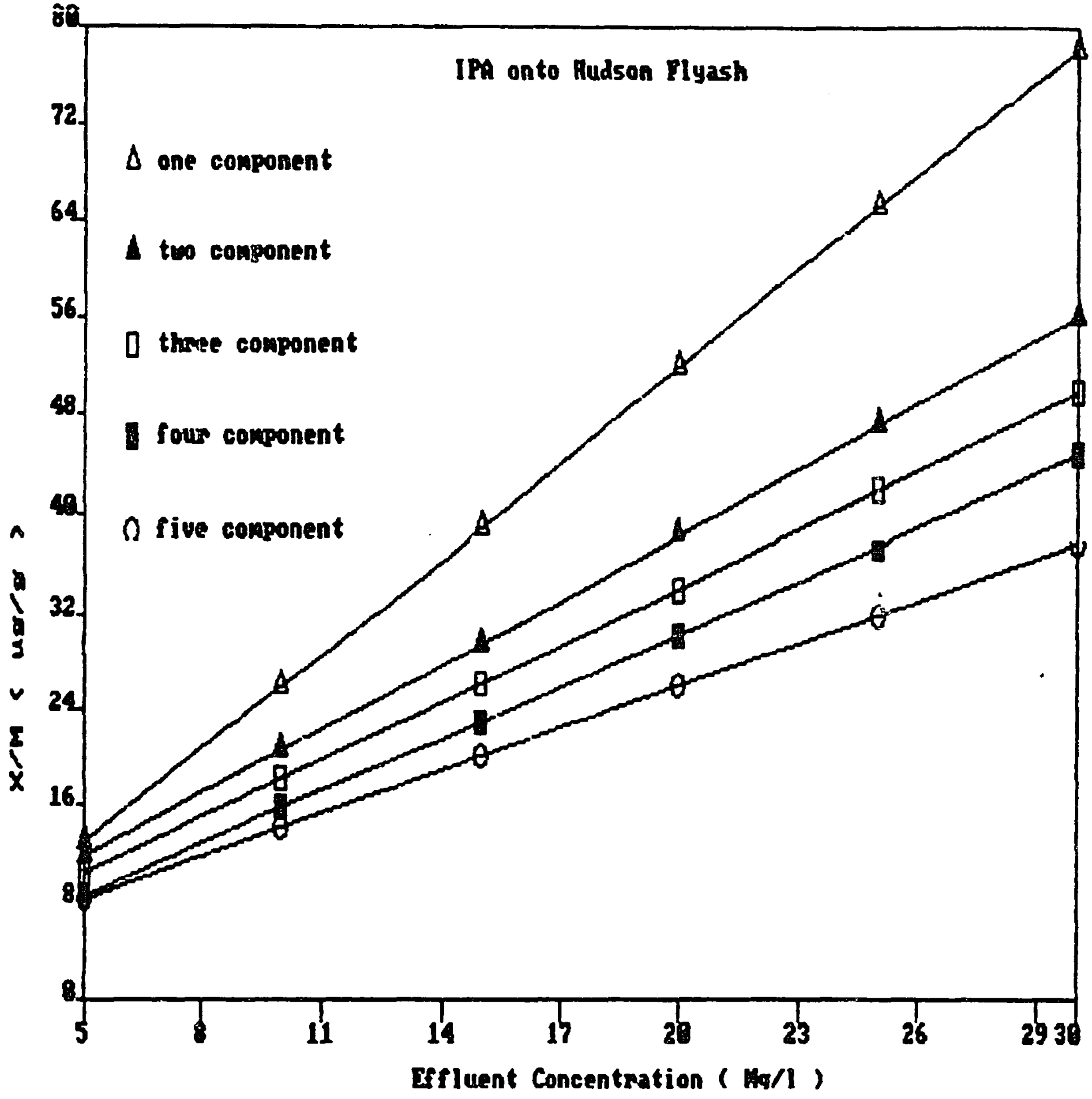


Figure E16. Multi-component Equilibria

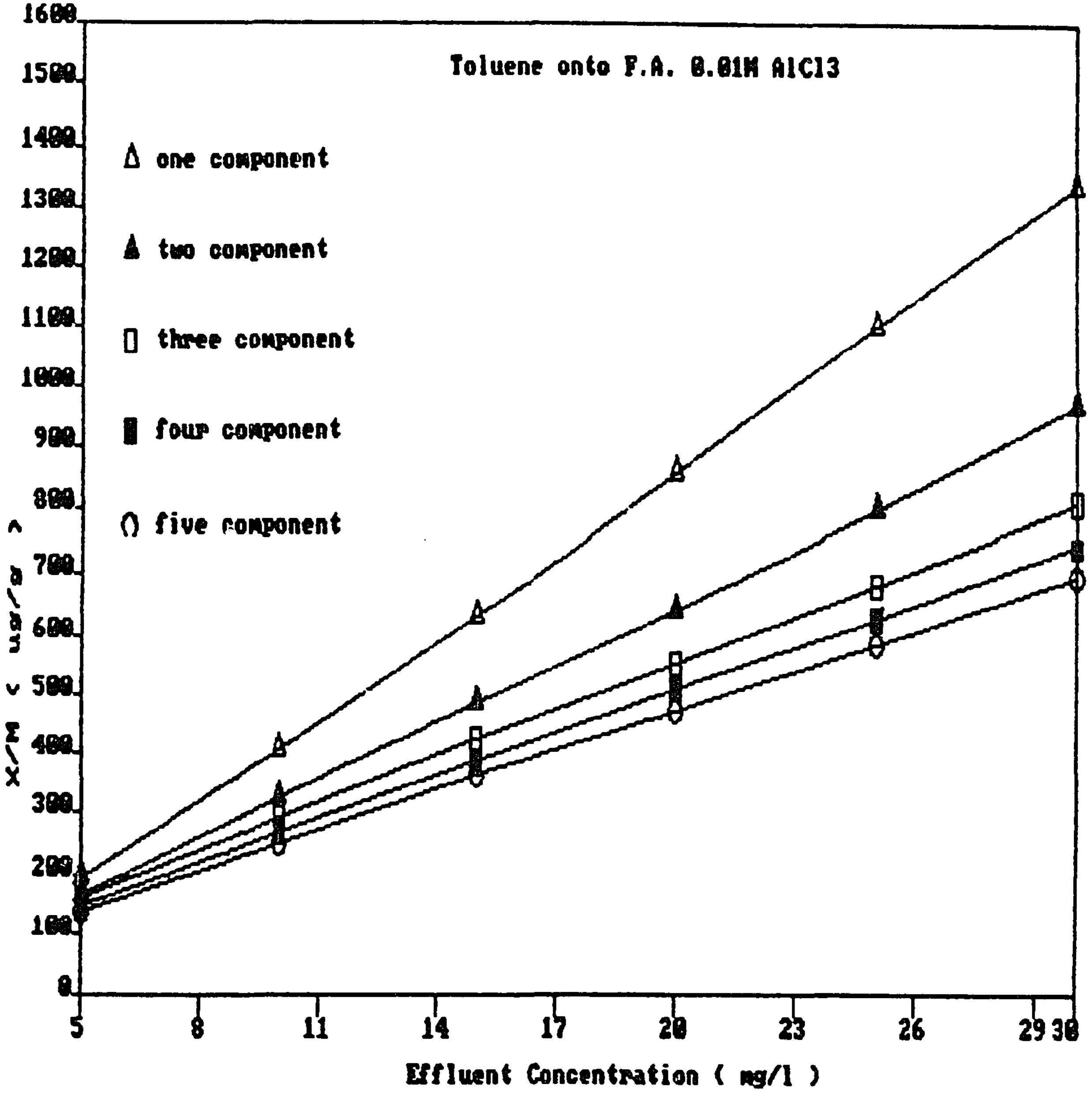


Figure E17. Multi-component Equilibria

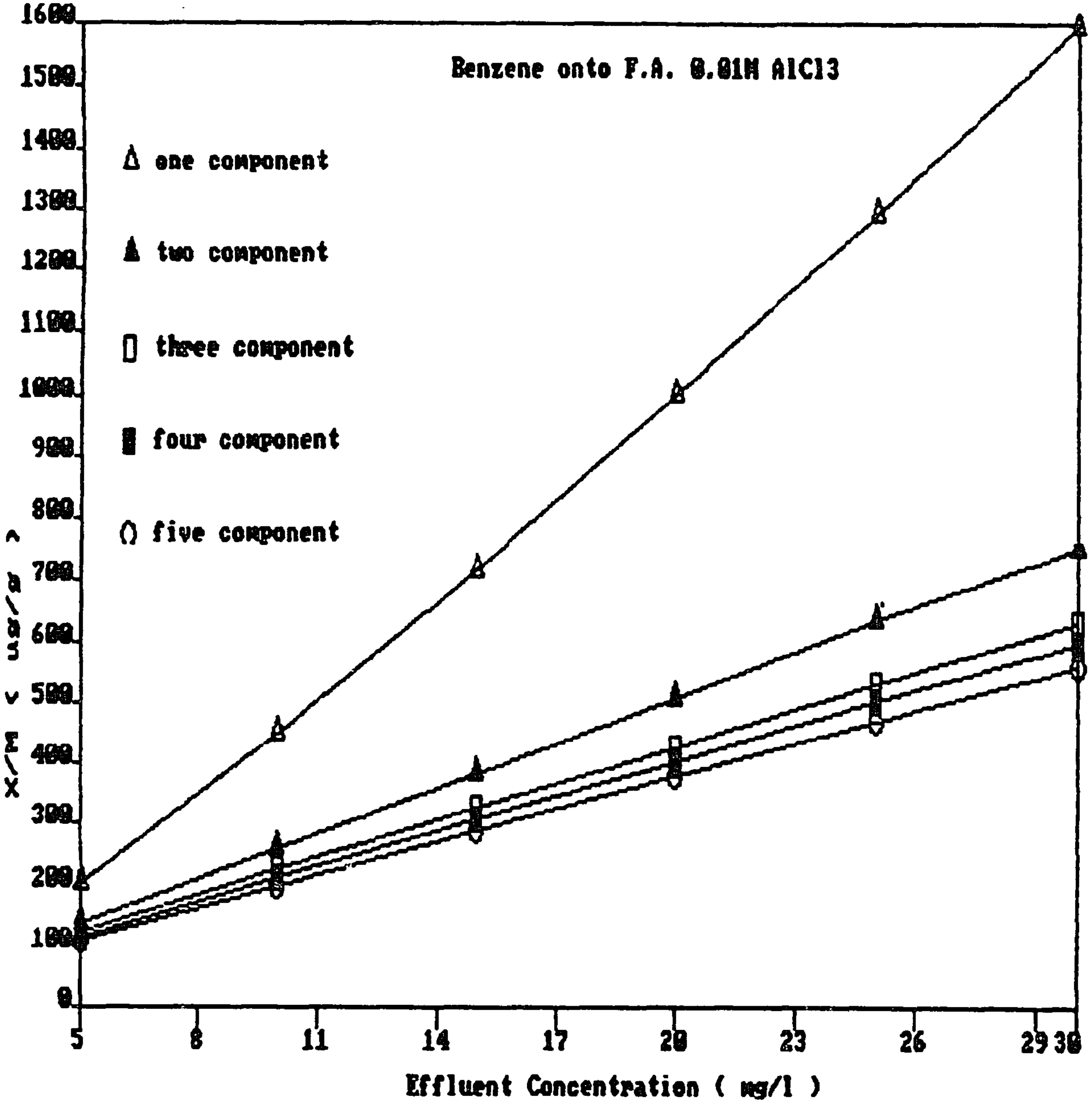
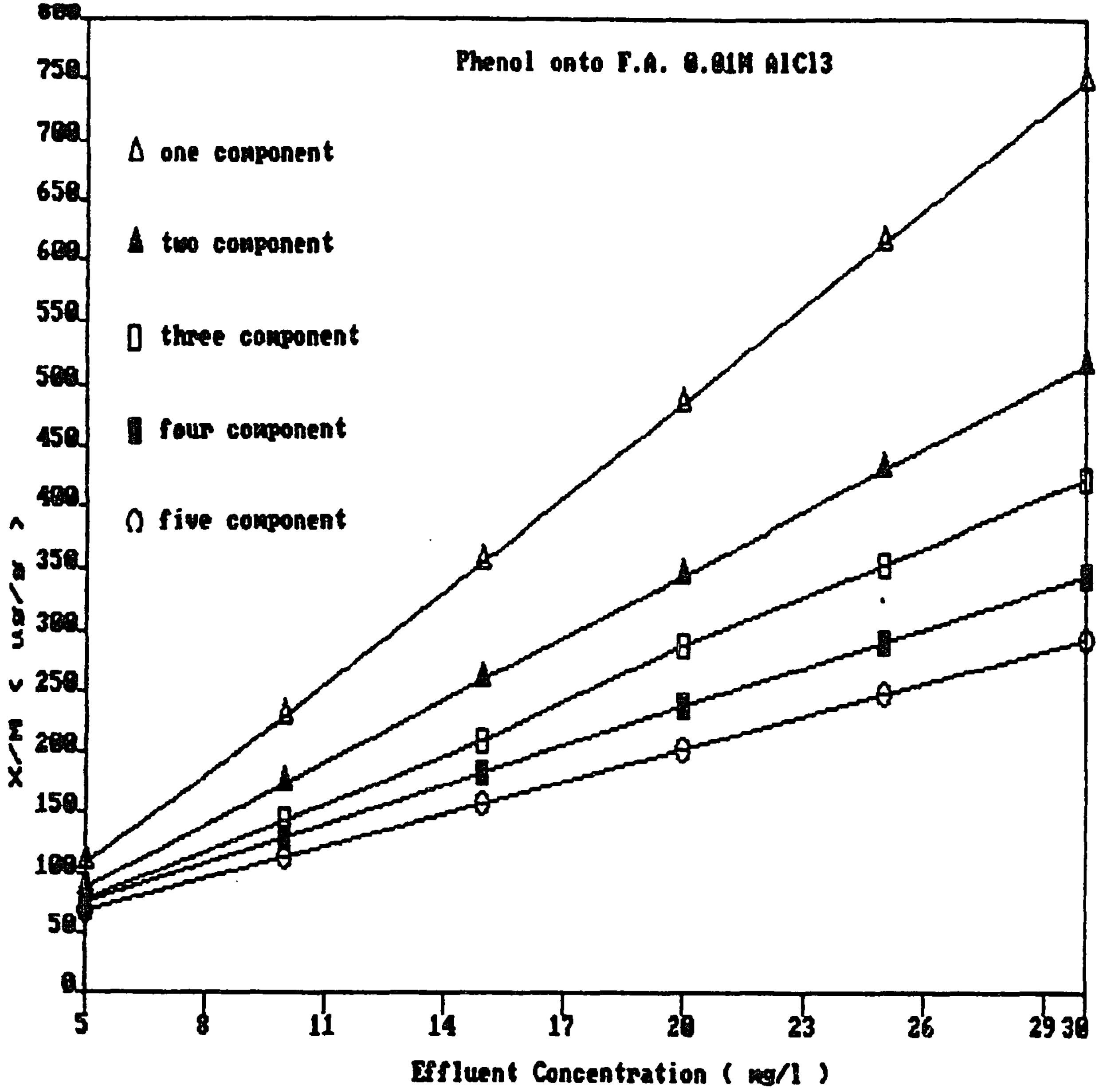


