

CHAPTER IV

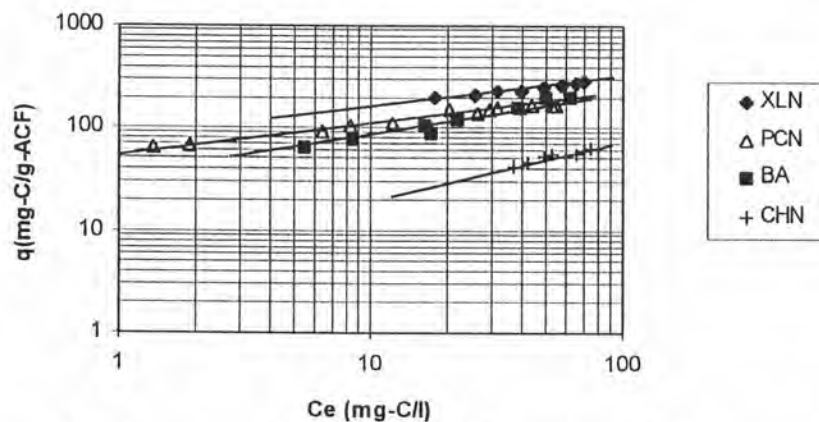
RESULTS AND DISCUSSION

In order to evaluate the applicability and suitability of this new approximate method to predict any breakthrough curve of interest relevant fundamental jar tests and, for validation, the corresponding fixed bed adsorption experiments are necessary.

In this work, comparison between the predicted and experimental characteristic breakthrough curves, including their break times, is carried out.

4.1 Adsorption Equilibrium Isotherms

The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature. For liquids, the concentration is often expressed in mass units, such as part per million. The concentration of adsorbate on the solid is given as mass adsorbed per unit mass of original adsorbent. The adsorptivity of each chemical substance is shown in Fig. 4-1. As shown in Appendix A 1.1 the Langmuir adsorption isotherm fits the sorption data reasonably well but not as well as the Freundlich isotherm.



	<u>XLN</u>	<u>PCN</u>	<u>BA</u>	<u>CHN</u>
k	87.02	56.95	24.68	6.66
n	3.65	3.56	1.95	1.93

Figure 4-1: Freundlich adsorption isotherm on ACF-15 ($q = kc^{1/n}$)

Regarding the adsorptivity of each single component , the order is : cyclohexanol < benzoic acid < p-chlorophenol< o-xylenol, which can be attributed to the difference in structural stericality and adsorption affinity. The more planar the molecular structure and the more lypophilic the adsorbate, the higher the adsorptivity on ACF.

4.2 Integral Adsorption Equilibrium Curve (IAEC) and Characteristic Distribution Curve (CDC)

Fig. 4-2 - 4-10 are the observed IAECs and the CDCs determined from them for the 7 synthetic solutions, 1 unknown multi-component solution (natural humic substance) and 1 industrial wastewater sampled from an oil refinery plant. In each of the figures the IAEC is shown on the left-hand side and the CDC on the right.

As seen from these figures, all of them show a monotonic decrease with respect to the increasing amount of adsorbent used. For simplicity, only the first term (n=1) of eqn.(2-15) was adopted to determine the simulating formula of the CDCs in this work.

The estimation of the parameters in eqn.(2-15) is carried out by minimizing the sum of absolute errors, namely,

$$E = \frac{1}{M} \sum_{i=1}^M \left| 1 - \frac{(C_T)_{i,cal}}{(C_T)_{i,exp}} \right| \quad (4-1)$$

The nonlinear Simplex search method was used to estimate the set of parameters (B, D, k, X_{min}, X_{max}) that minimize eqn. (4-1). The values of the parameters estimated from each IAEC are shown in **Table 4-1**.

4.3 Breakthrough Curve and Break Time

The breakthrough curves calculated with eqns.(2-29) - (2-31) from the CDC of each solution are compared with the experimental curves shown in **Fig. 4-11 - Fig. 4-29**.

As expected from the fundamental concept of adsorption technology, the order of the breakthrough time of each individual chemical species is the same as the adsorptivity order : o-Xylenol >p-Chlorophenol > Benzoic acid > Cyclohexanol. The higher the adsorptivity, the longer the breakthrough time. Examples of calculation results shown in the Appendix (A1.4) clearly indicate that a higher adsorptivity is generally accompanied by a faster adsorption rate and thus a narrower and slower-moving adsorption zone. Furthermore, it shows that the mass transfer zone for the ACF packed bed adsorber is very narrow.

As seen from the comparison between each pair of the predicted and experimental breakthrough curves, most of the pairs as well as their breaktimes in **Table 4-2** agree rather well for all the three single component systems. But in the cases of binary, tertiary, natural humic substance and refinery wastewater, the agreement between the calculated and the observed curves are not that good.

Of the two binary solutions shown here, the first consists of PCN and CHN (strongly and weakly adsorbed species) while the second is composed of PCN and XLN, two comparably strongly adsorbed species. In addition, the tertiary solution is comprised of XLN, PCN and BA, three comparably strongly adsorbed species. In both types of these cases, the observed and predicted breakthrough curves are rather different, as seen in **Fig. 4-23 - Fig. 4-25**. These may have resulted from competitive interaction among the individual species. These results reveal the limitation of the present model. In fact, the model has been developed for describing the adsorptive characteristics of a solution containing a sufficiently large number of adsorbates, which makes the concentration density a continuous function while assuming instantaneous adsorption equilibrium between the liquid phase and adsorbent phase. Thus, in the cases of two or three components, the individual species have competitive interactions, including the possibility that instantaneous adsorption equilibrium may not occur for all components.

By the way, both of the unknown multicomponent systems (natural humic substance, and oil refinery wastewater) yield a breakthrough curve of similar pattern. In both cases, the adsorption of the unknown adsorbates onto ACF is rather limited because ACFs-15 contains mostly micropores (mean radius = 0.45 nm), while many of

Table 4-1 : Values of the parameters of the Integral Adsorption Equilibrium Curve (IAEC) estimated in the present work

Initial guess: $B = -0.9748144$ $D = 34.39801$ $k = 0.8550539$

$X_{max} = 1.099647$ $X_{min} = 28.008113$

Search termination criteria: $CRJ = 0.1$ $EPSI = 0.001$

Note : 1. The parameters of Wastewater A [Okazaki (1989)] were used as the starting point (initial guess)

2. CRJ and EPSI values for the refinery wastewater were 0.01 and 0.000001, respectively.

Estimated Parameters	Run No. of Adsorption System										
	1	5	9	13	17	19	21	23	27		
X_{LN}	11.11	11.06	10.95	11.06	11.09	11.02	10.50	5.84	20.54		
X_{LN}	11.11	11.06	10.95	11.06	11.09	11.02	10.50	5.84	20.54		
A	-8.3597E-03	-5.0049E-03	-3.4228E-03	-6.0515E-03	-5.0805E-03	-3.4563E-02	-3.9756E-03	-1.9981E-02	-3.2424E-03		
B	-1.7380E+00	-8.2315E-01	-9.2350E-01	-9.2325E-01	-8.2344E-01	-1.1181E+00	-1.2945E+00	-1.1392E+00	-1.4280E+00		
D	3.2346E+01	3.3677E+01	3.3299E+01	3.4458E+01	3.3370E+01	3.3109E+01	3.3011E+01	3.2203E+01	3.4794E+01		
k	2.5059E-03	1.5220E-03	8.7173E-04	1.9078E-04	2.4503E-03	1.9327E-03	2.4317E-03	5.0305E-05	9.9737E-06		
X_{min}	3.9603E+00	3.6583E+00	3.2454E+00	6.1576E+00	6.0958E-04	2.1049E-02	1.7494E-03	4.7643E+00	2.0020E+00		
X_{max}	1.0045E+01	1.3385E+01	1.6640E+01	1.3222E+01	1.2312E+01	3.5612E+00	1.3480E+01	6.3998E+00	2.5142E+01		
Fitting Error	2.4503E-01	9.6212E-02	9.8427E-02	4.2369E-02	1.2959E-01	8.9406E-02	2.0288E-01	1.4368E-02	0.0000E+00		

Table 4-2 : Summary of the experimental and predicted breakthrough times*

<u>Type</u>	<u>Run No.</u>	<u>Solution</u>	<u>IAEC</u>		
			Experimental (hr.)	Prediction (hr.)	Relative error (%)
<i><u>Single</u></i>	1	XLN	12.87	12.15	-5.59
	2		40.54	36.60	-9.72
	3		21.95	18.31	-16.58
	4		20.52	18.30	-10.82
	5	PCN	7.33	7.73	5.46
	6		25.82	23.22	-10.07
	7		12.79	11.62	-9.15
	8		12.72	11.61	-8.73
	9	BA	6.19	4.50	-27.30
	10		14.82	13.52	-8.77
	11		7.39	6.77	-8.39
	12		7.00	6.76	-3.43
	13	CHN	1.52	1.42	-6.58
	14		4.64	4.26	-8.19
	15		1.52	2.14	40.79
	16		2.35	2.13	-9.36
<i><u>Binary</u></i>	17	XLN + PCN	9.95	6.27	-36.98
	18		3.33	3.14	-5.71
	19	PCN + CHN	2.22	1.08	-51.35
	20		0.85	0.54	-36.47
<i><u>Tertiary</u></i>	21	XLN+PCN+BA	9.37	6.93	-26.04
	22		4.18	3.45	-17.46

* Here the breakthrough time is taken to be the times at which the outlet solute concentration reaches up to 10 % of the inlet concentration

the adsorbate molecules apparently either are too bulky to readily enter the micropores because of structural stericity or exhibit weak adsorptive affinity. Even when ACFs-20 with bigger pore radius (mean radius = 0.50 nm), was used as adsorbent, the obtained breakthrough curve for NHS still gave the same pattern as shown in **Fig.4-30**. In these cases, ACF adsorption is not directly suitable for the treatment of these samples. A secondary treatment, such as activated sludge unit, should be used to break down these molecules in advance of the tertiary treatment. Alternatively, large-pore adsorbents may be used instead.

In the case of tapwater, Most of the contaminants in it are inorganic compounds which have low lypophilicity . So they adsorb only weakly on ACF. Thus breakthrough occurs quickly and its breakthrough curve is as shown in **Fig.4-31**.

4.4 Design calculation of an industrial ACF adsorber

Activated carbon adsorption systems, widely used in the chemical process industries for several decades, are now playing an important role in cleaning up plant effluents and municipal wastewaters.

Typically, the designing of fixed bed adsorber even for a single-solute system can be difficult and time consuming in some cases. The complete engineering approach involves a four step progression - studying its adsorption equilibrium and isotherm , running laboratory column tests, followed by pilot-scale tests, and finally designing the commercial unit. The task becomes more complicated when the system is binary or multi-solute. The conventional design approach is inapplicable to an unknown multi-solute system and it would be necessary to rely heavily on extensive column tests to scale up the design.

Here two practical and simplified methods for designing the fixed bed ACF adsorber, Okazaki's method (see section 4.4.1) and bed-depth service time method will be adopted.

4.4.1 Okazaki's method

Okazaki's approach needs only the information from simple jar tests to predict the transient outlet concentration of the adsorption column. What follows is a design example using Okazaki's method.

Design basis A medium-scale water treatment plant wants to produce drinking water from groundwater containing unknown multiple solutes whose jar test characteristics are assumed to be essentially the same as that containing o-xylenol, p-chlorophenol and benzoic acid (refer to Fig.4-8). Design an adsorption column of activated carbon fibers that will operate for at least 10 days before breakthrough occurs. The relevant technical data are as follows.

Total initial concentration (TOC)	10 mg-C/l
Total flowrate	102 m ³ /day
Superficial velocity (design value)	15 m/hr
Voidage of ACF column	0.50

Solution :

- The required cross-sectional area = $[(4/\pi)(102/15)]^{1/2}$
= 0.60 m.
- The various model parameters are the same as those given in section 4.2, table 4-1. Based on Okazaki's method, the relationship between the service time (consider breakthrough as outlet $C/C_o = 0.1$) and bed length is obtained as shown as below

Run No.	Bed length (m.)	Service time (day)
1	1.0	6.19
2	1.5	9.28
3	2.0	12.38
4	1.62	10.0

so the bed length required for service time of 10 days is $(1.62 \times 1.2) = 2.0$ m. (here the safety factor is 20%)

4.4.2 Bed-depth service time method

Another simplified design approach for fixed-bed adsorbers is available that correlate the service time with the operation variables. One such model is the Bed-Depth Service Time (BDST) model (R.A. Hutchins ,1973) that simplifies and speed up the design process using the information from column test. Basically, it is a means

for predicting the effects of different feed concentrations, flowrates or effluent compositions on the breakthrough time based on the results of lab-scale column tests.

$$t_b = N_0/(C_0V) [Z - V/(kN_0)\ln(C_0/C - 1)] \quad (4-2)$$

or $t_b = aZ+b \quad (4-3)$

- Which ;
- a = slope = $1990 N_0/(C_0V)$, hr./m.
 - b = Ordinate intercept = $-16.018/(kC_0)[\ln(C_0/C-1)]$, hr.
 - t_b = Service time at breakthrough time, hr.
 - Z = Bed length, m.
 - N_0 = Initial adsorptive capacity of ACF, kg impurity/m.³ of carbon
 - C_0 = Feed impurity concentration, ppm.
 - V = Linear flowrate, m³/hr.m².
 - k = Adsorption rate constant, m³. of liquid treated per kg of impurity feed to system per hr.
 - C = Impurity concentration in effluent at breakthrough point, ppm

Design basis Assume that the operating conditions are similar to that mentioned in case 4.4.1 Okazaki's method

Solution :

a) From the experimental conditions of the column test (Run No.21).