Figure E18. Multi-component Equilibria



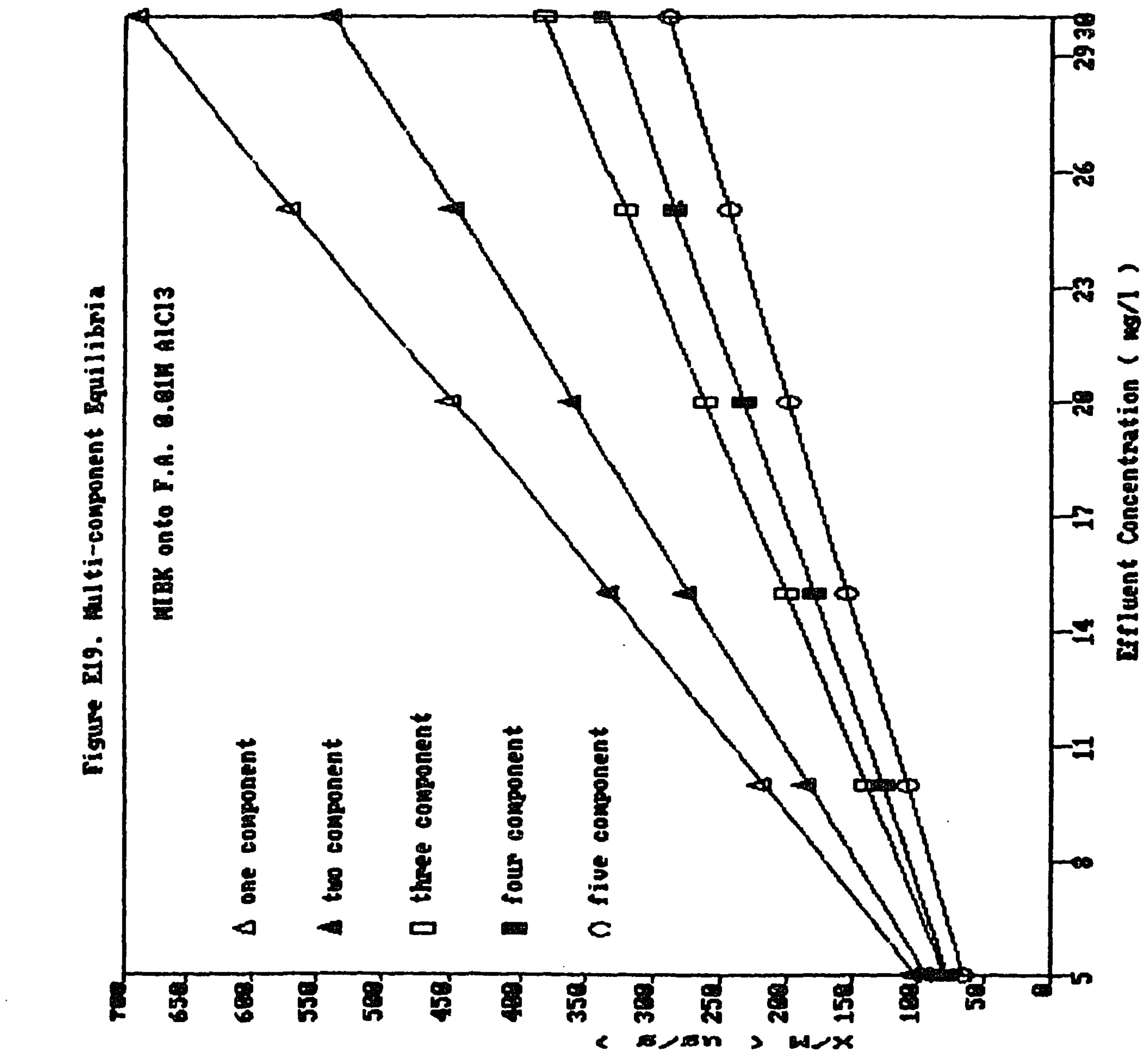


Figure E19. Multi-component Equilibria

MIBK onto F.A. 0.01M AlCl3

Figure E20. Multi-component Equilibria

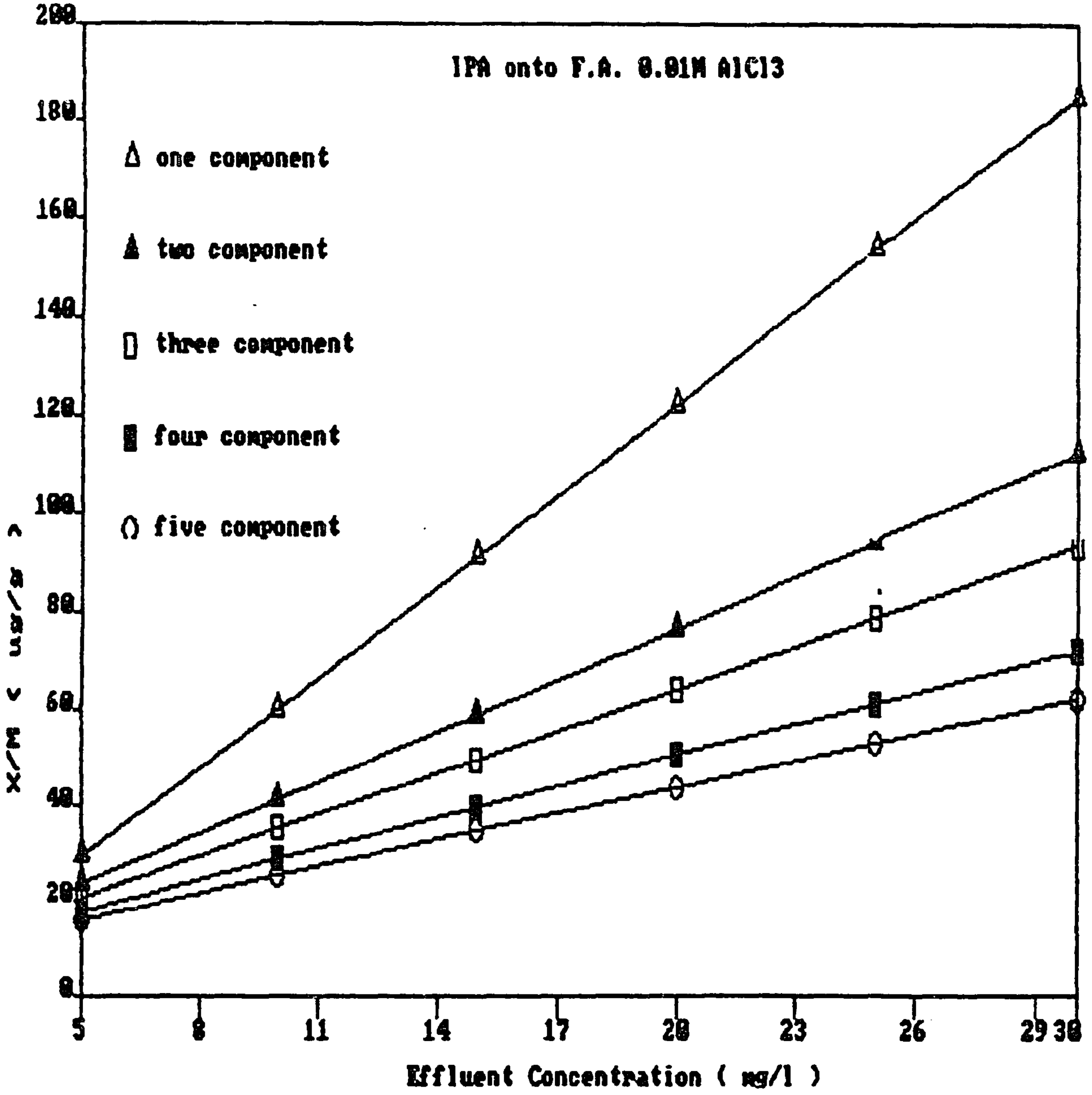


Figure E21. Effect of Concentration of NaCl on Multi-solute Adsorption

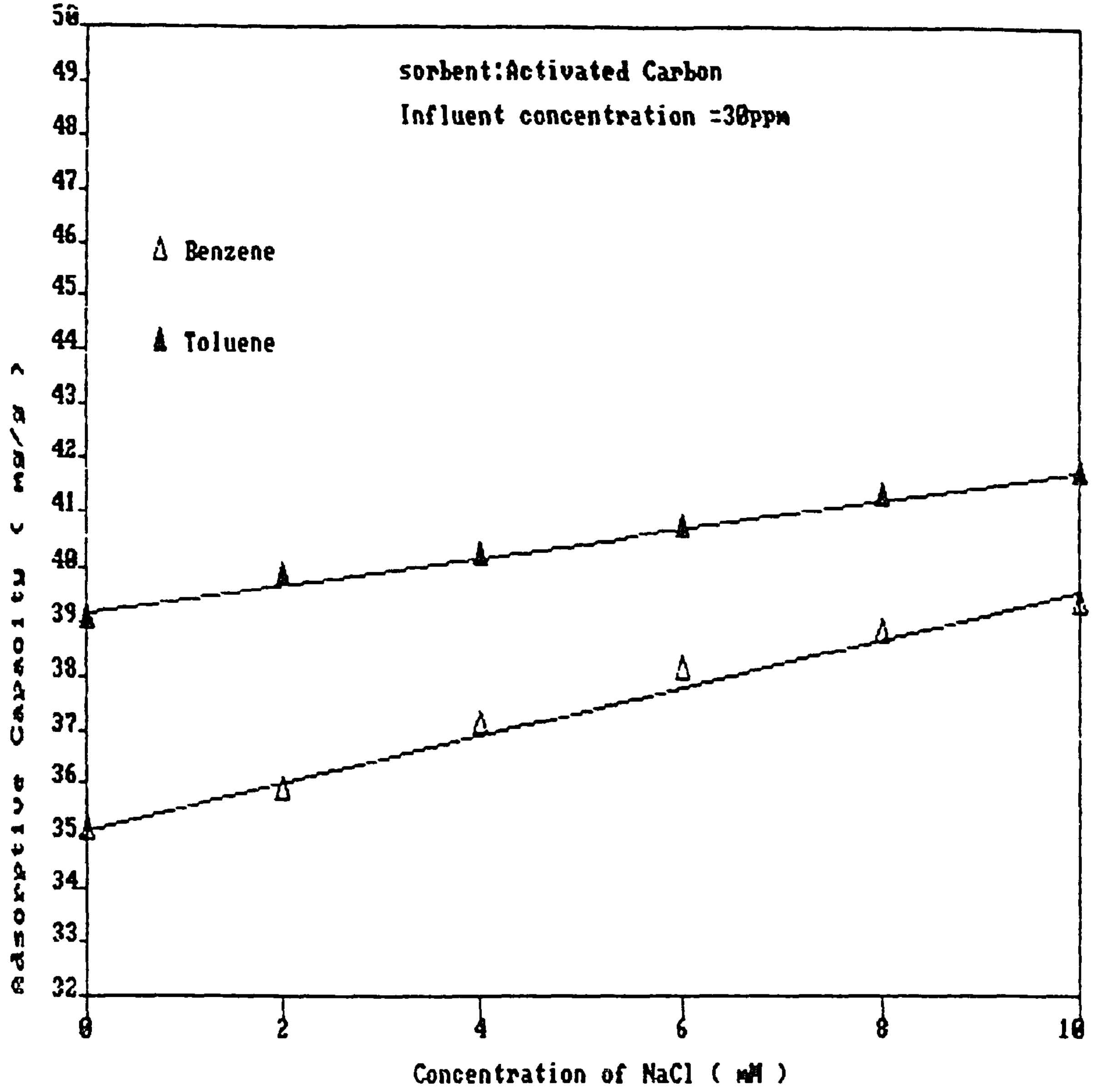