Initial TOC concentration	=	10	ppm
Column diameter	=	0.4	cm.
Bed length	=	10	cm.
Superficial velocity	=	14.32	m/hr.
Packing density	=	0.159	gm/cm. ³
Adsorption capacity	=	157.86	mg-C/g-ACF

(N_0 from adsorption equilibrium)

By solving using eqn. (4-2), we obtain

$$k = 0.030 \text{ m}^3 \text{ of liquid treated / kg of impurity .hr.}$$

b) Operating conditions of industrial are the as same as the example in section

4.4.1

Solution

Initial TOC concentration	=	10	ppm
TOC concentration at effluent	=	1	ppm (at breakpoint $C/C_0 = 0.1$)
t_b	=	10	day (240 hr.)
N_0	=	157.86	mg-C/g-ACF
	=	23.93	kg-C/m ³ -ACF
V	=	102	m ³ /day

From eqn. (4-2) we get ; $Z = 1.56$ m.

Thus, the bed length required for the service time of 10 days is $(1.56*1.2) = 1.87$ m.
(here the safety factor is 20%).

Pressure Drop through the fixed bed

Since the fiber diameter is small, pressure drop through the ACF bed may become critical in long-term operation. There has not been much work done in this area but a rough estimation can be made (Perry, 1984).

$$\Delta P/L = [2f_m G^2 (1-\epsilon)^2] / [D_p g_c \rho \phi_c^2 \epsilon^3] \quad (4-4)$$

which

f_m	=	$100/N_{Re}$
G	=	fluid superficial velocity = 15 m/hr
L	=	bed length , m = 2.0 m.
ρ	=	fluid density = 1000 kg/m ³
μ	=	fluid viscosity = 10 ⁻³ kg/m.s
ϕ_c	=	shape factor
	=	0.38 (fiber shape)
ϵ	=	void fraction = 0.50

For laminar flow ($N_{Re} < 10$)

$$N_{Re} = D_p G / \mu = \text{Reynolds number}$$

For non spherical particles

$$D_p = 6(1-\varepsilon) / (\phi_c S) \text{ , m.}$$

S = specific surface area, or area of particle surface per unit volume of bed

$$= S_0(1-\varepsilon)$$

S_0 = area of particle surface per unit volume of solid (m^2/m^3)

Substitution of the above values into equation (4-4) gives

$$\Delta P = 0.025 \text{ bar}$$

Thus the pressure is acceptable.

From the above design results, it can be concluded that both design methods give very close agreement, i.e. a required adsorber length of 1.62 m. vs 1.56 m. However, Okazaki's method is definitely simpler because it does not require any column test results. So Okazaki's method is preferable for the above system and any system in which the assumption of instantaneous adsorption is valid.

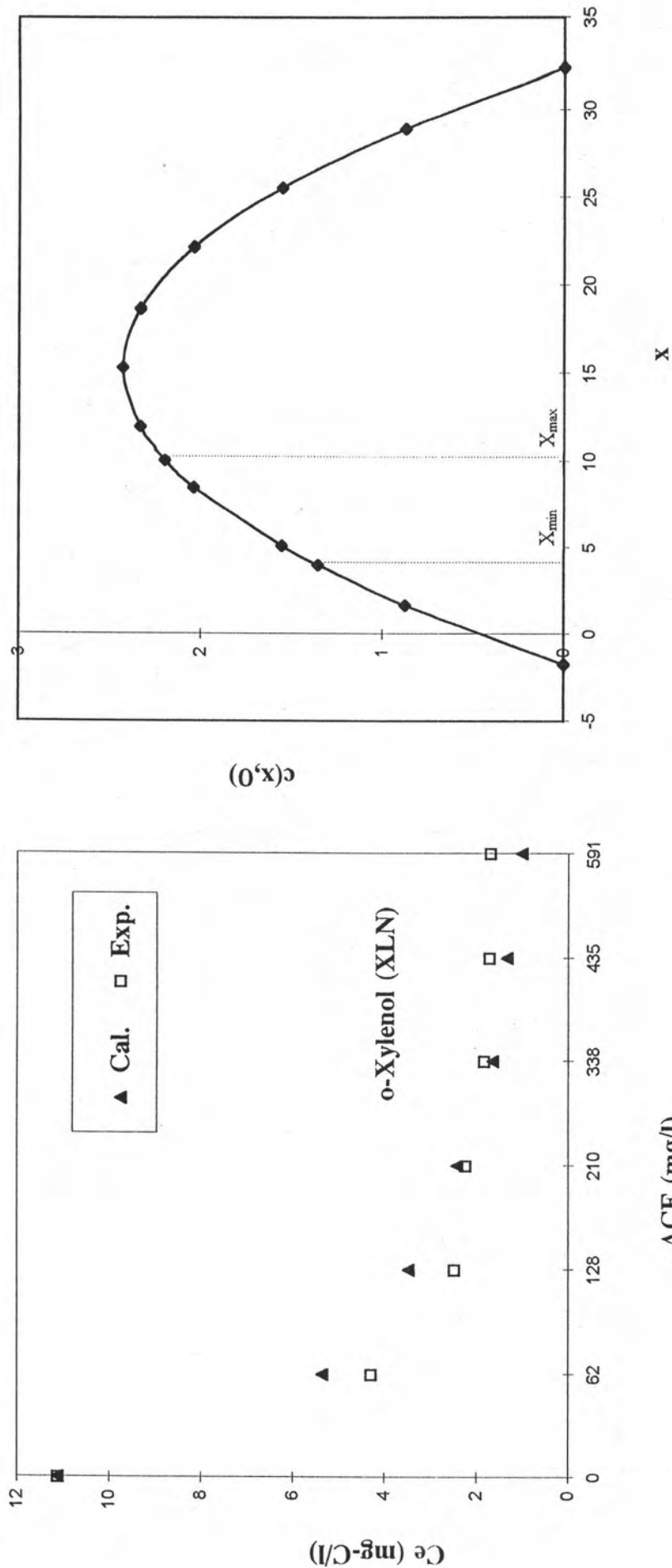


Fig.4-2 IAEC and CDC for XLN solution

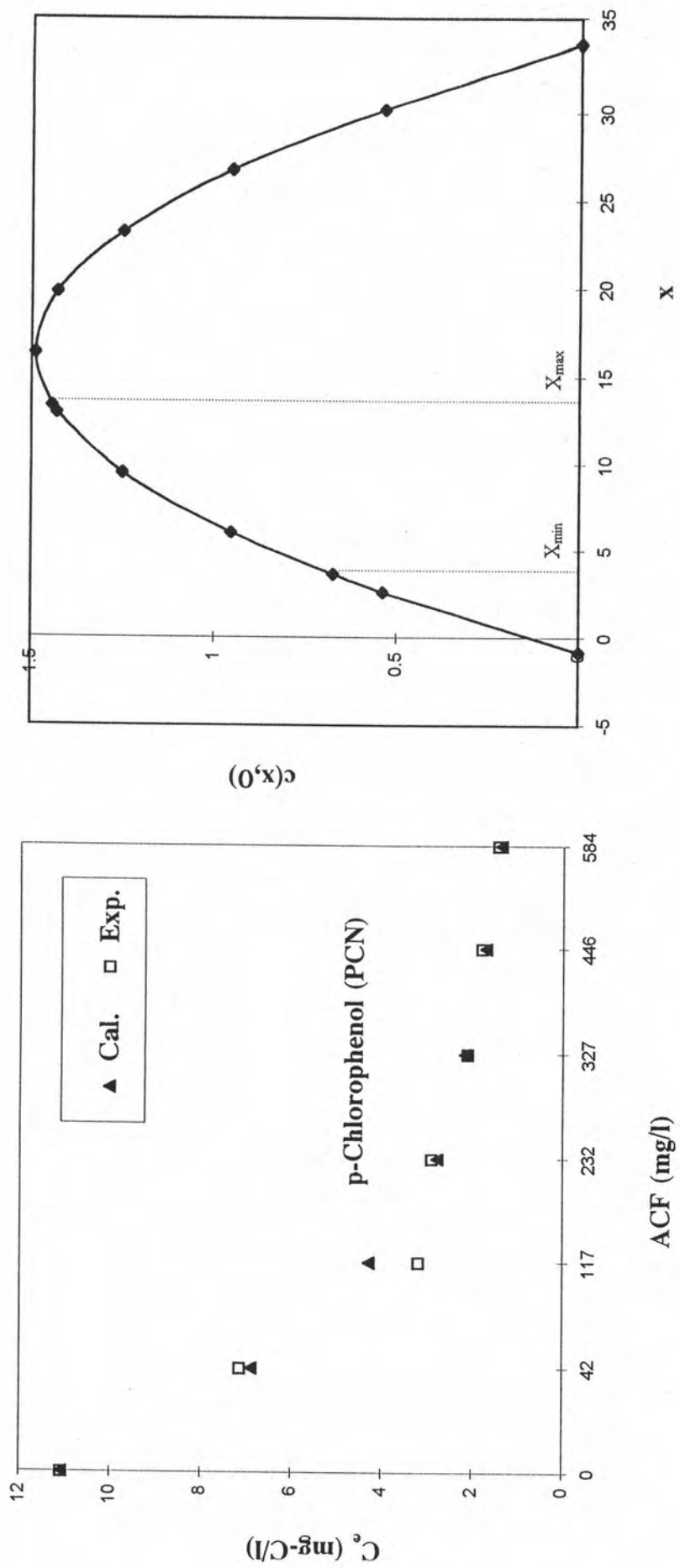