Figure E22. Effect of Concentration of NaCl on Multi-solute Adsorption

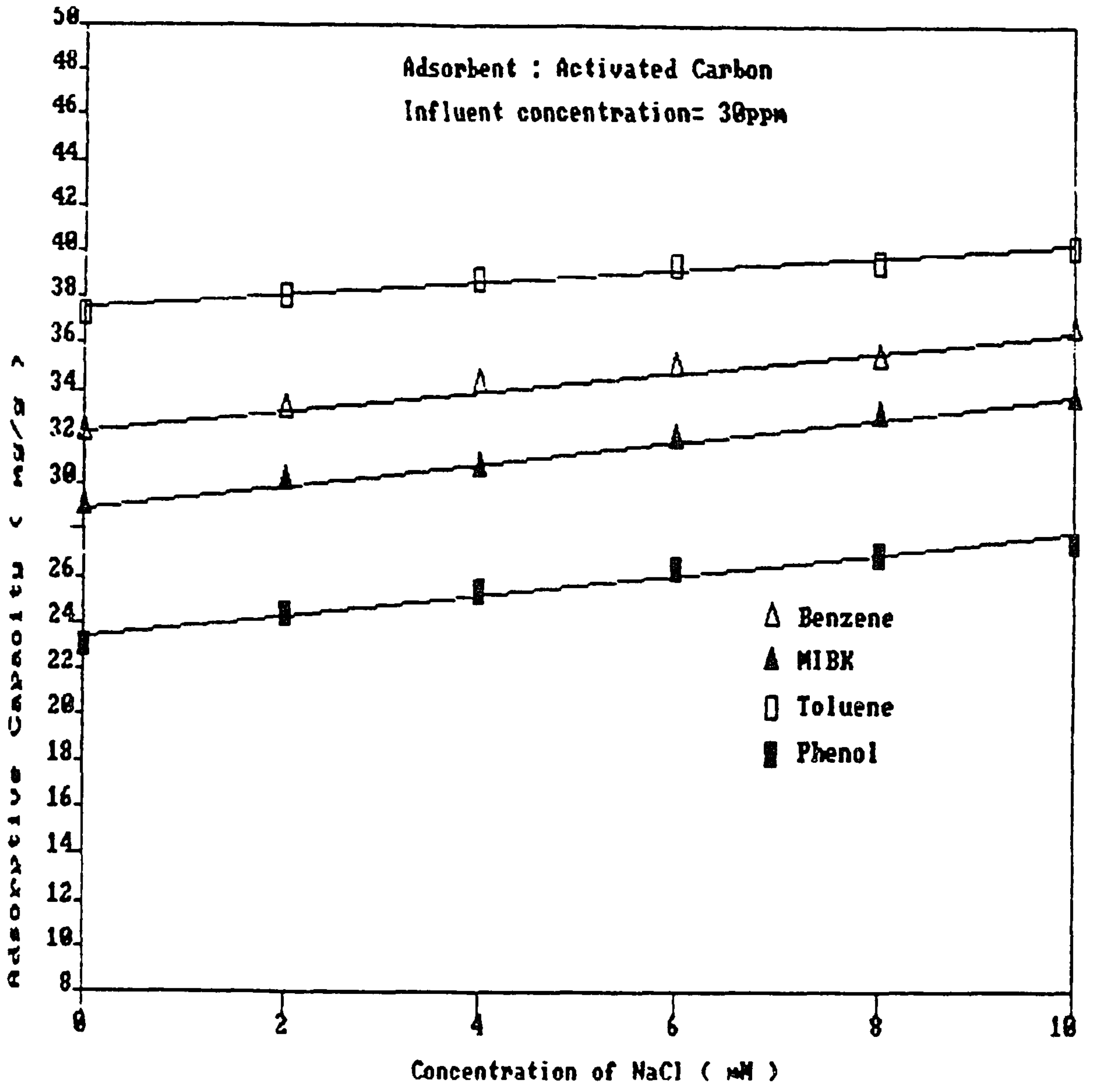


Figure E23. Effect of Concentration of AlCl$_3$ on Multi-solute Adsorption

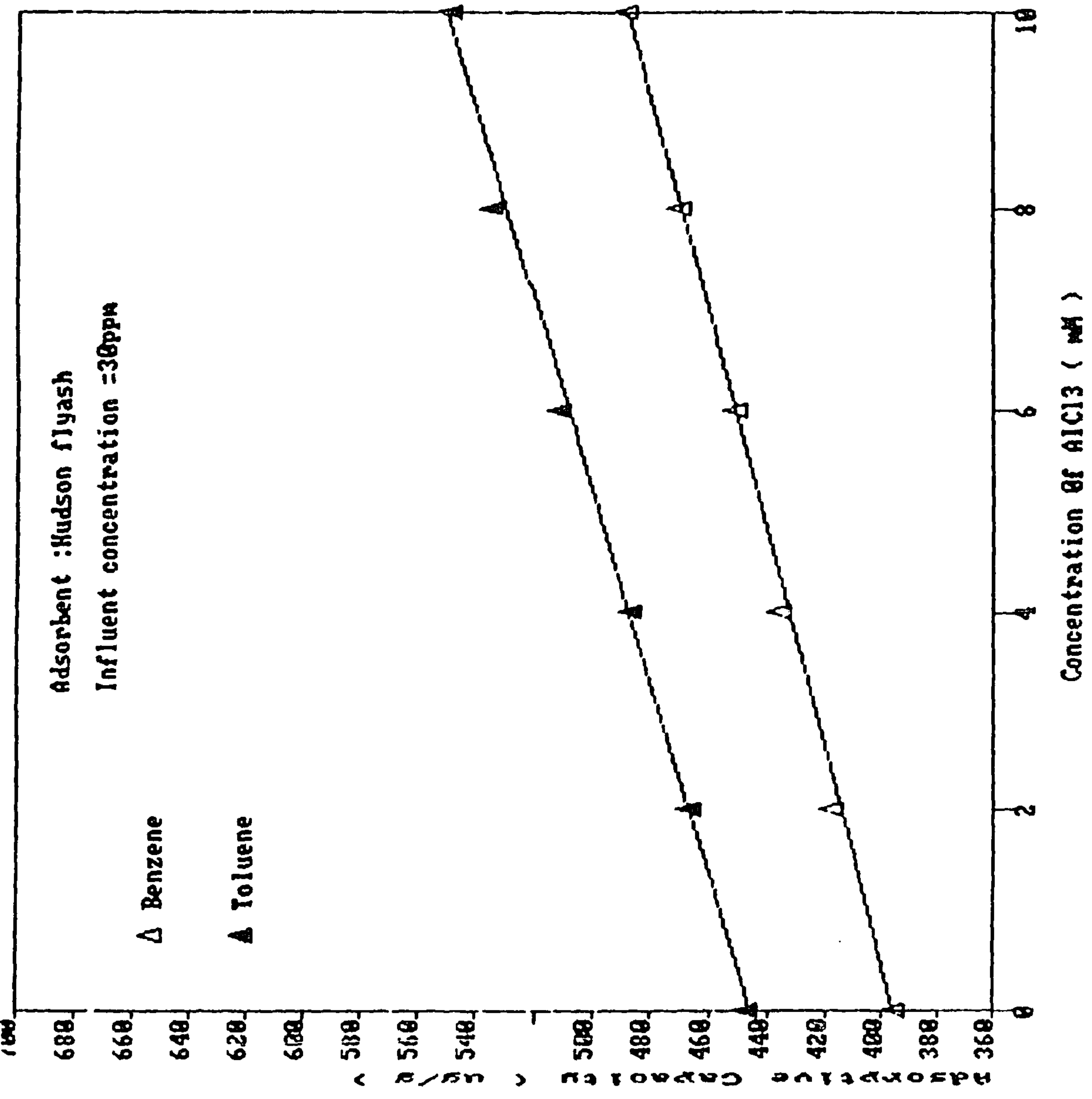
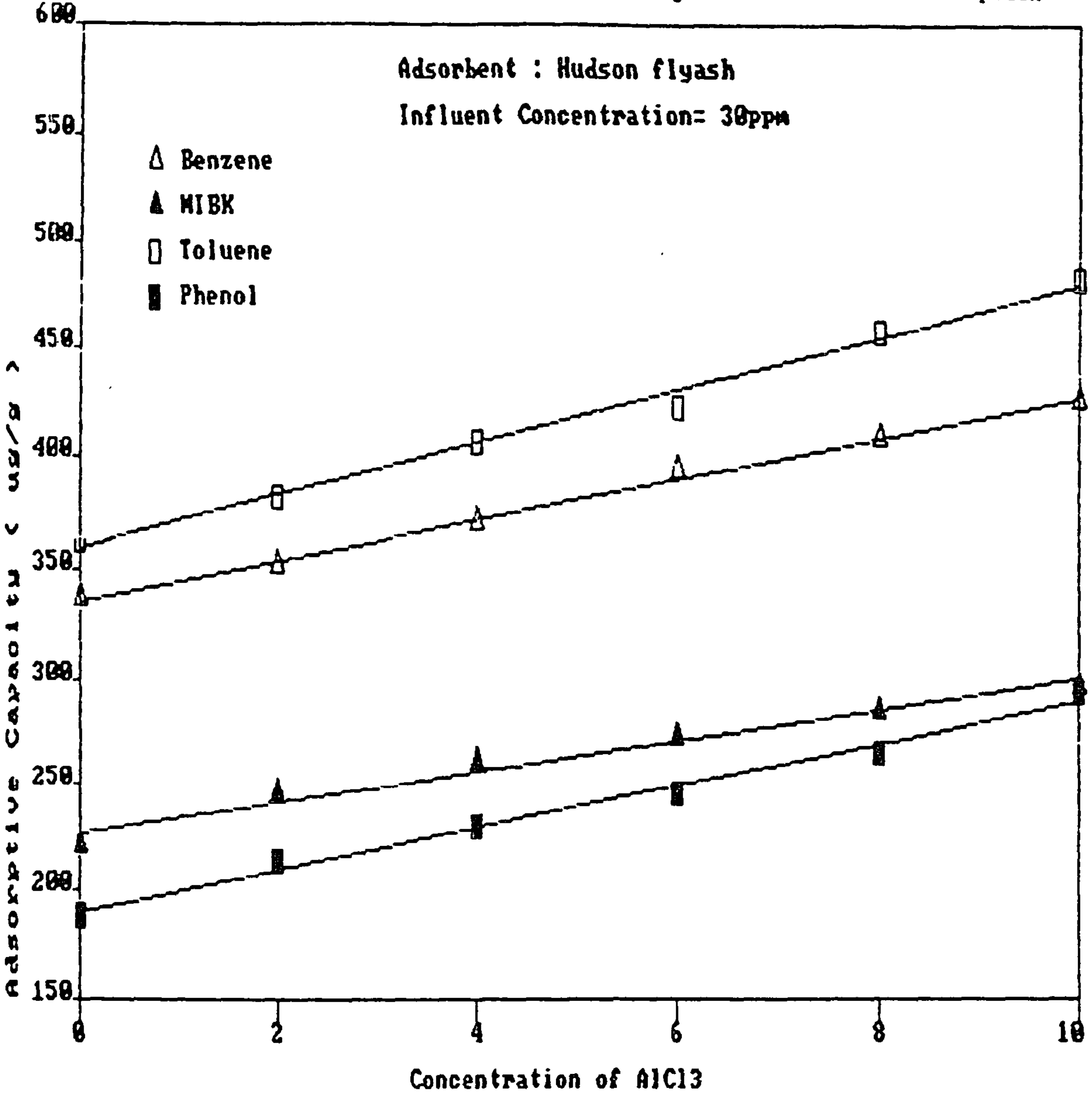


Figure E24. Effect of Concentration of $AlCl_3$ on Multi-solute Adsorption

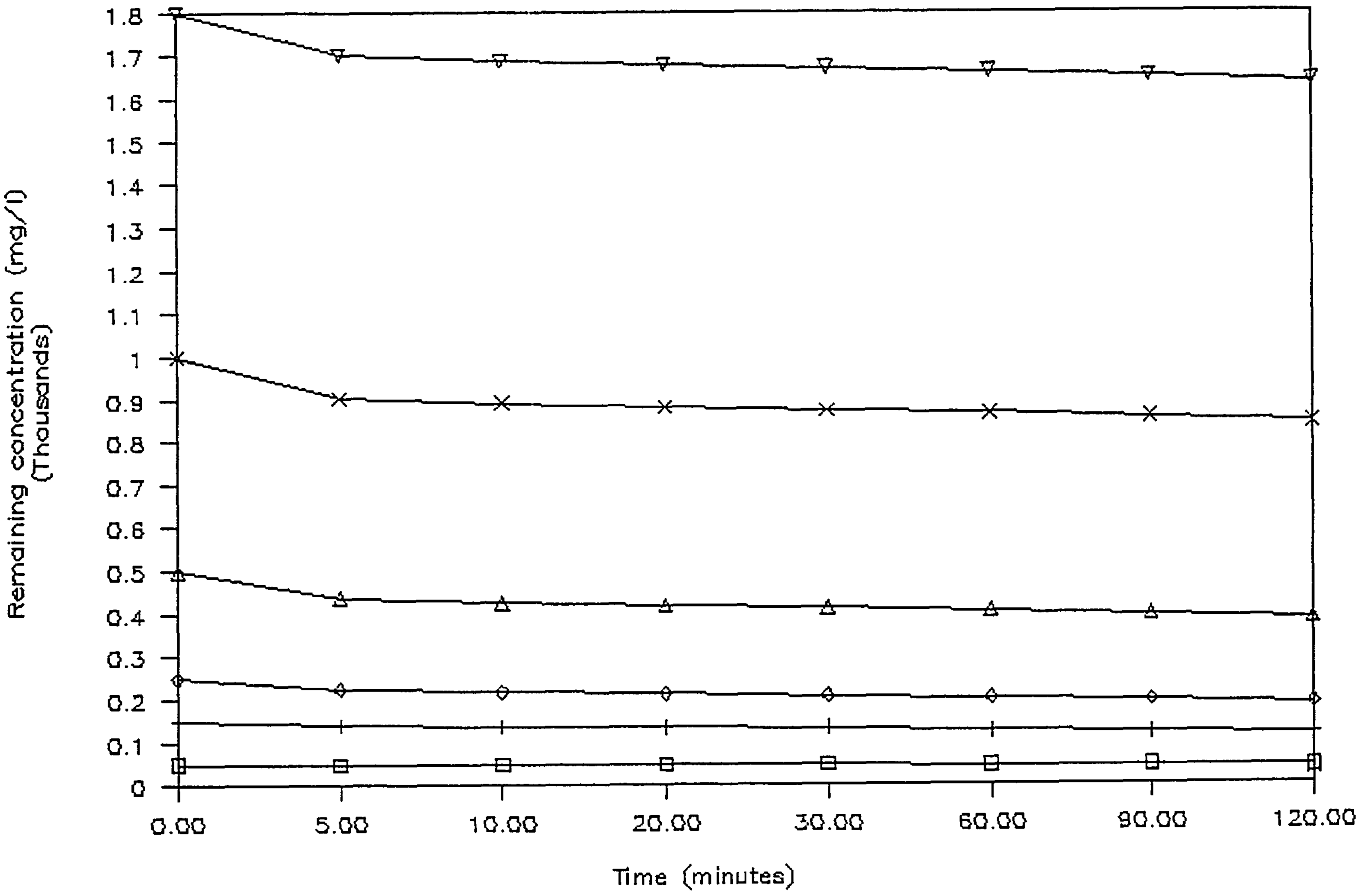


APPENDIX - 'F'

KINETIC STUDIES

Figure F1. Kinetic study

Phenol onto Activated Carbon, no salt



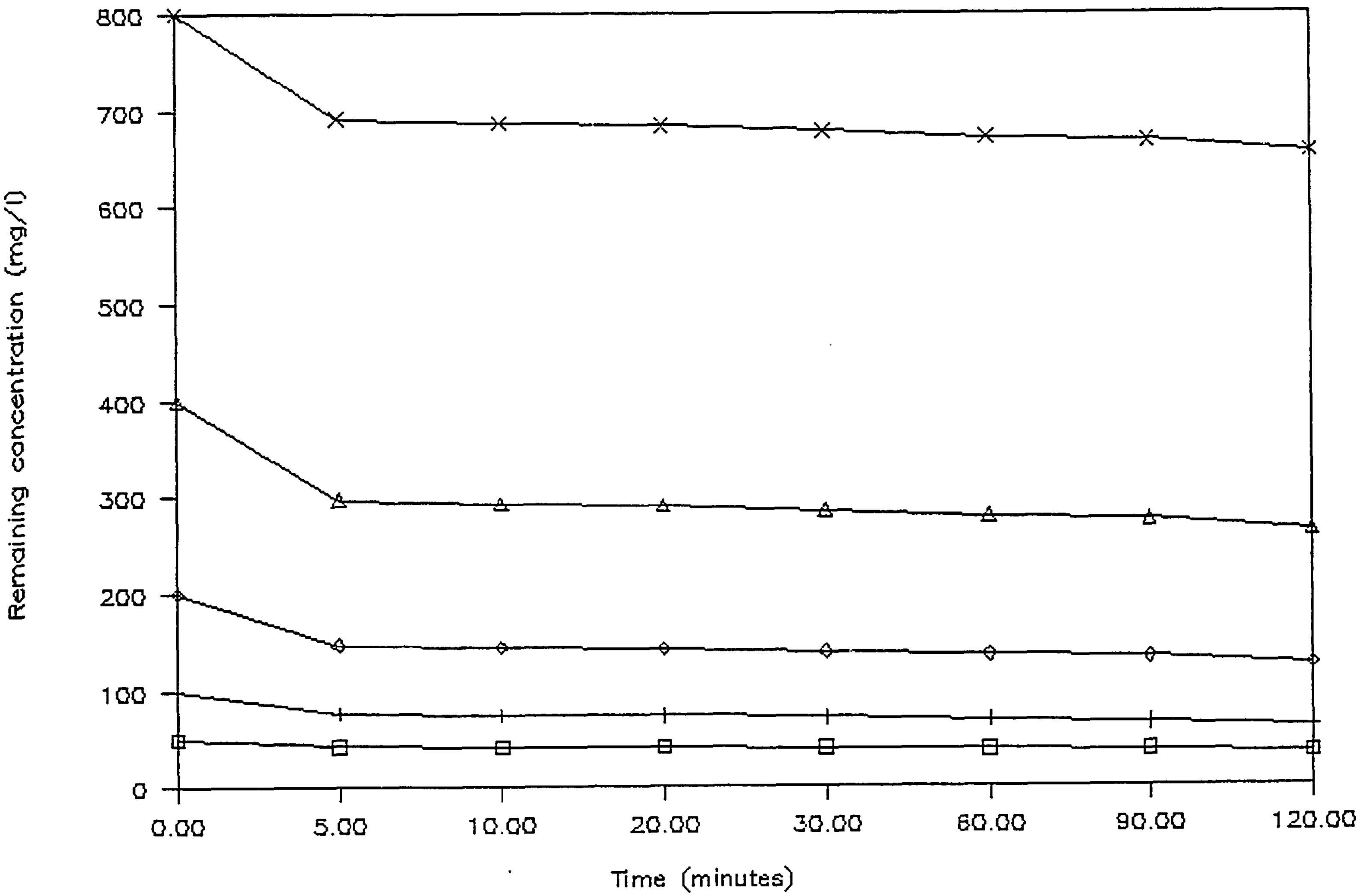


Figure F2. Kinetic study

MIBK onto Activated Carbon, no salt

Figure F3. Kinetic study

Phenol onto Flyash, no salt

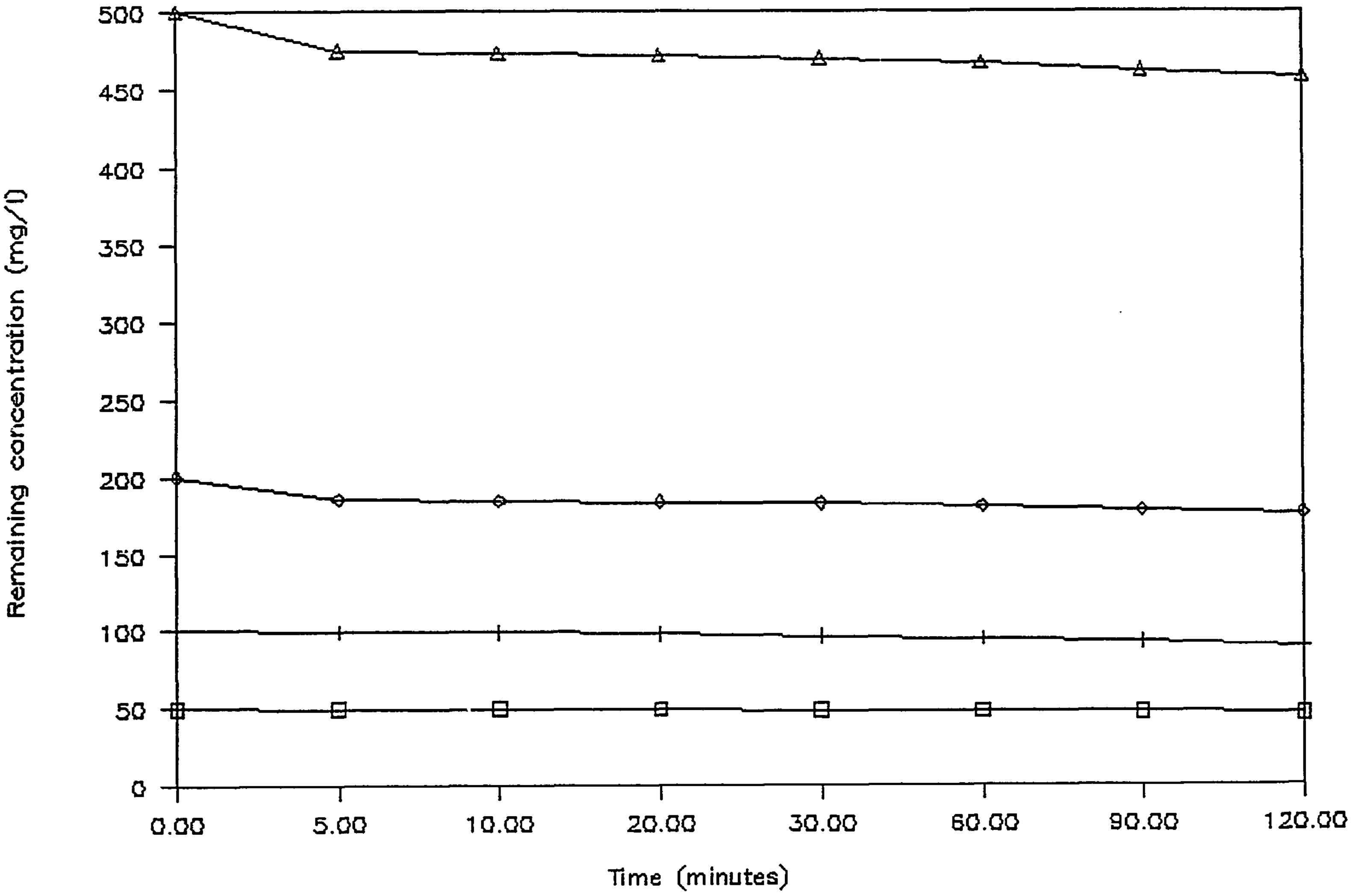


Figure F4. Kinetic study

MIBK onto Flyash, no salt

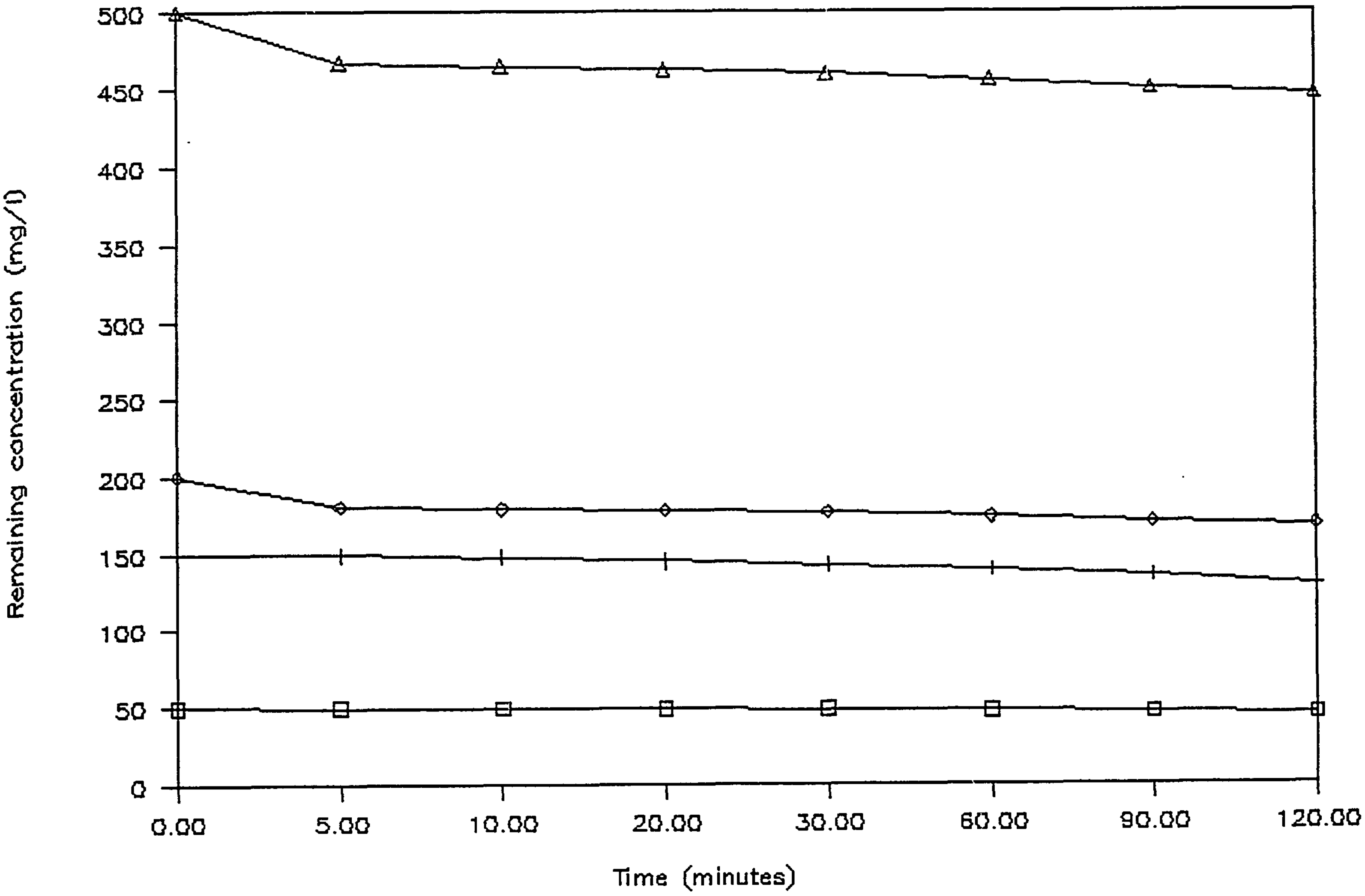


Figure F5. Kinetic study

Phenol onto Activated carbon,.01 M NaCl

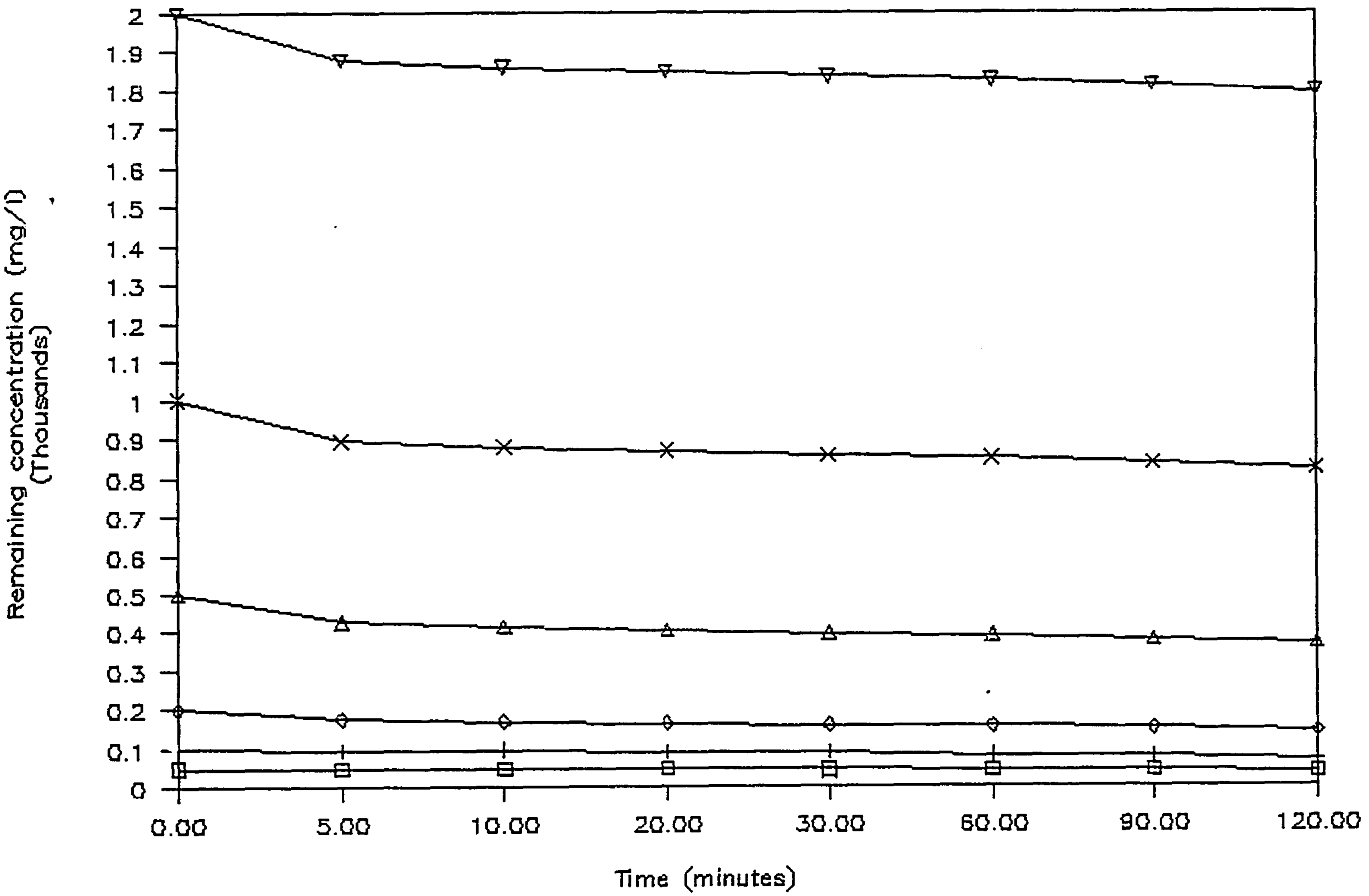


Figure F6. Kinetic study

MIBK onto Activated carbon, 0.01 M NaCl