Fig. 4-3 IAEC and CDC for PCN solution

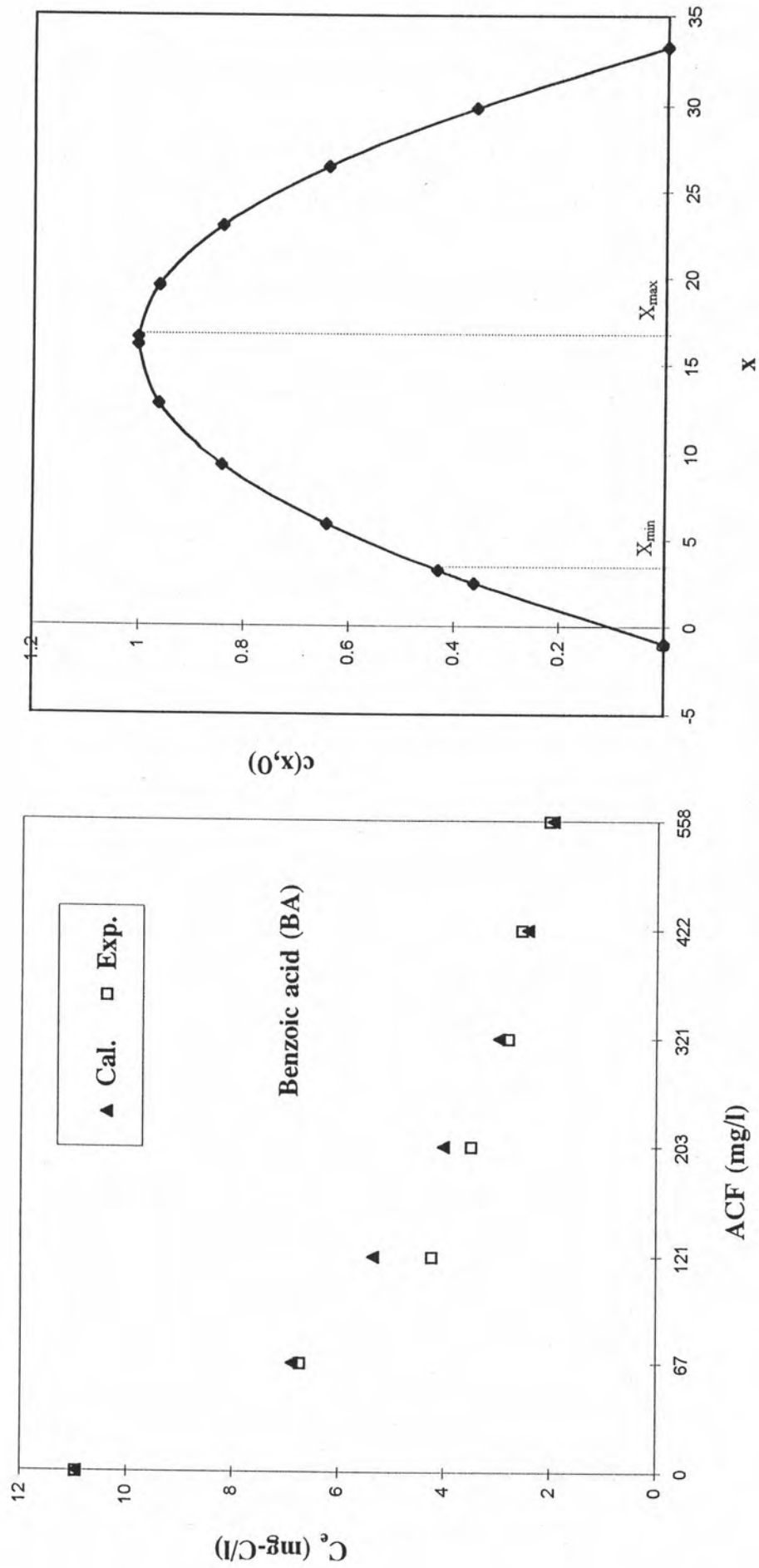


Fig.4-4 IAEC and CDC for BA solution

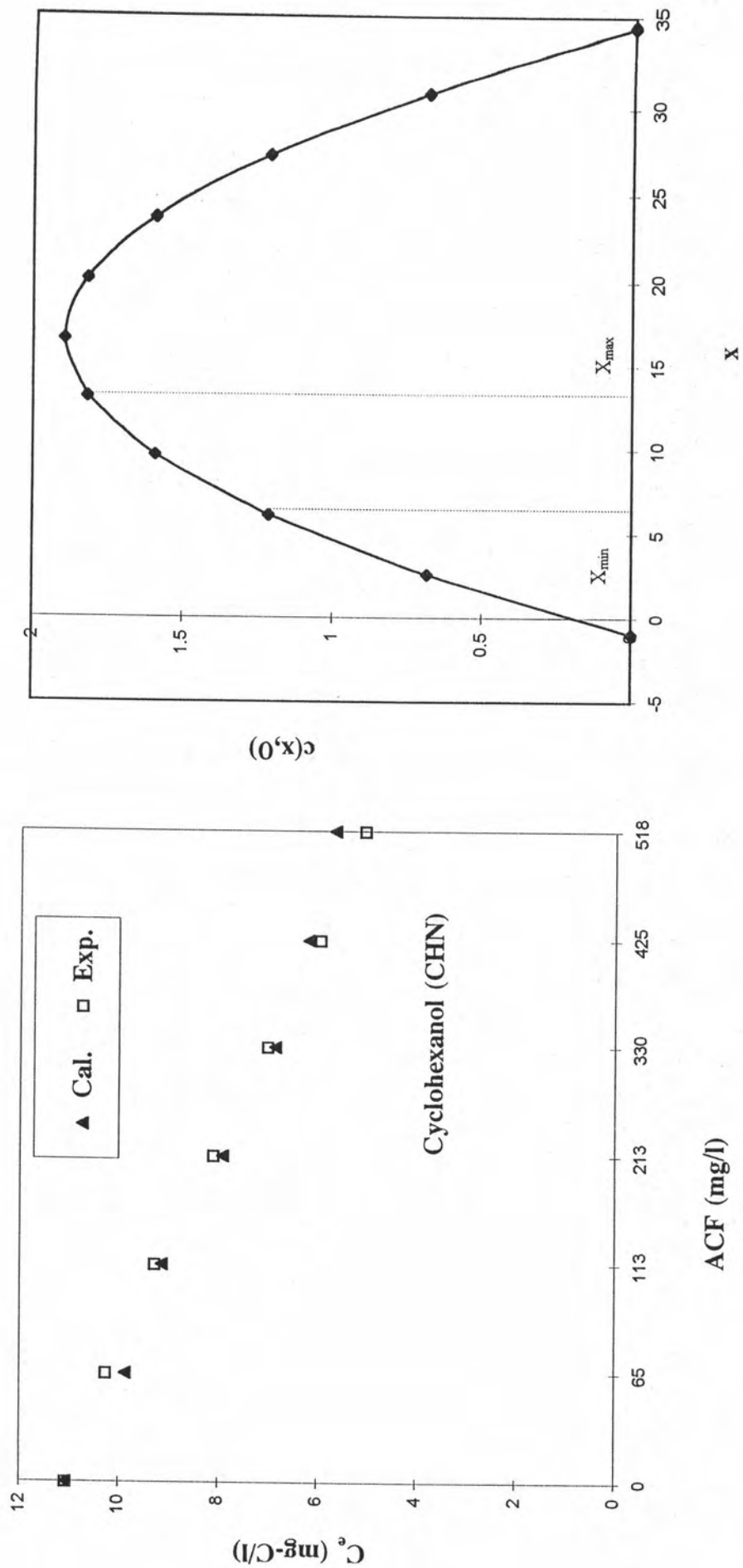


Fig. 4-5 IAEC and CDC for CHN solution

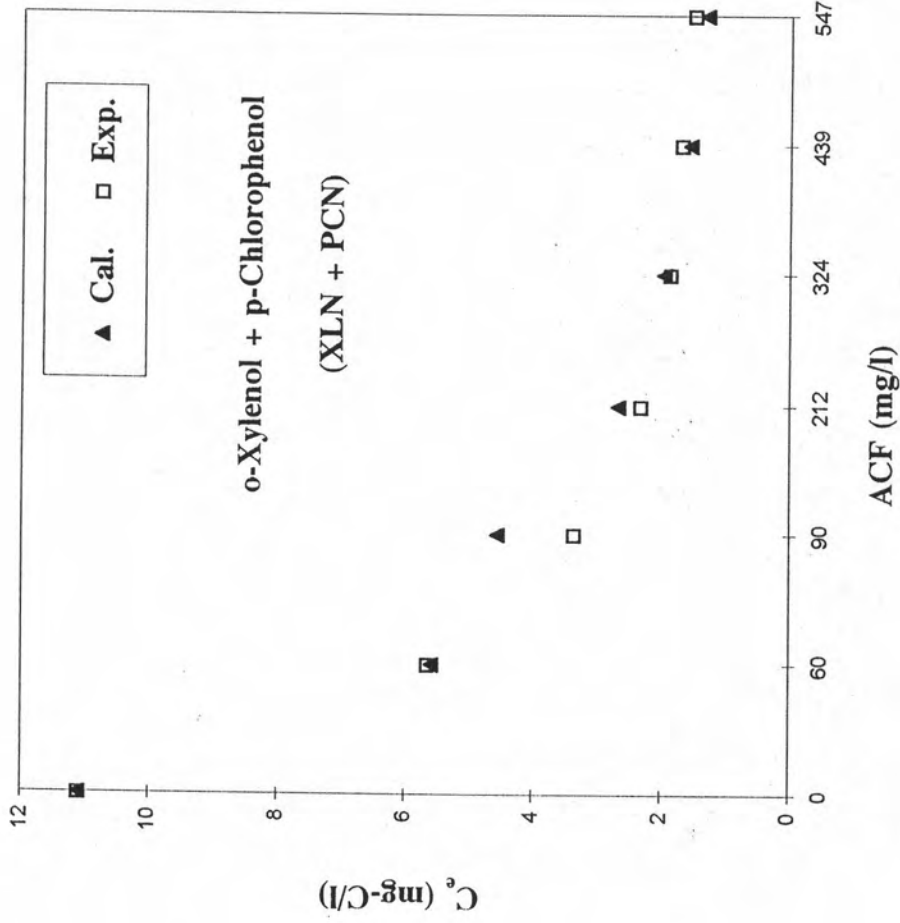
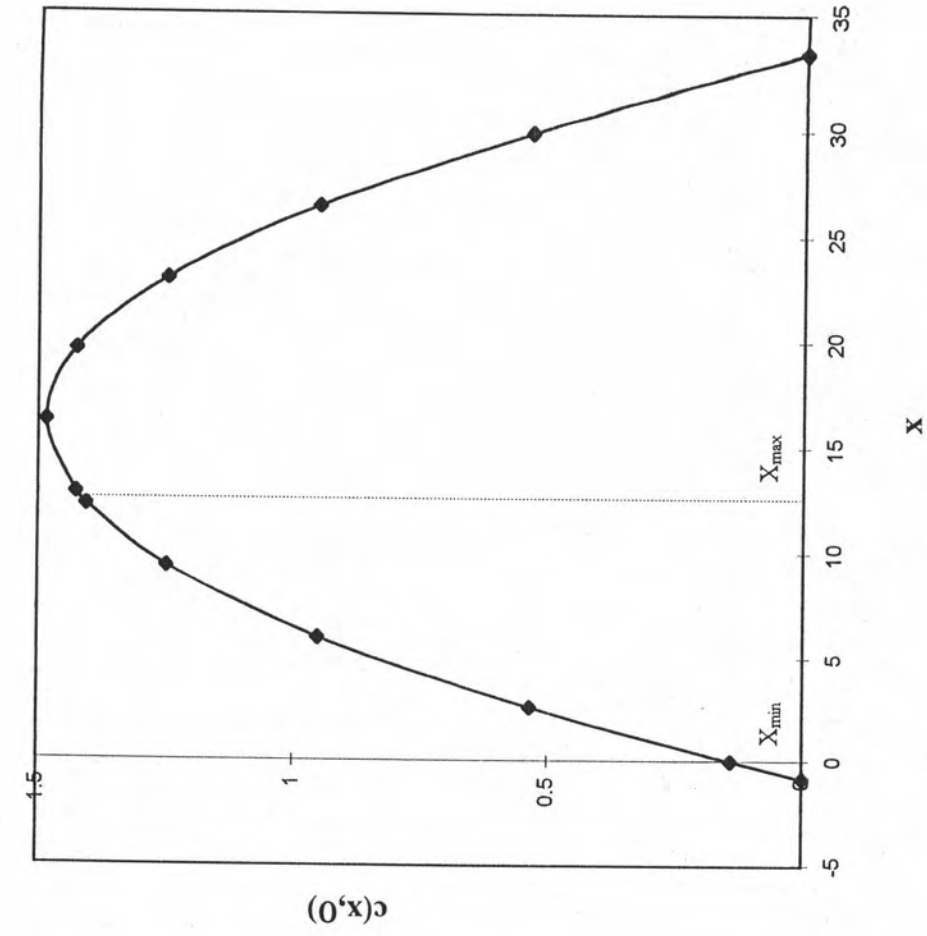