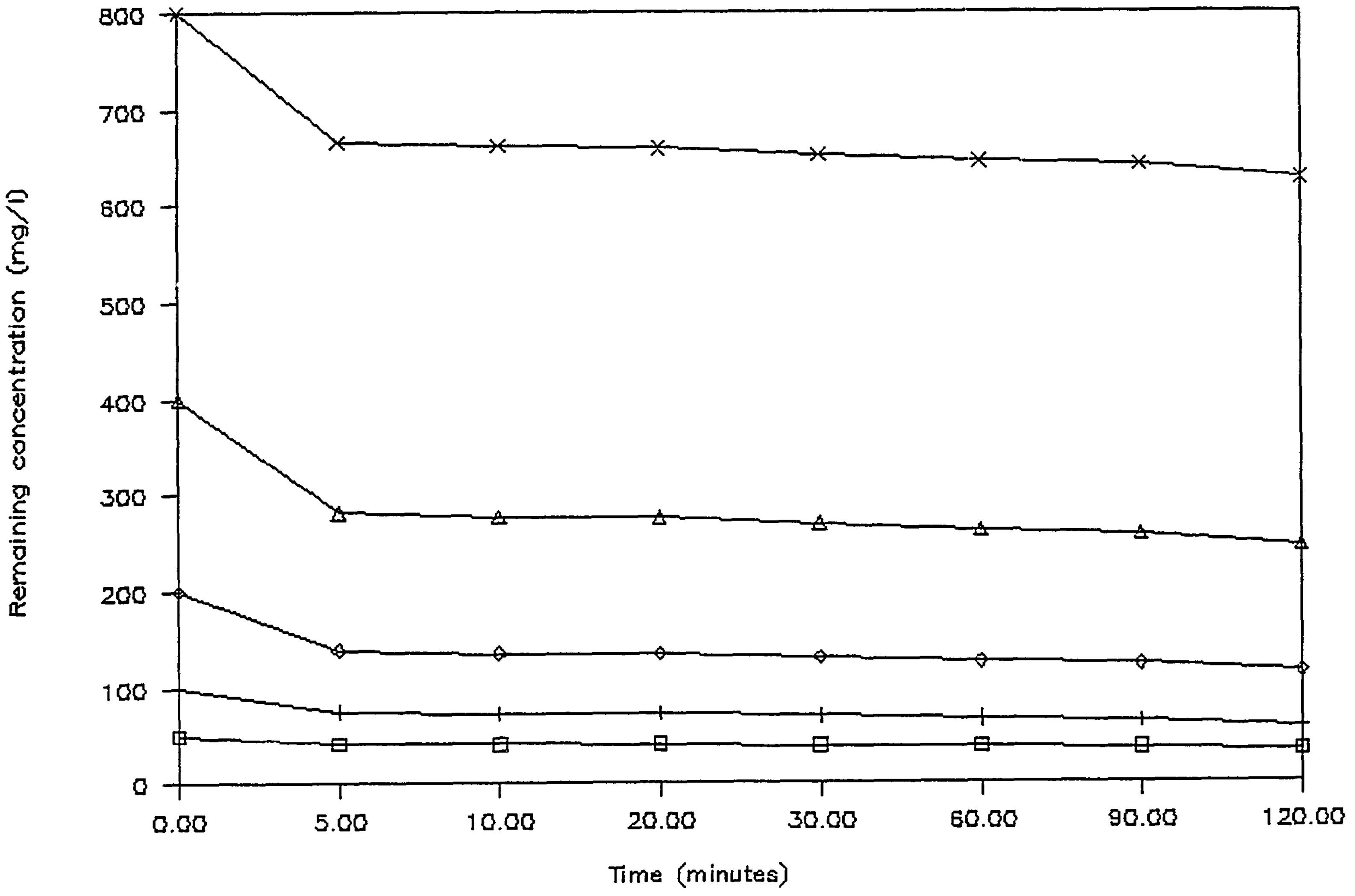


Figure F7. Kinetic study

Phenol onto Flyash, 0.01 M AlCl3

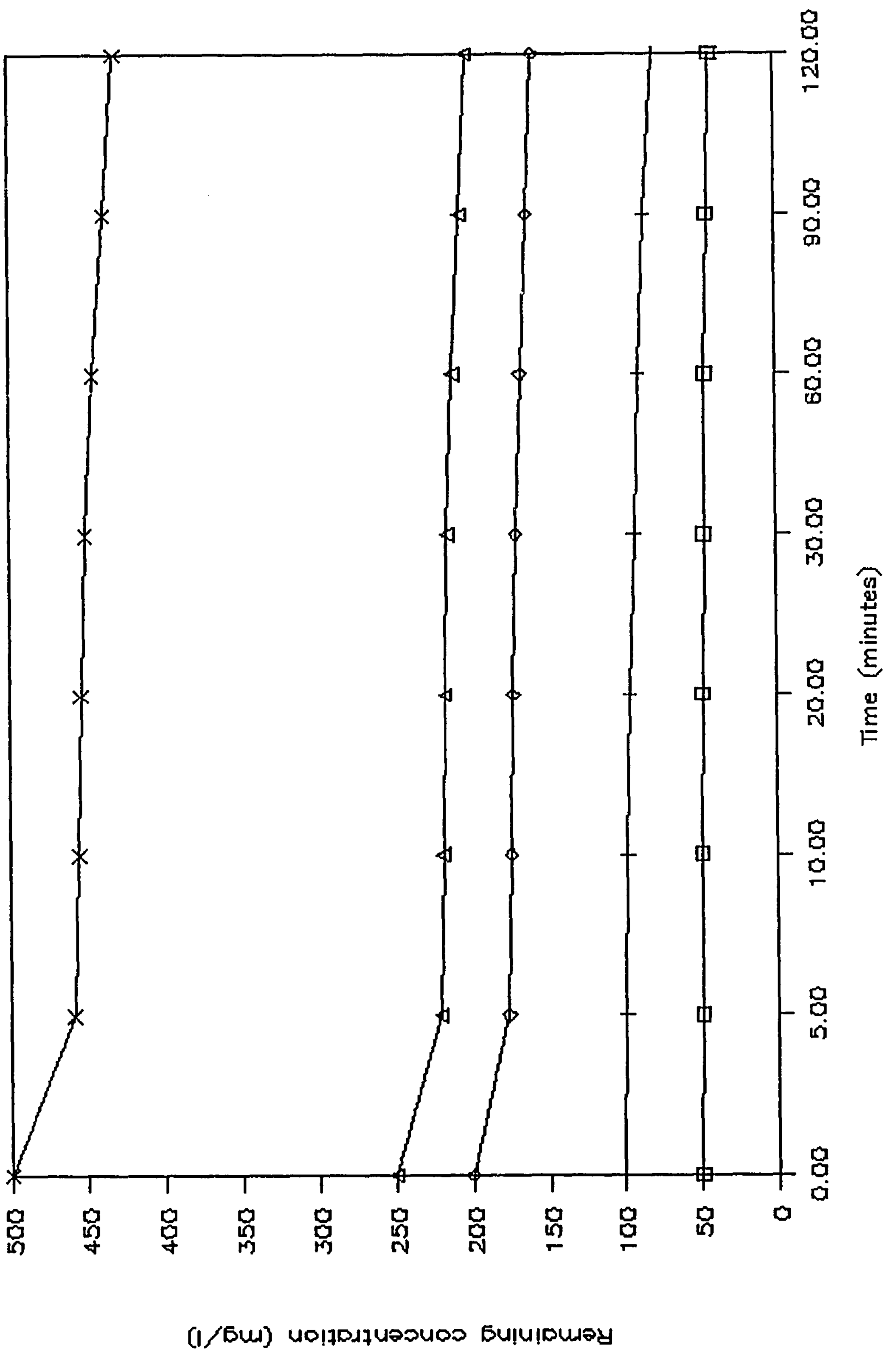


Figure F8. Kinetic study

MIBK onto Flyash, 0.01 M AlCl3

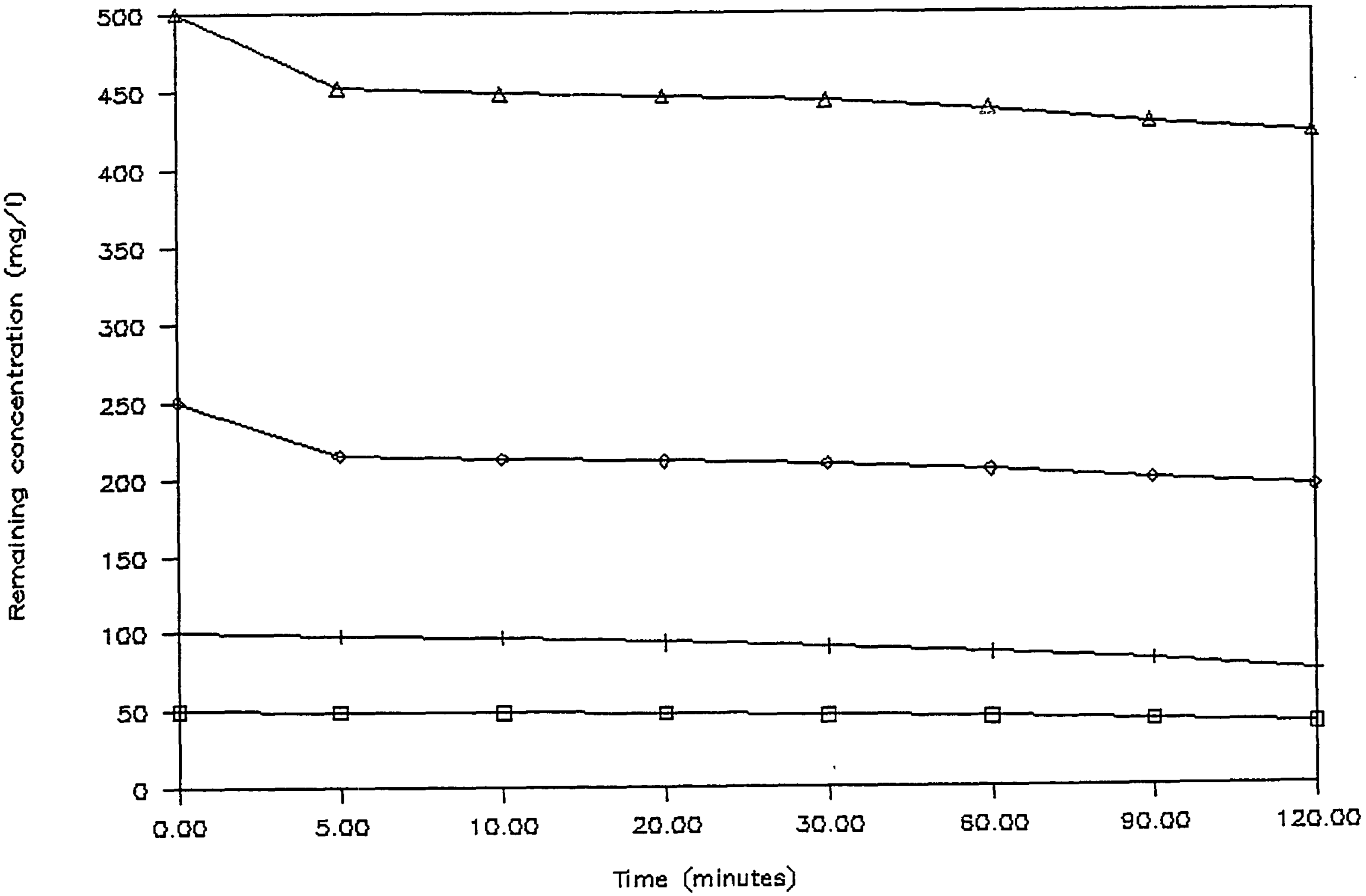


Figure F9. Salts' Effect on Adsorption Kinetics

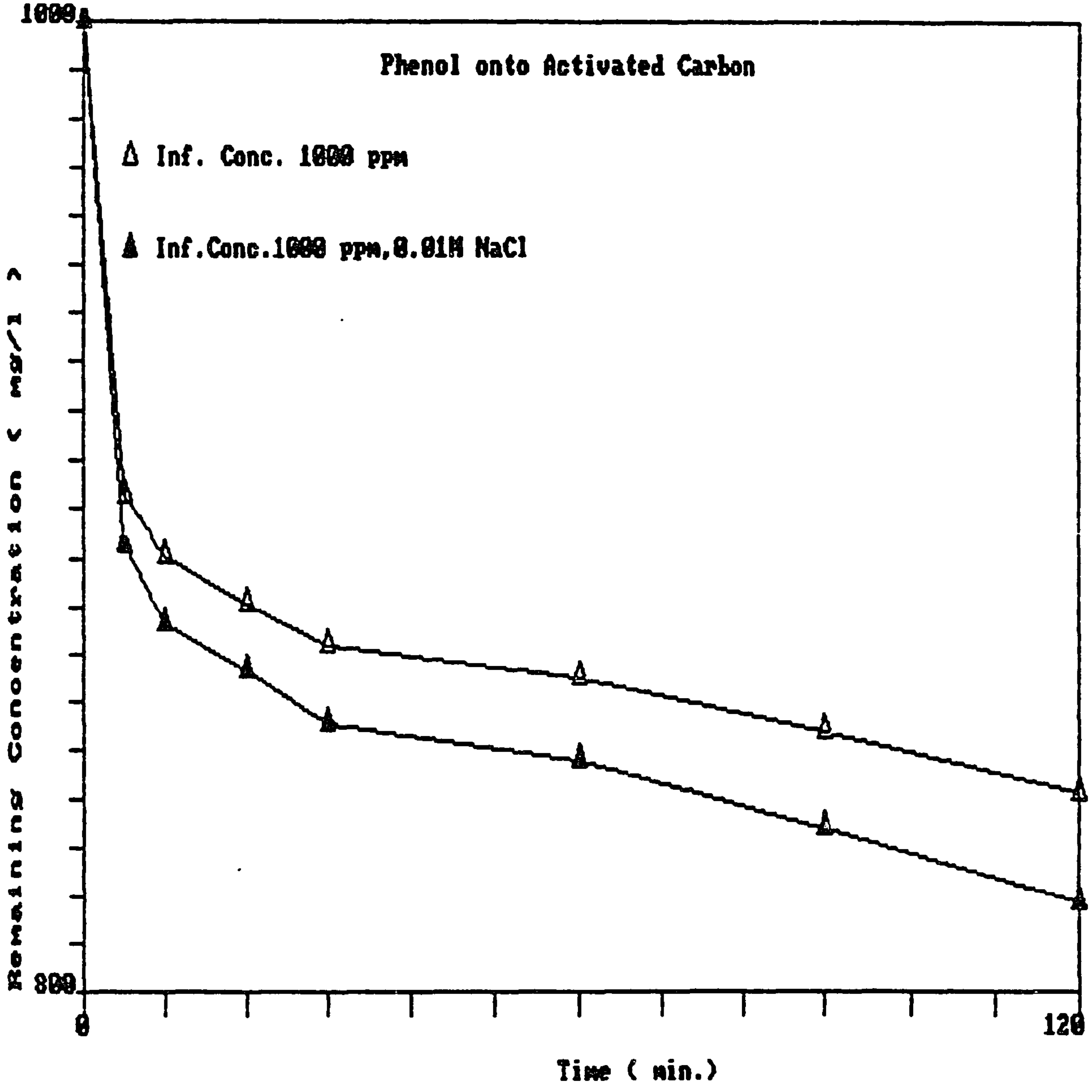


Figure F10. Salts' Effect on Adsorption Kinetics

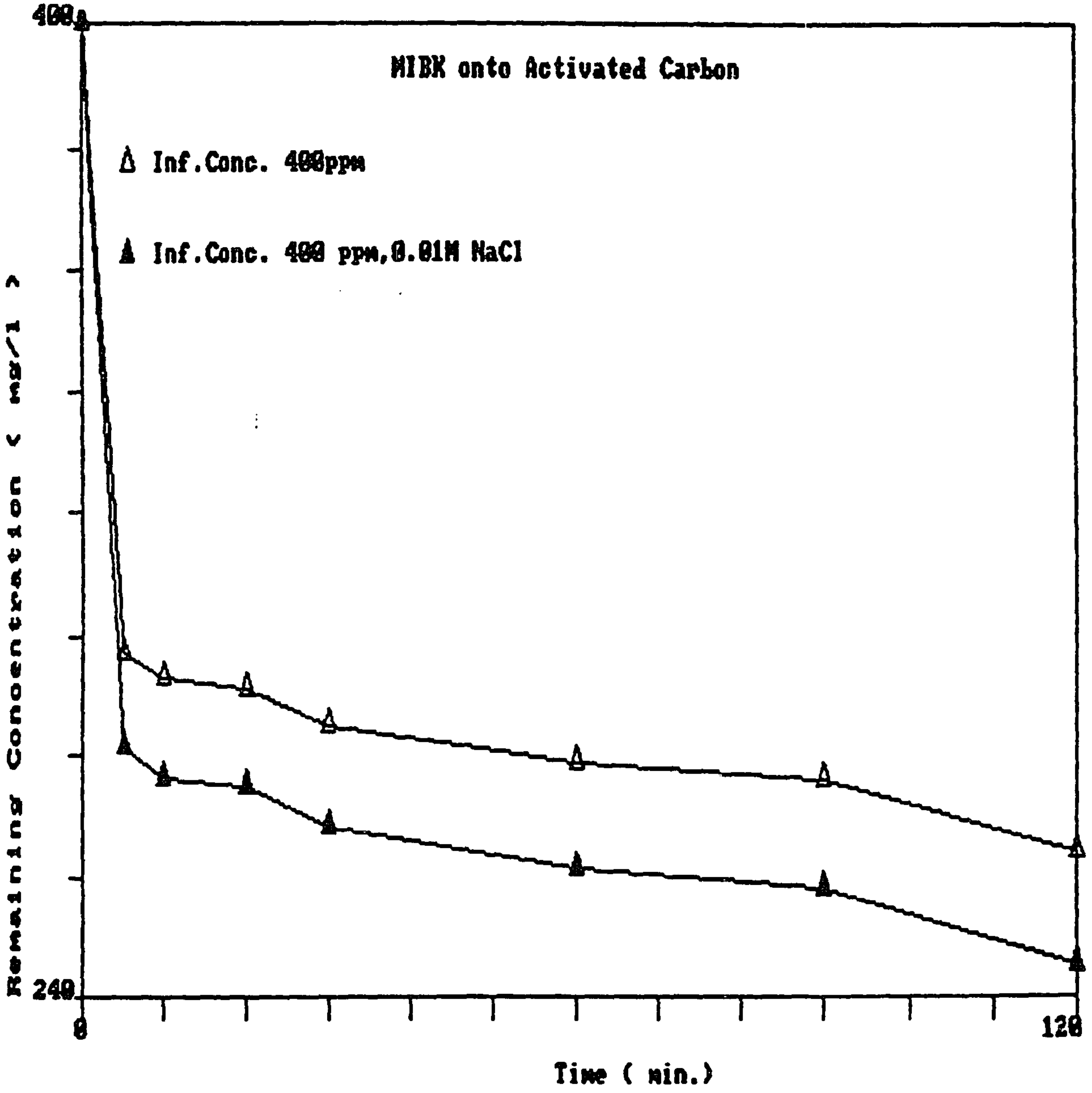


Figure F11. Salts' Effect on Adsorption Rate Const.

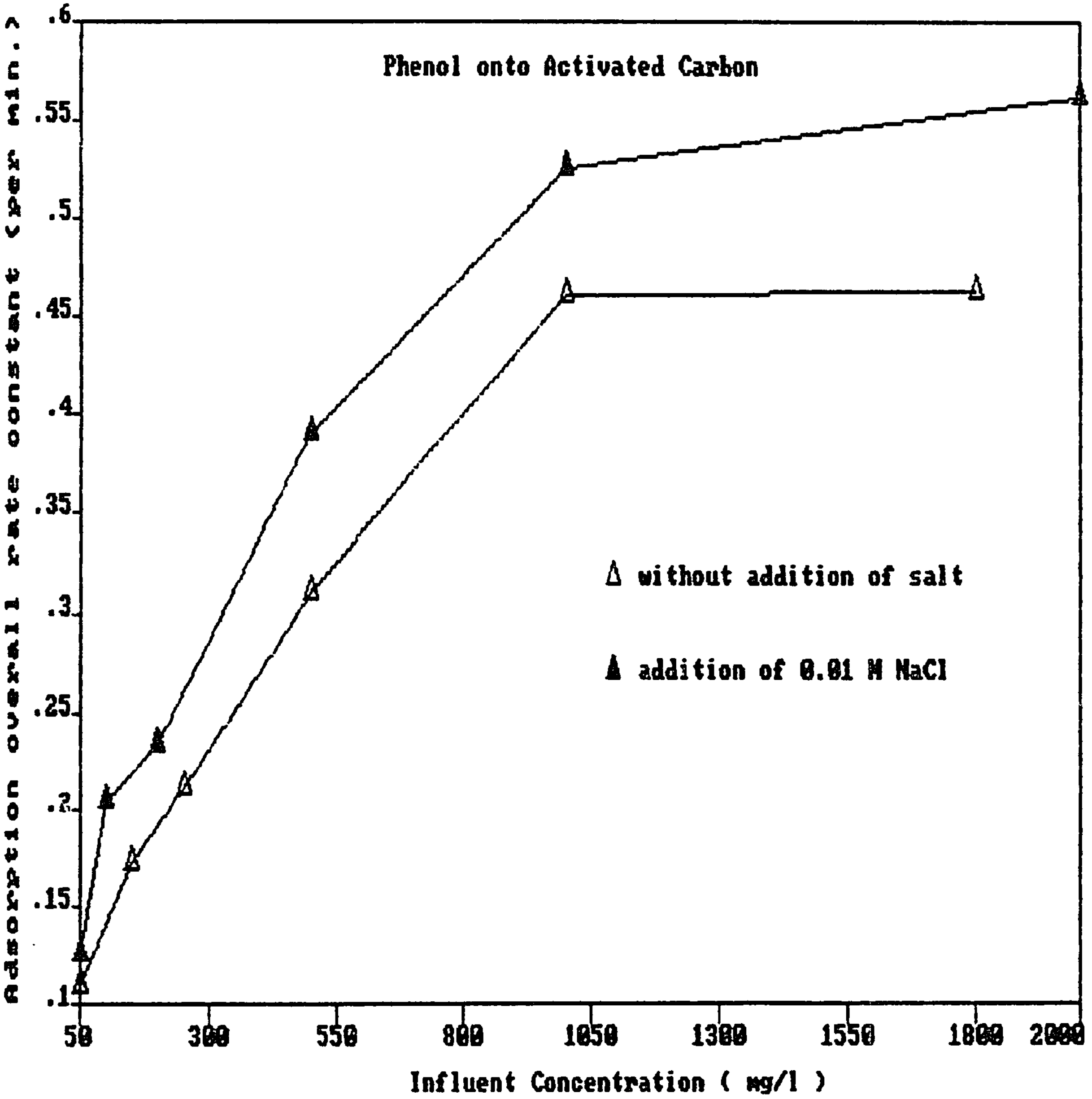


Figure F12. Salts' Effect on Adsorption Rate Const.