Fig. 4-6 IAEC and CDC for XLN+PCN solution

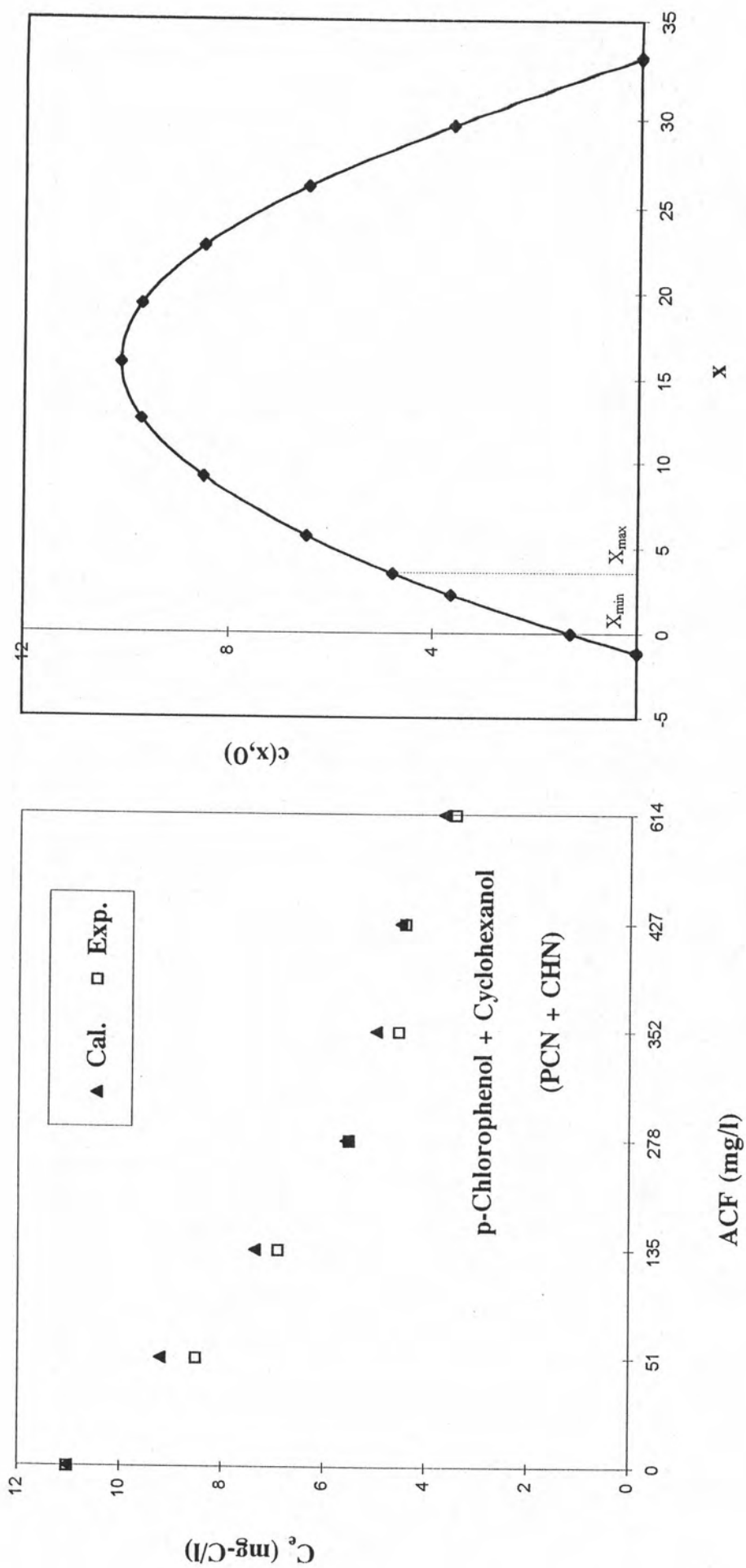


Fig.4-7 IAEC and CDC for PCN+CHN solution

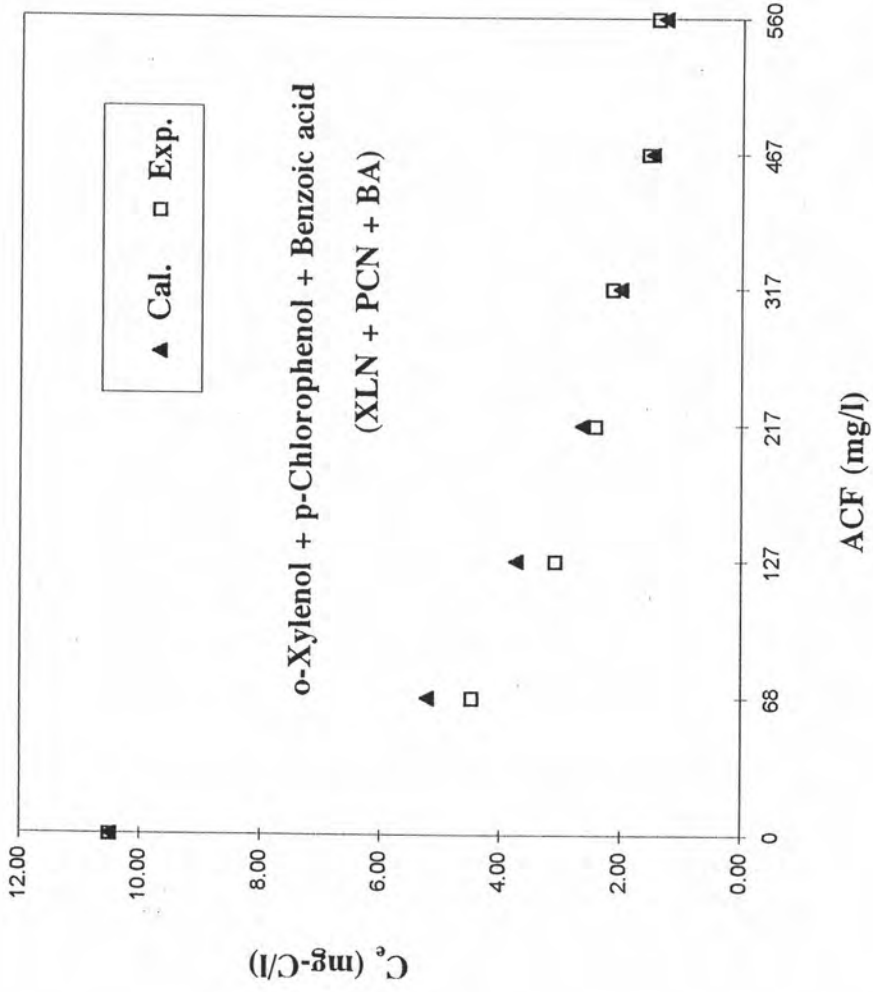
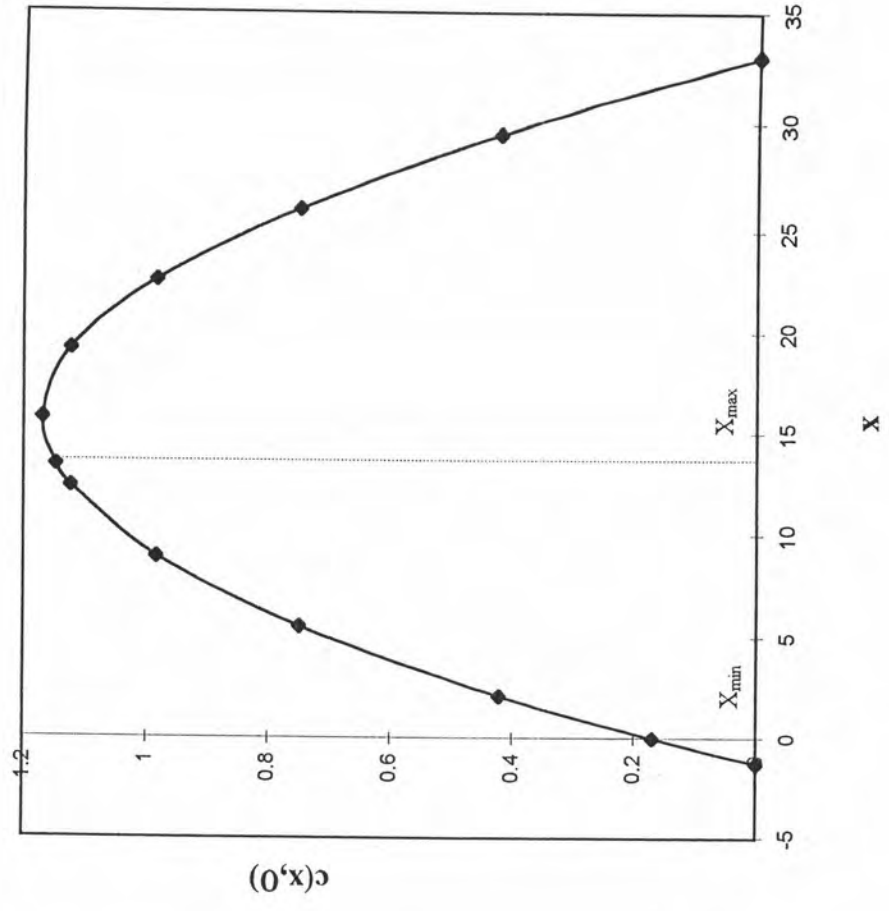