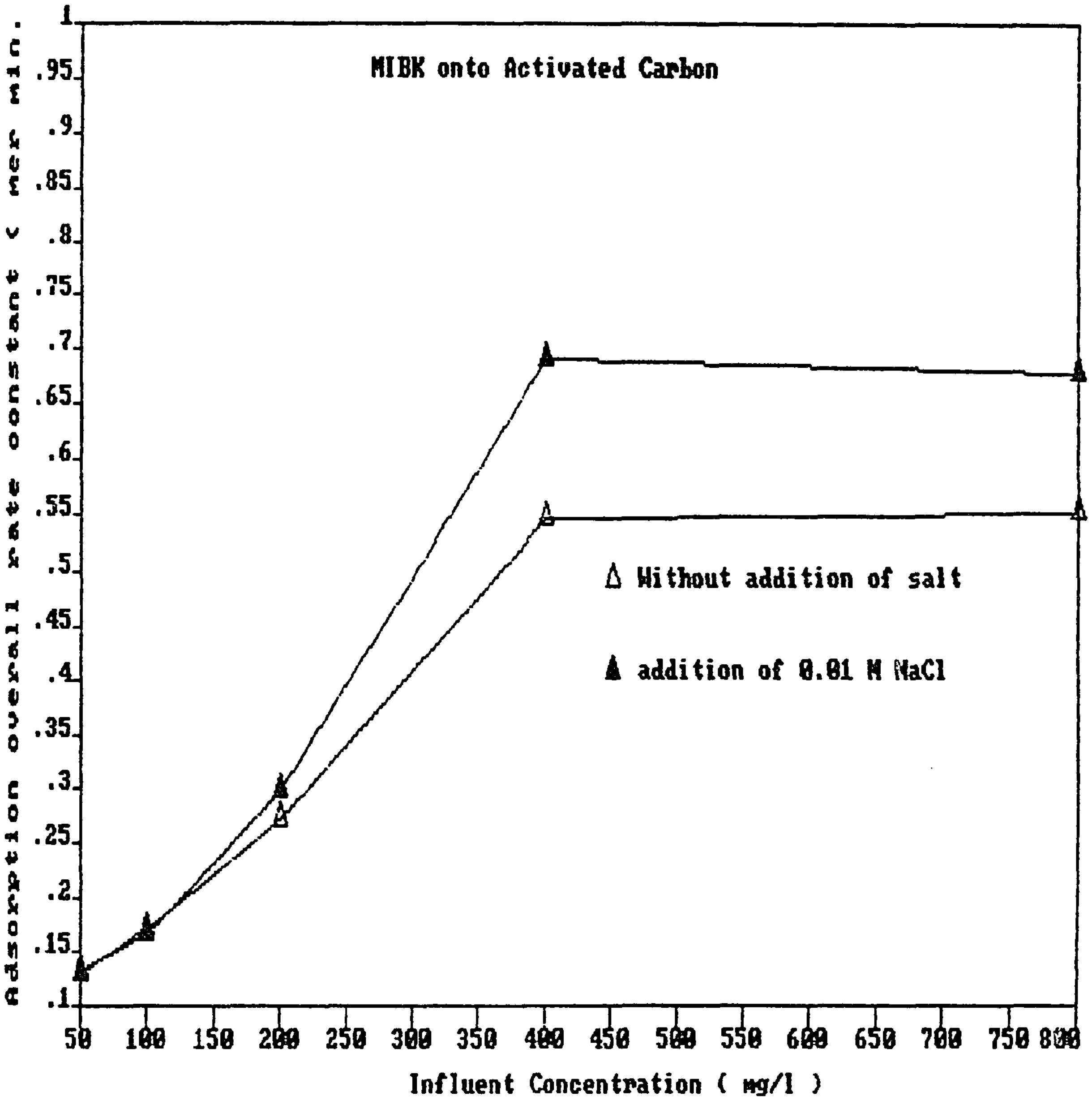


Figure F13. First Order Reversible Kinetic Fit

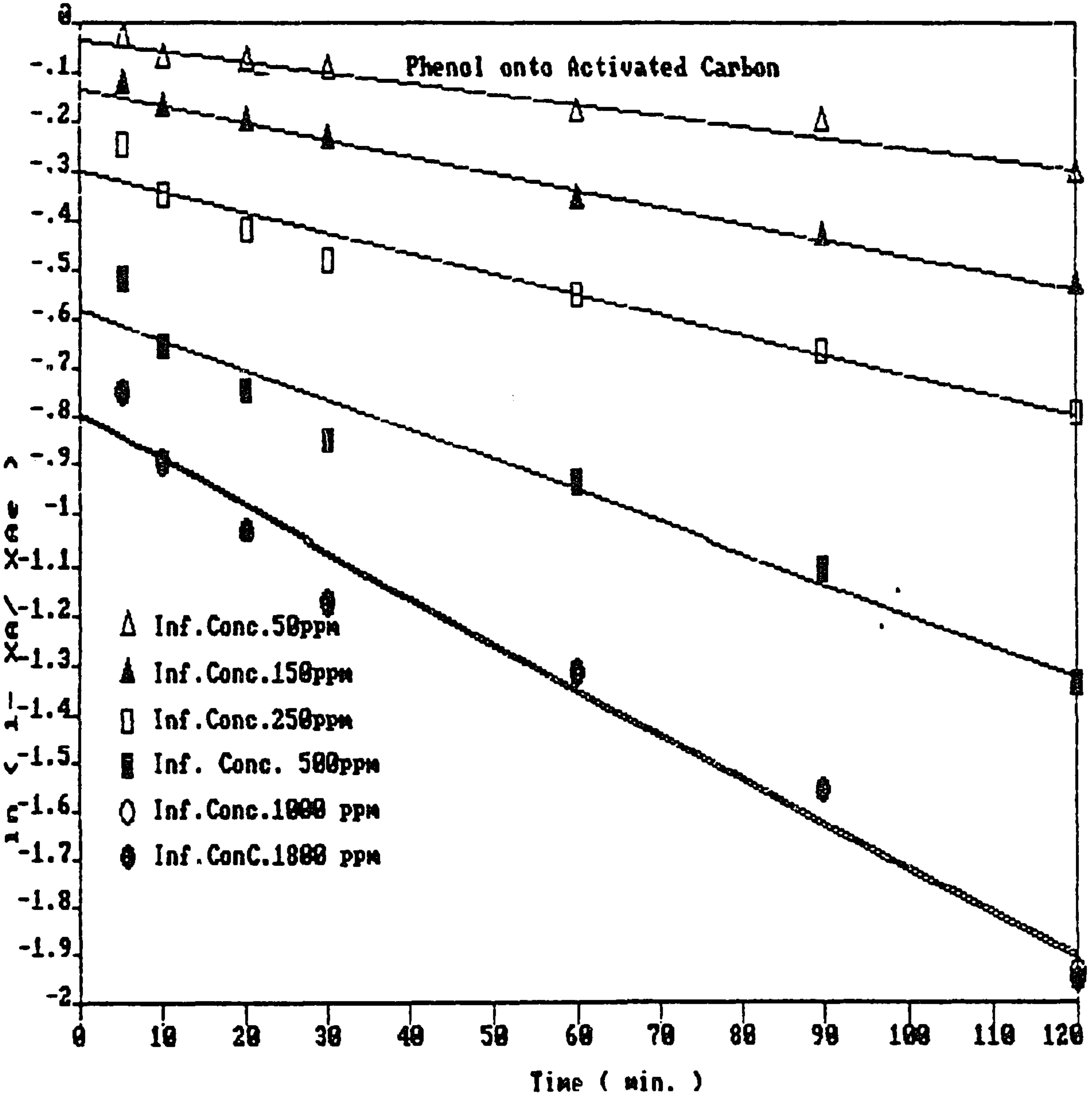


Figure F14. First order Reversible Kinetic Fit

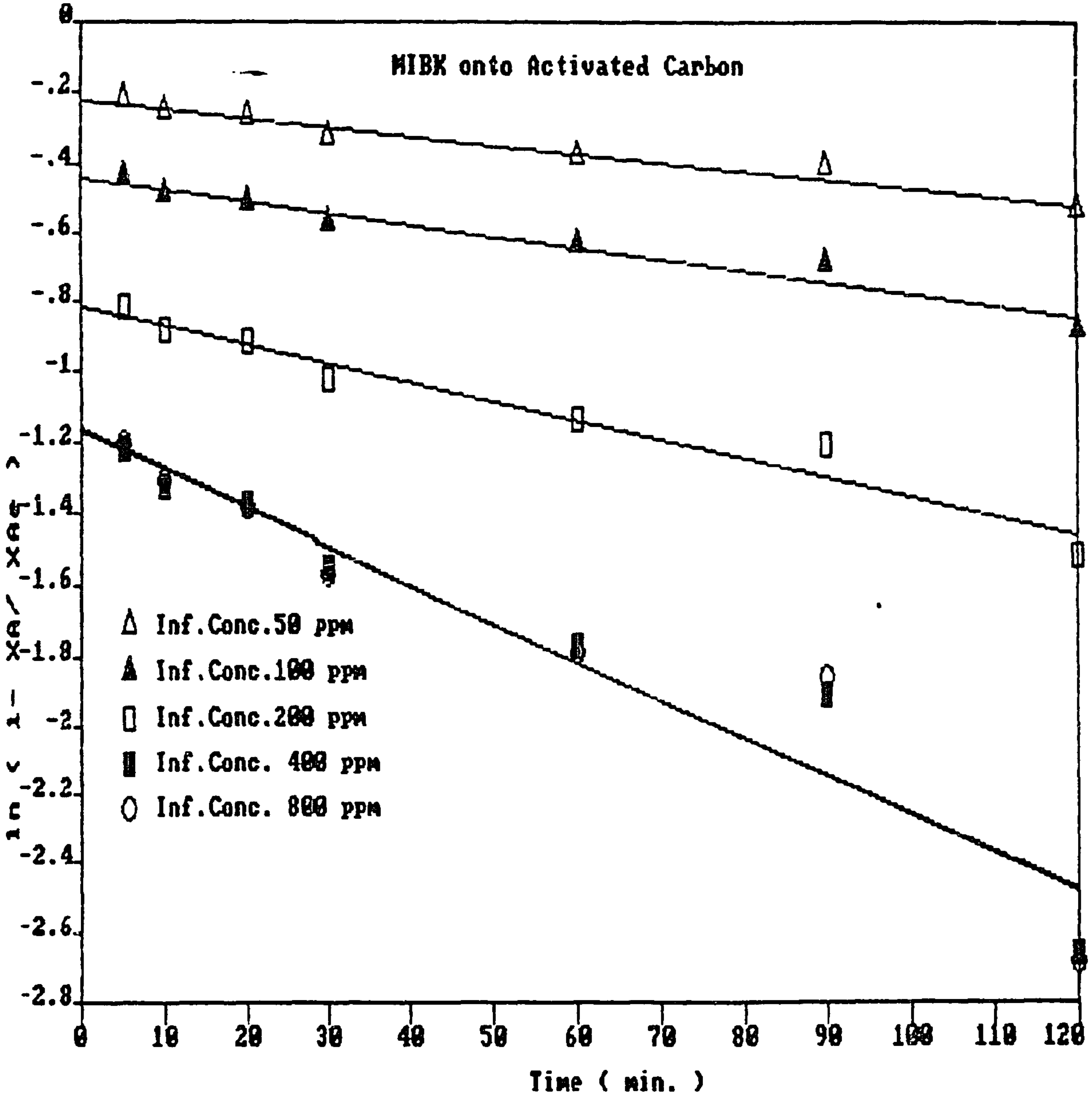


Figure F15. First order Reversible Kinetic Fit

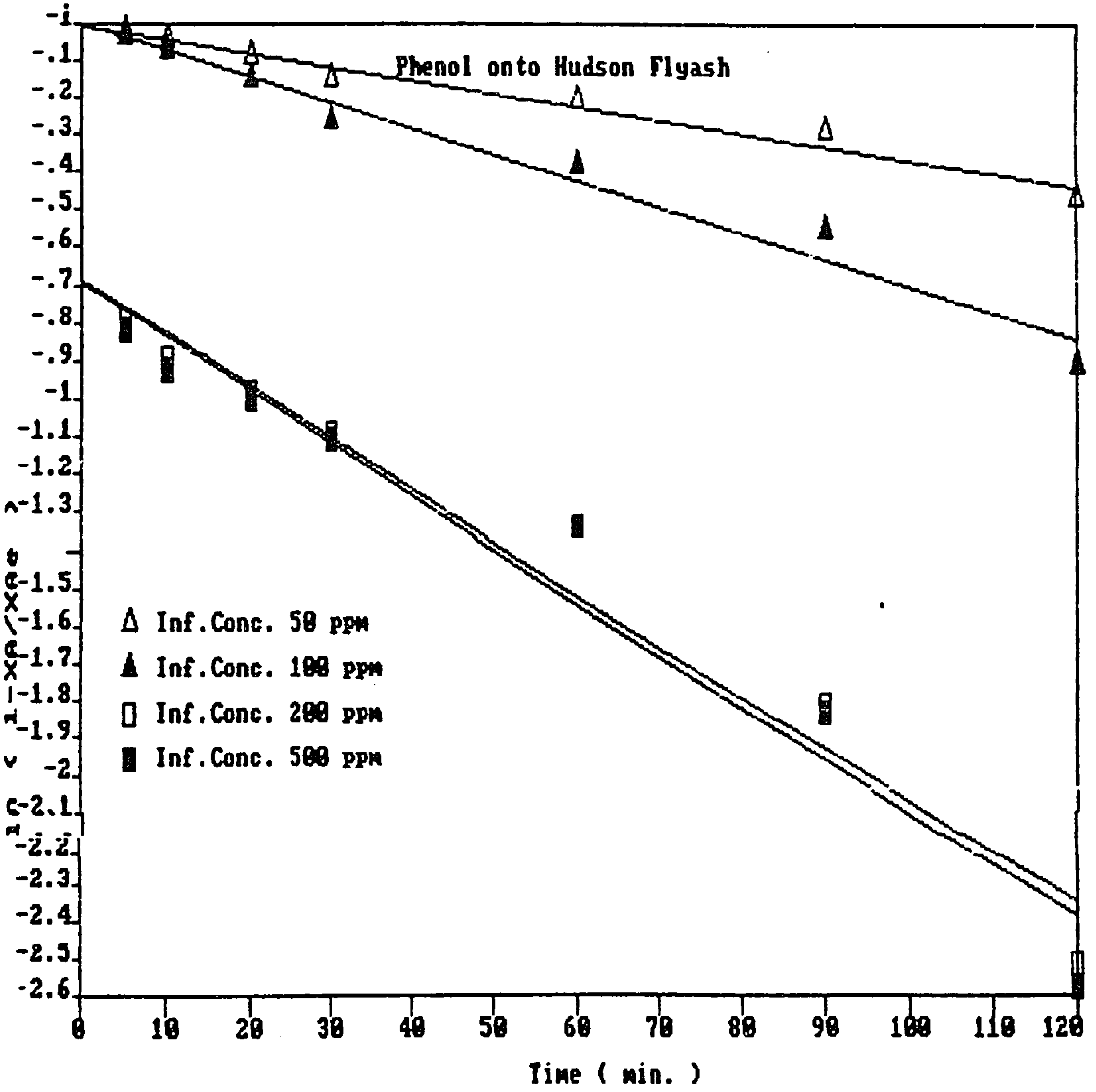


Figure F16. First order Reversible Kinetic Fit

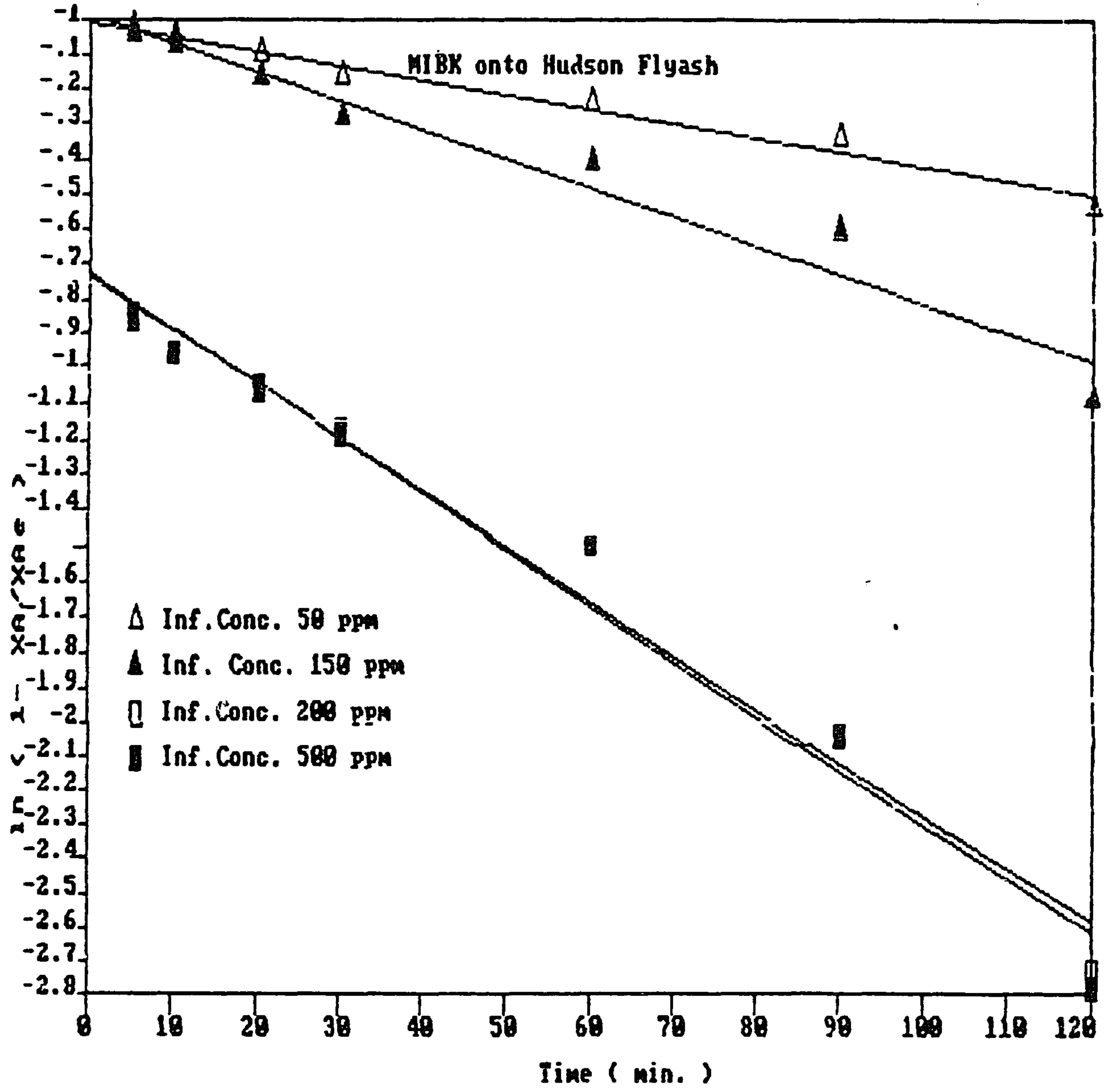


Figure F17. First order Reversible Kinetic Fit

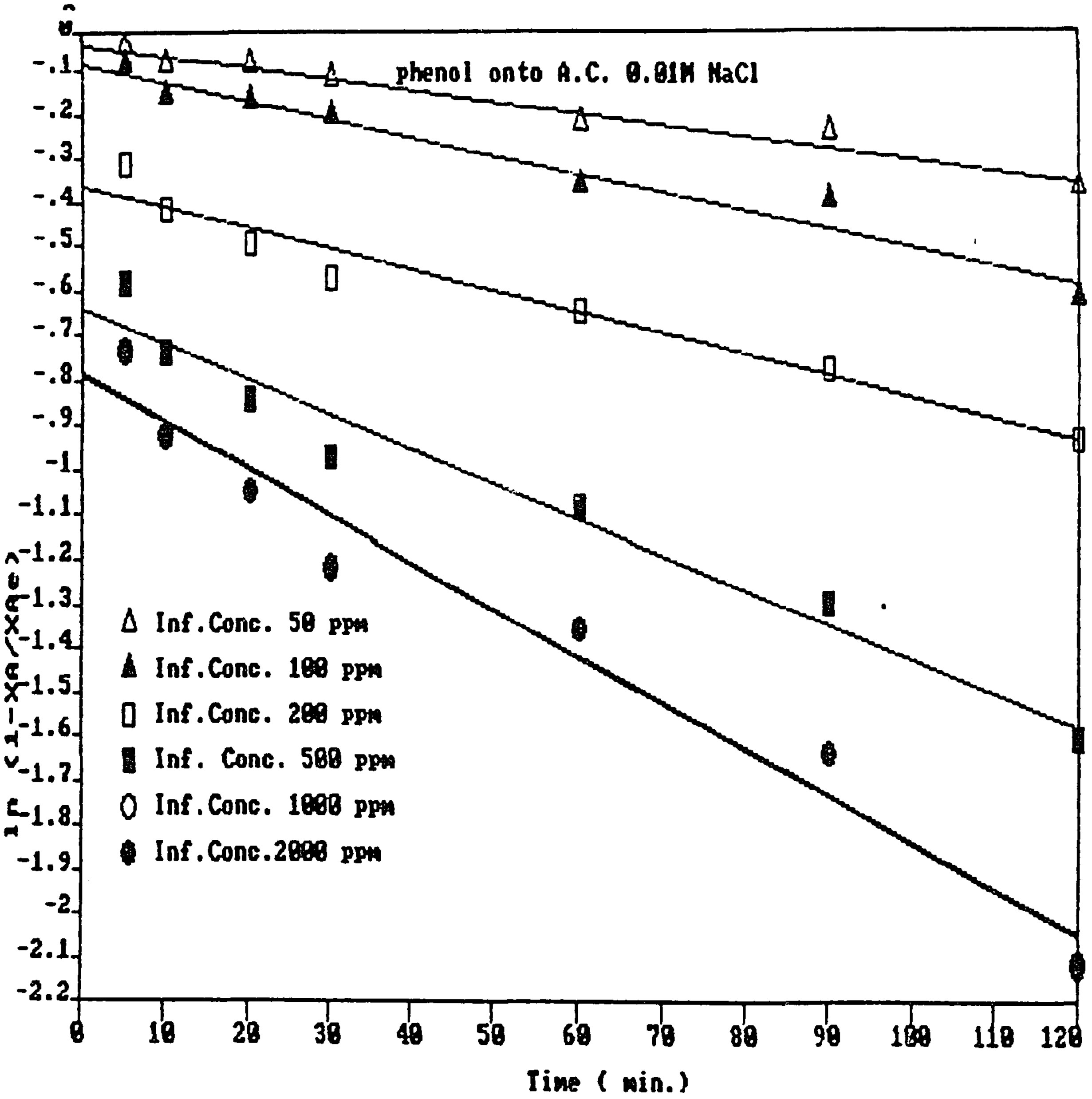


Figure F18. First order Reversible Kinetic Fit

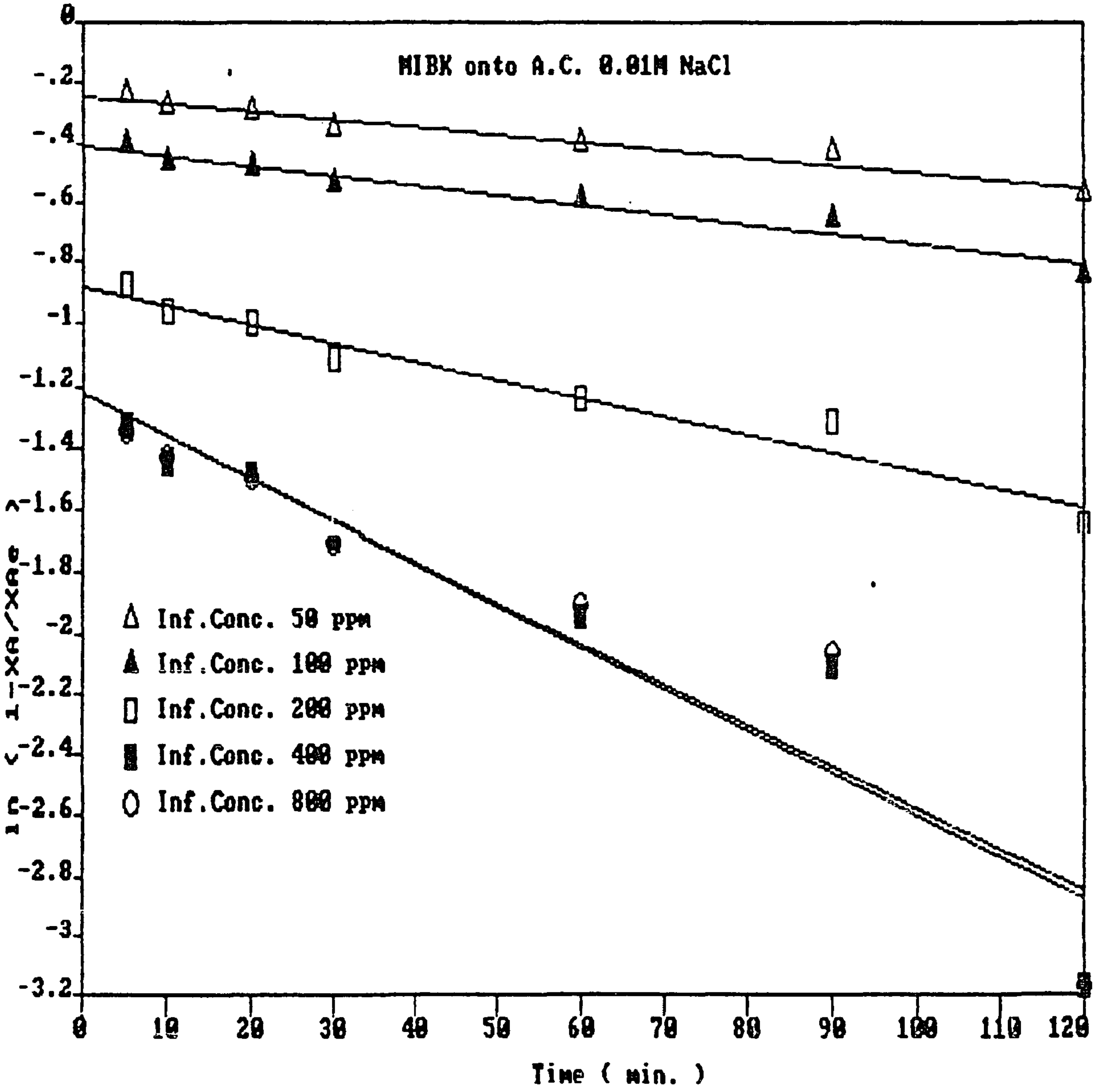


Figure F19. First order Reversible Kinetic Fit

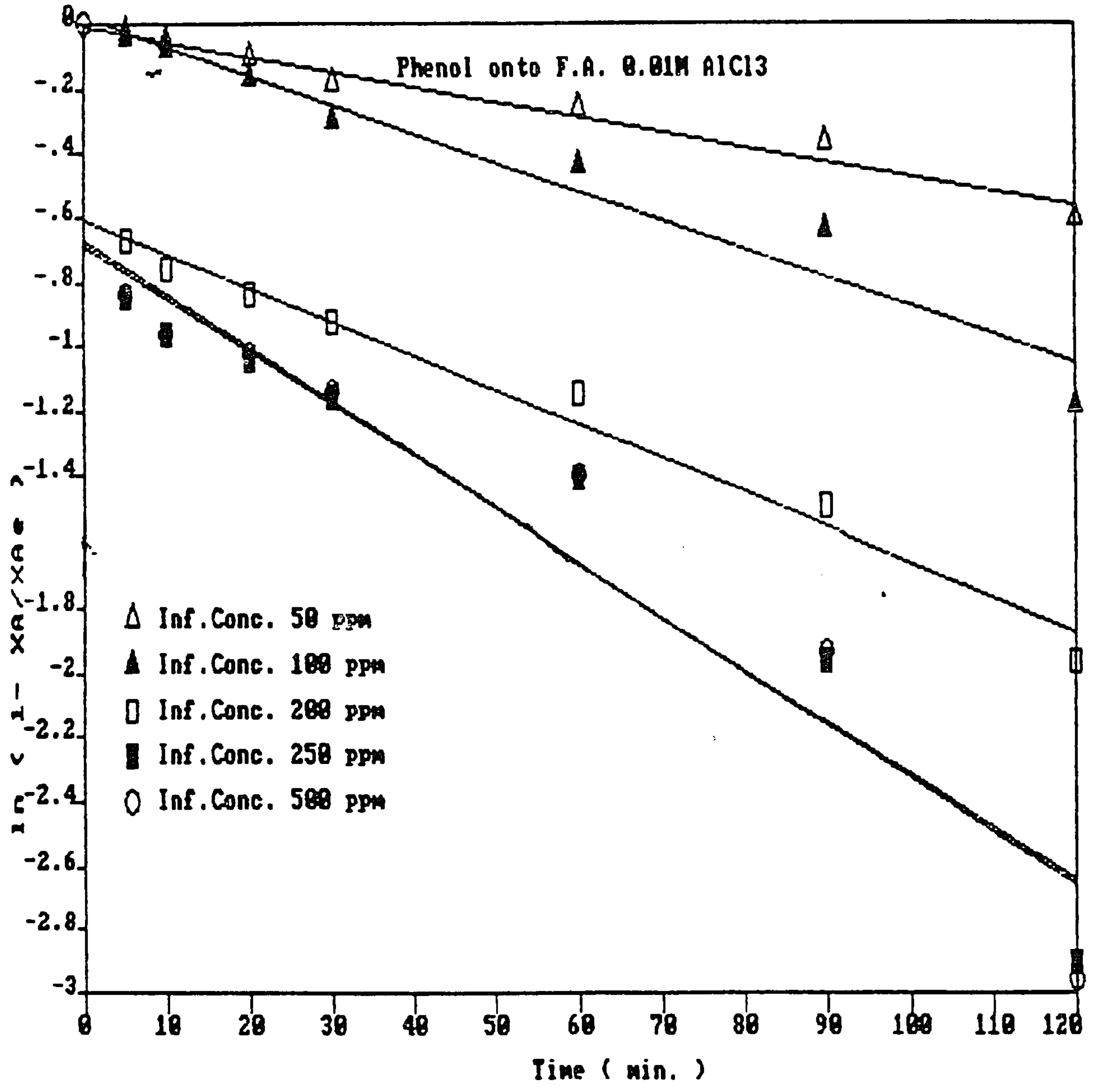
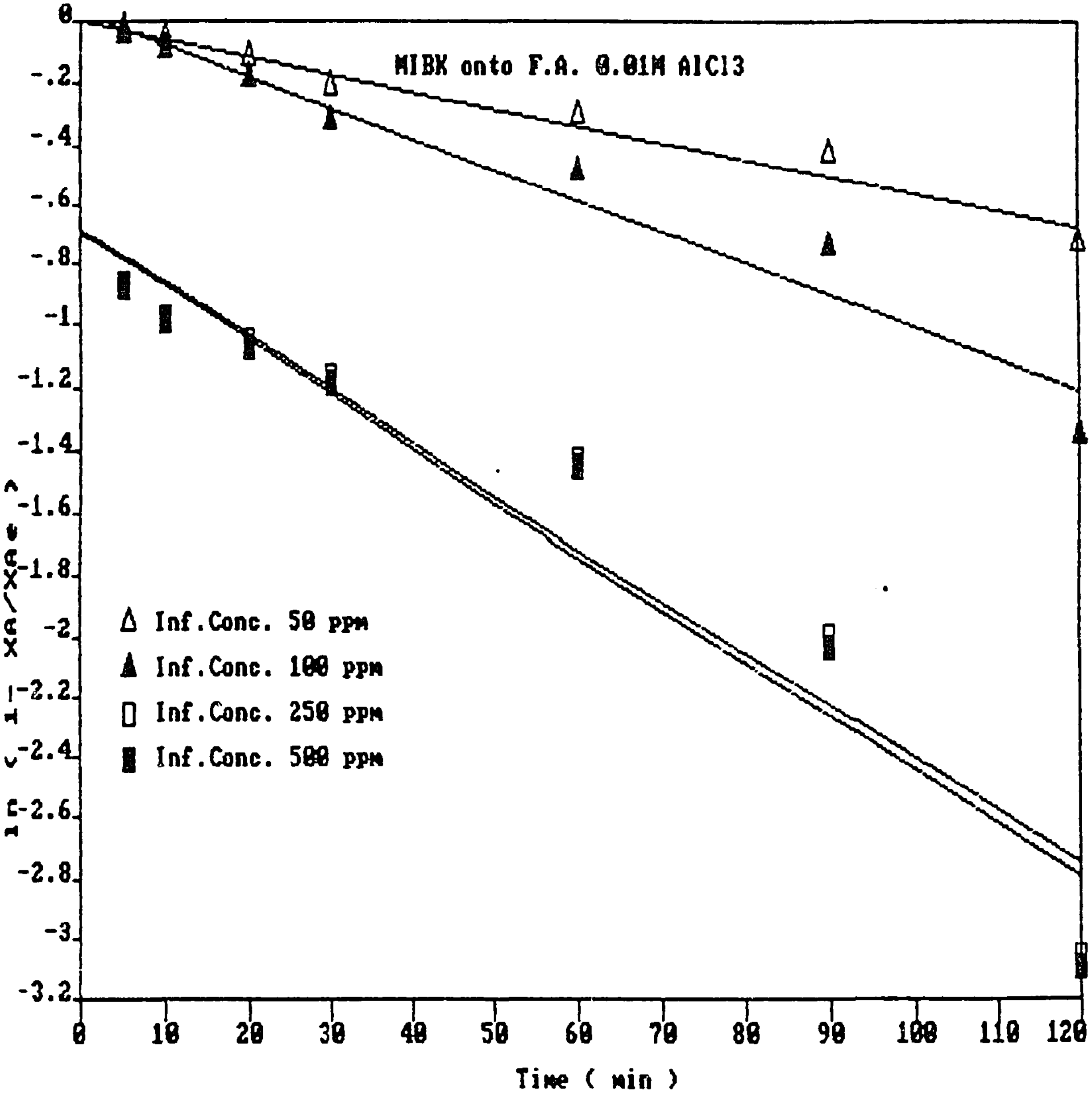


Figure F28. First order Reversible Kinetic Fit



APPENDIX - 'G'

RELATIONSHIP AMONG SALT CONCENTRATION, OVERALL SORPTION RATE CONSTANT , AND ADSORPTIVE CAPACITY

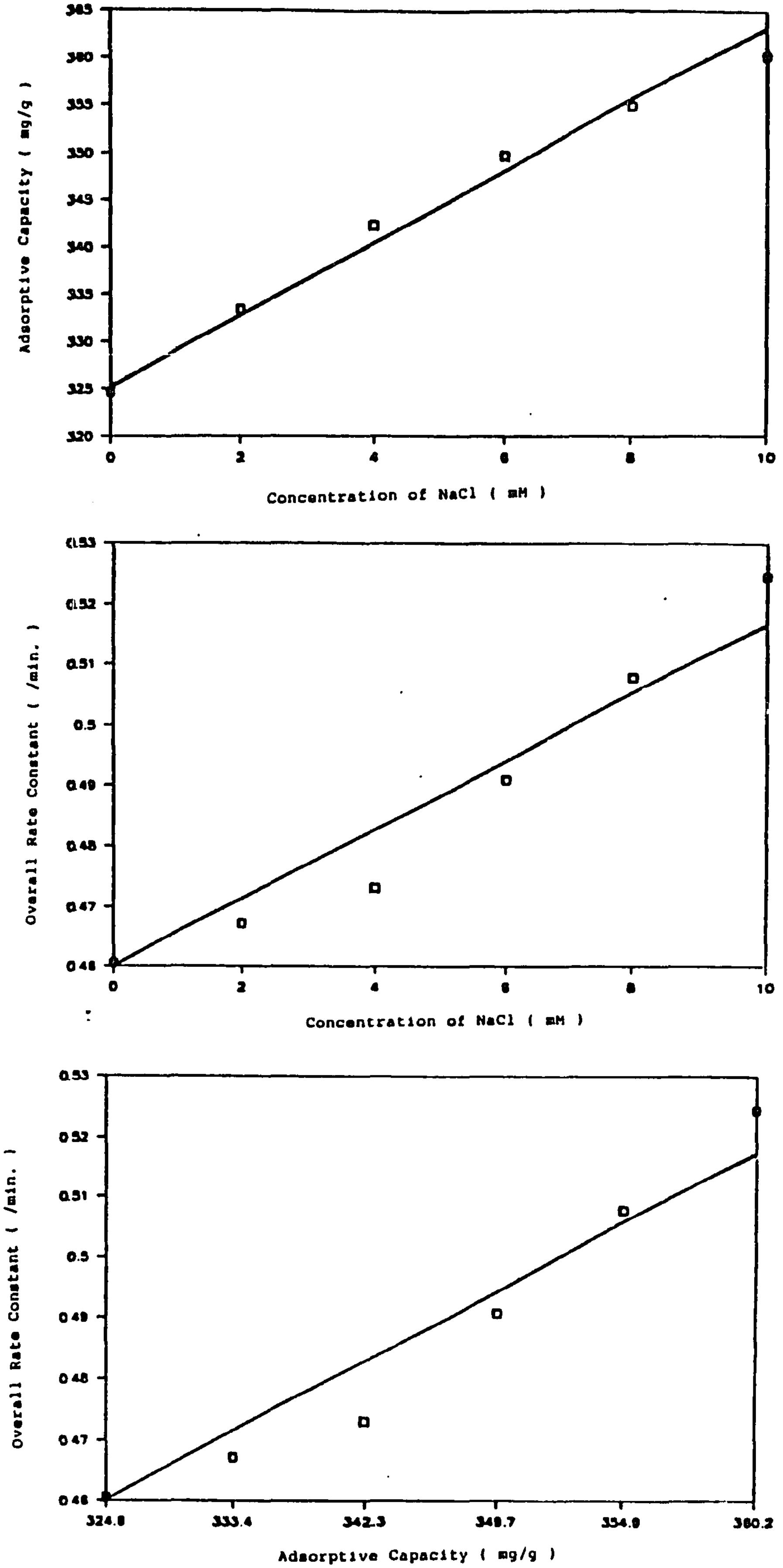


Figure G1. Relationship among Salts' Concentration, Overall Sorption Rate Constant, and Adsorptive Capacity. (1000 ppm Phenol, NaCl, Activated Carbon)

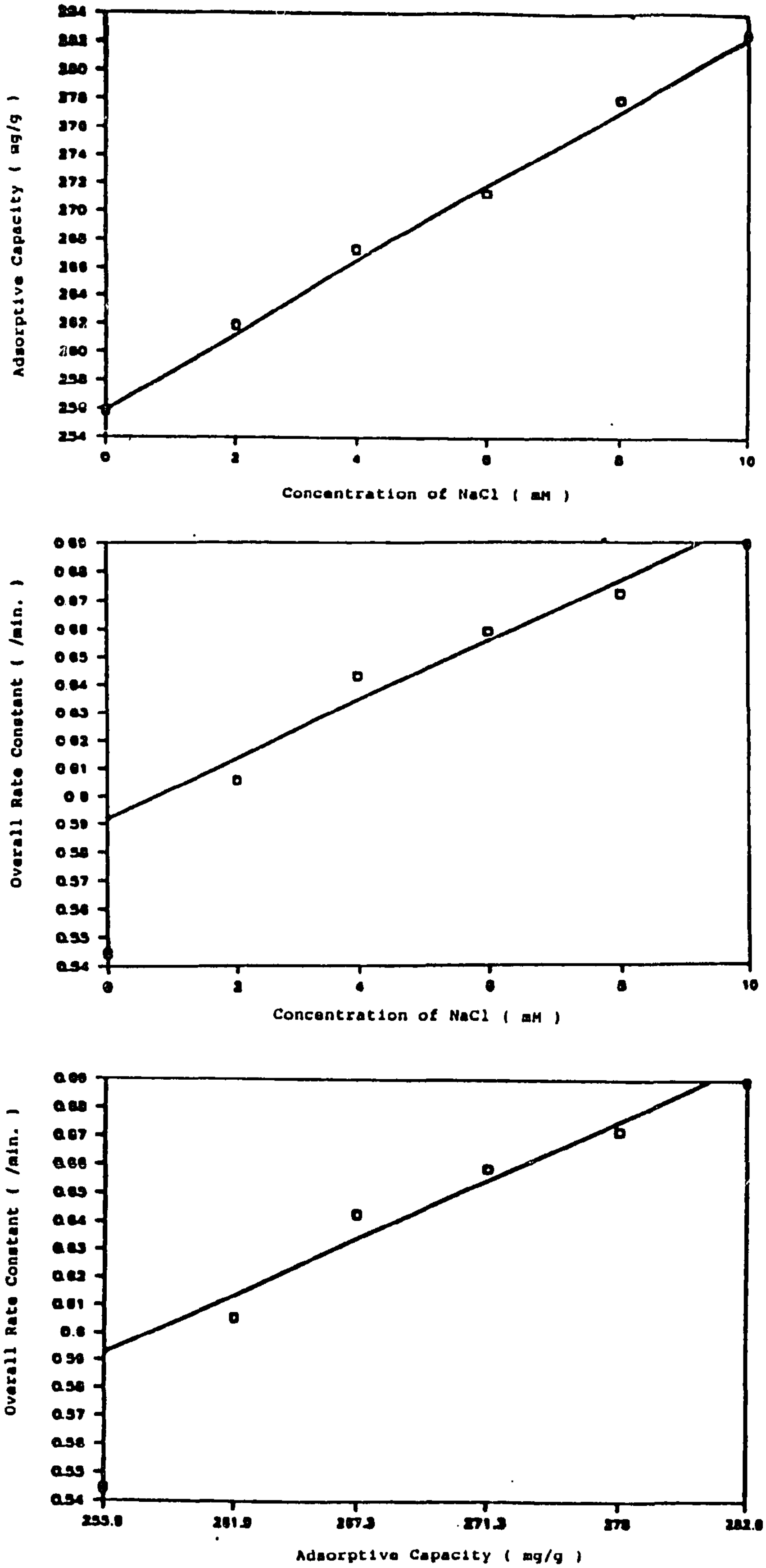


Figure G2. Relationship among Salts' Concentration, Overall Sorption Rate Constant, and Adsorptive Capacity. (400 ppm MIBK, NaCl, Activated Carbon)

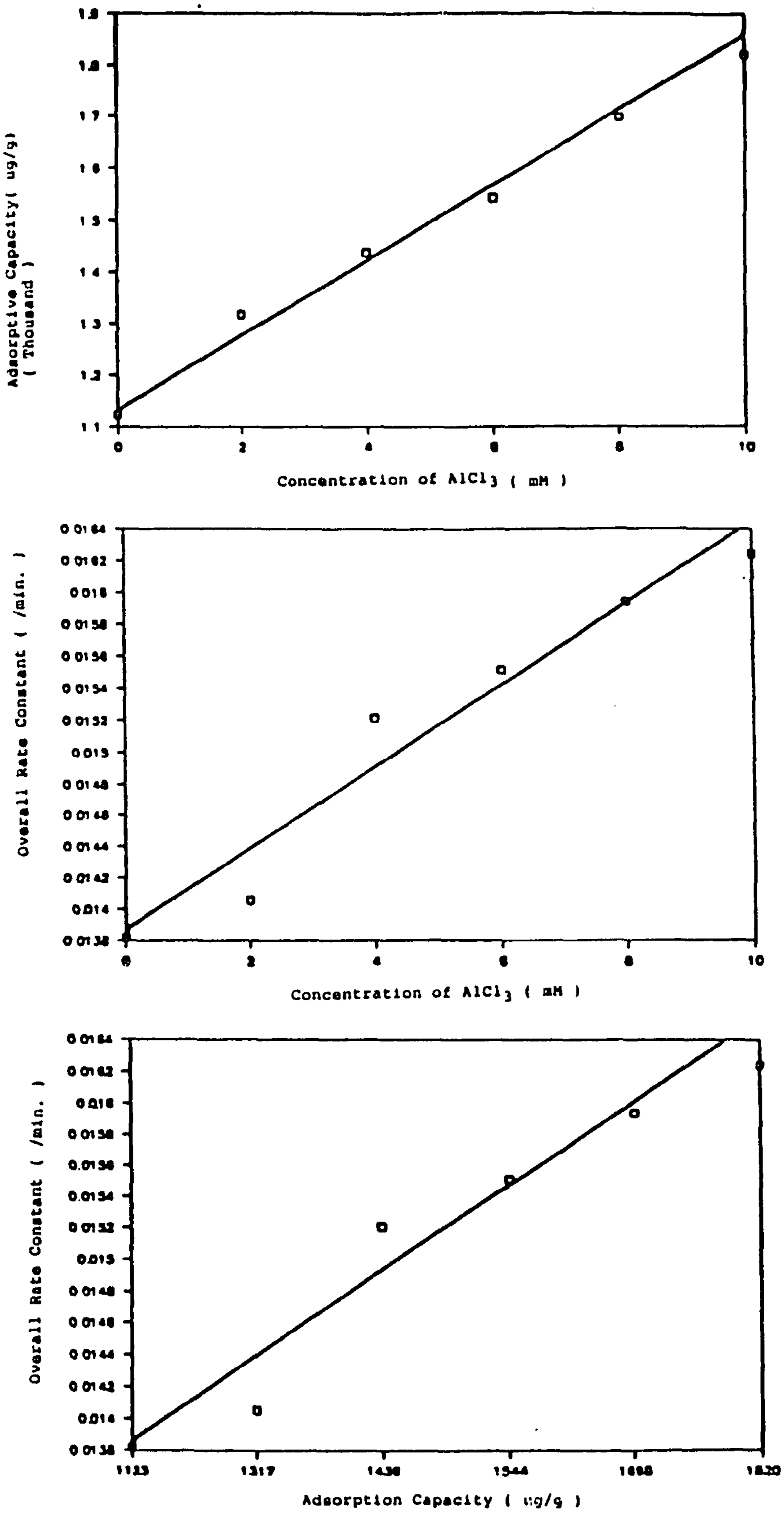


Figure G3. Relationship among Salts' Concentration, Overall Sorption Rate Constant, and Adsorptive Capacity.(250 ppm phenol, AlCl3, Hudson flyash)

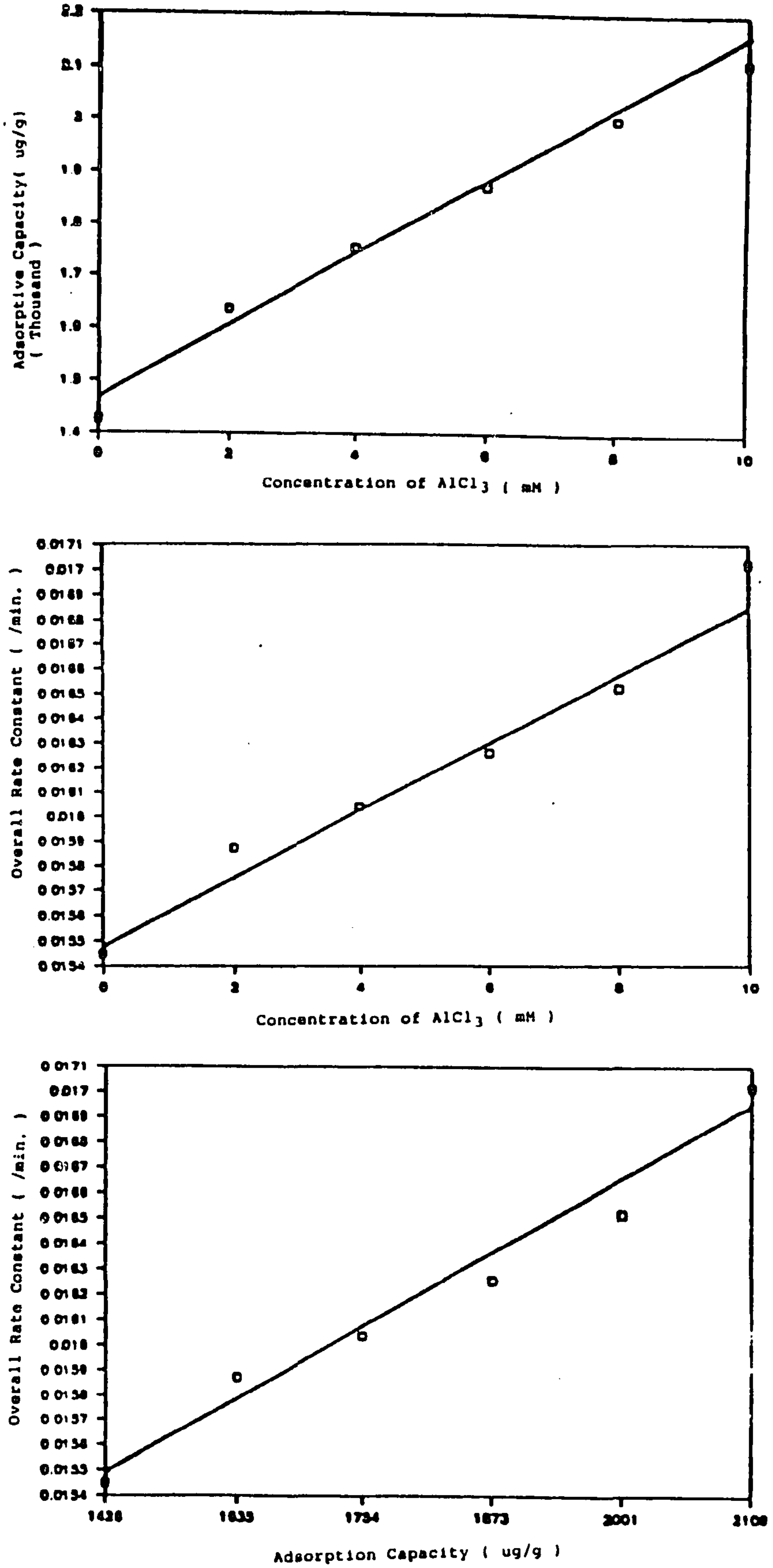


Figure G4. Relationship among Salts' Concentration, Overall Sorption Rate Constant, and Adsorptive Capacity. (250 ppm MIBK, AlCl3, Hudson flyash)