Fig.4-8 IAEC and CDC for XLN+PCN+BA solution

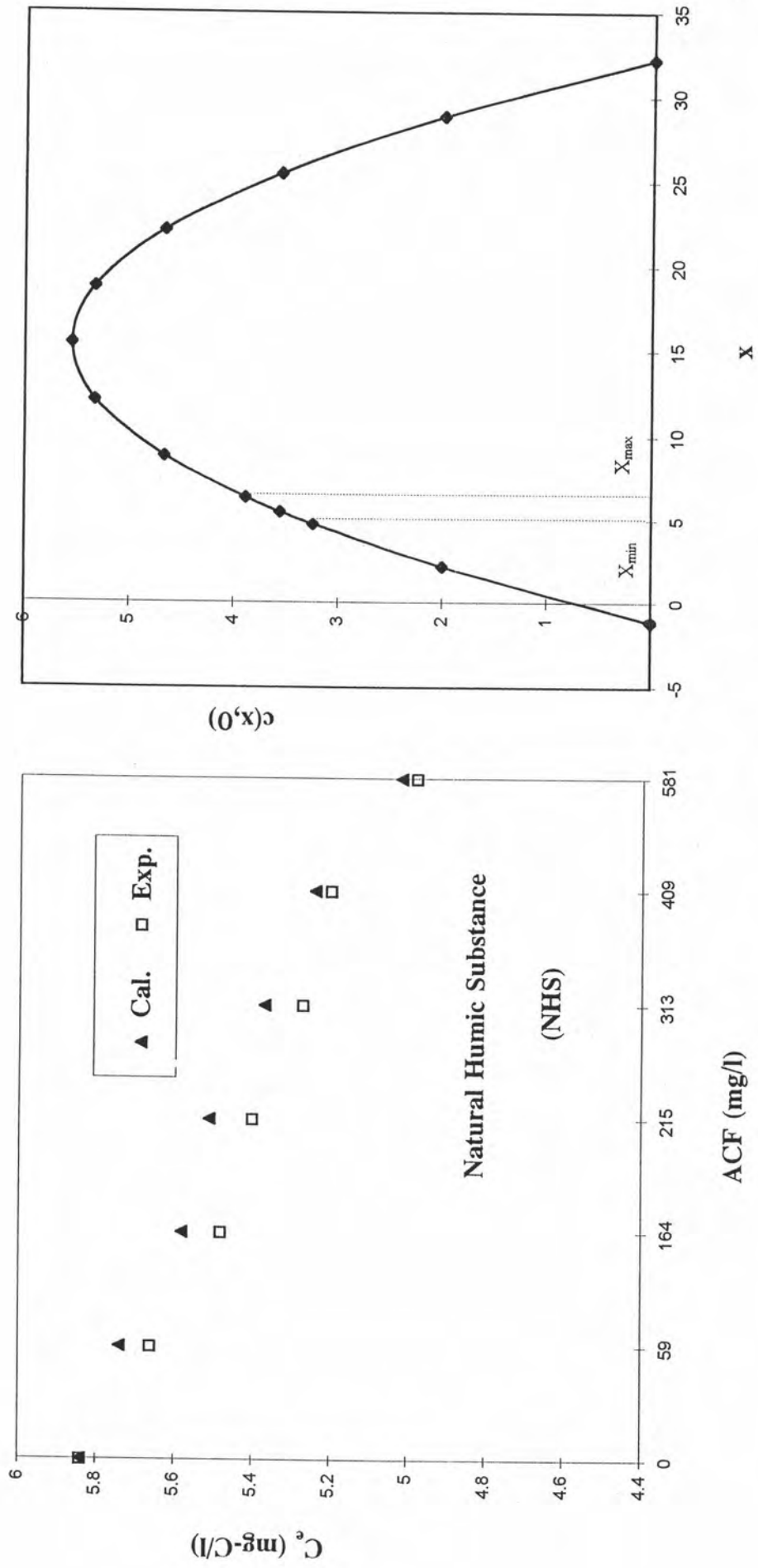


Fig.4-9 IAEC and CDC for NHS solution

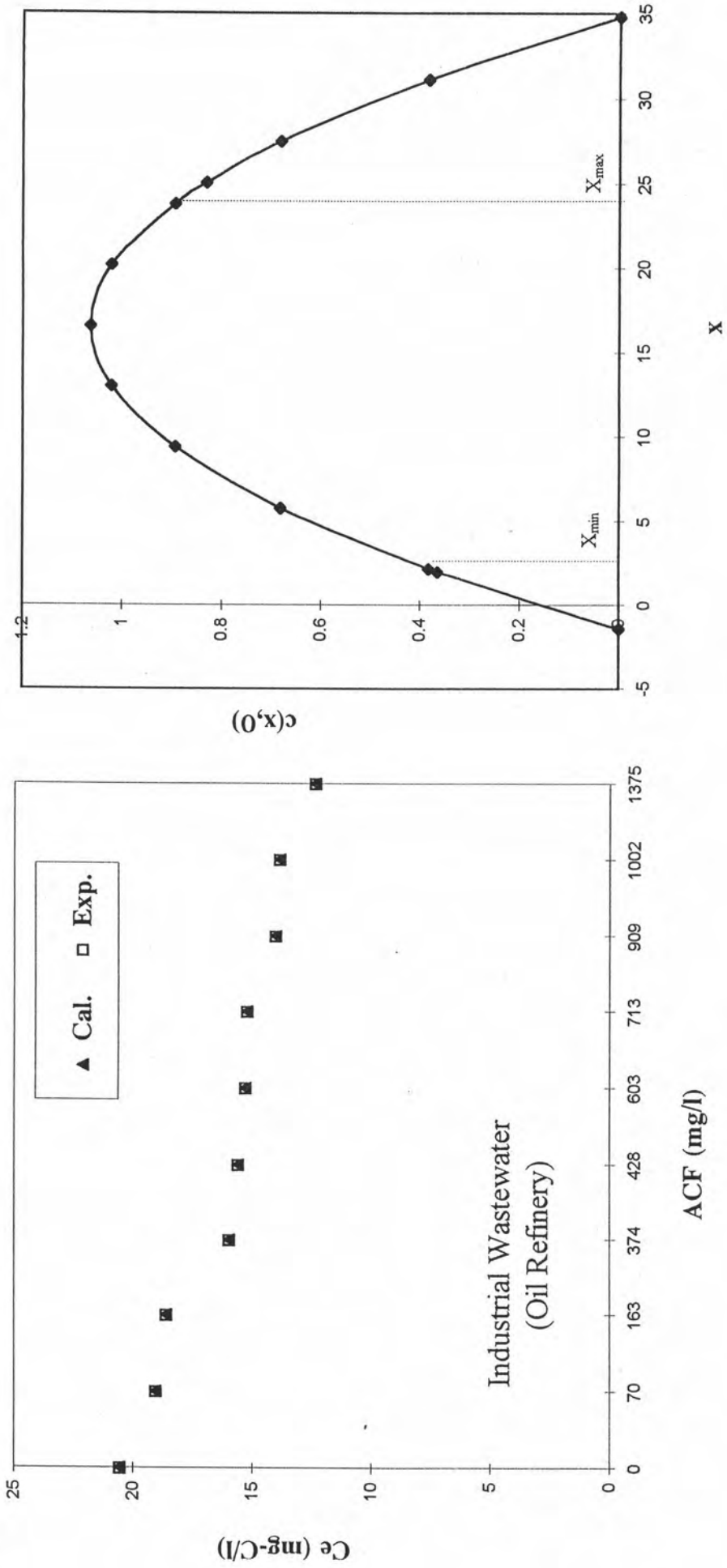


Fig.4-10 IAEC and CDC for an Industrial wastewater

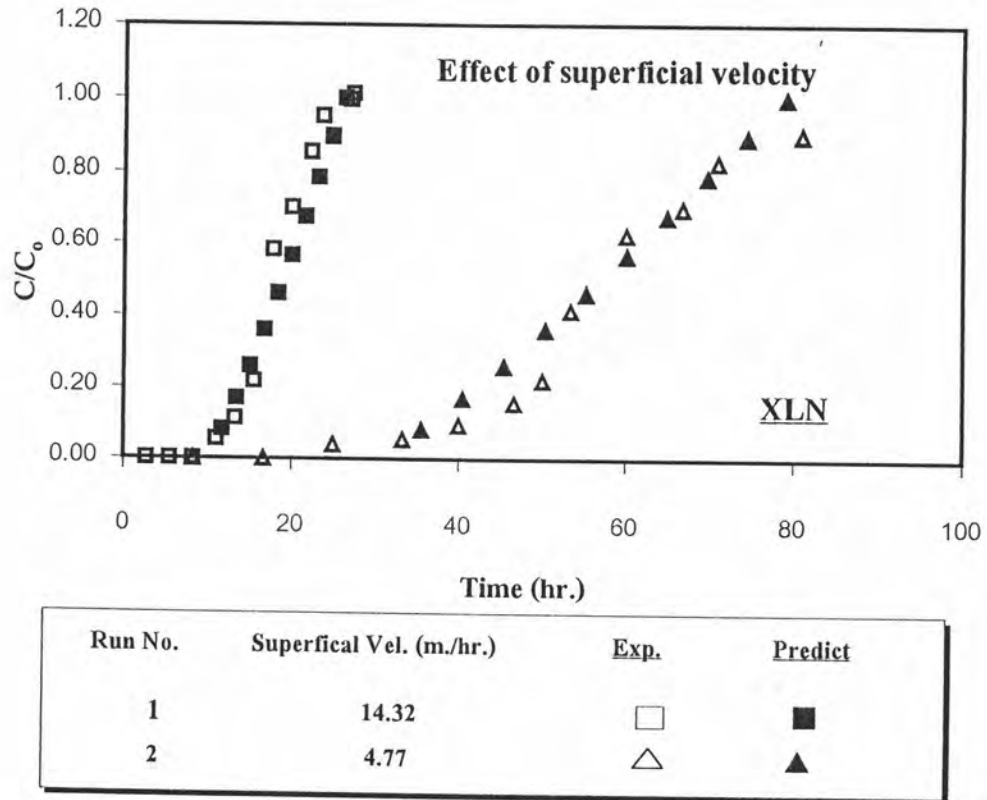


Figure 4-11 Breakthrough curves of XLN solution (Effect of superficial velocity)

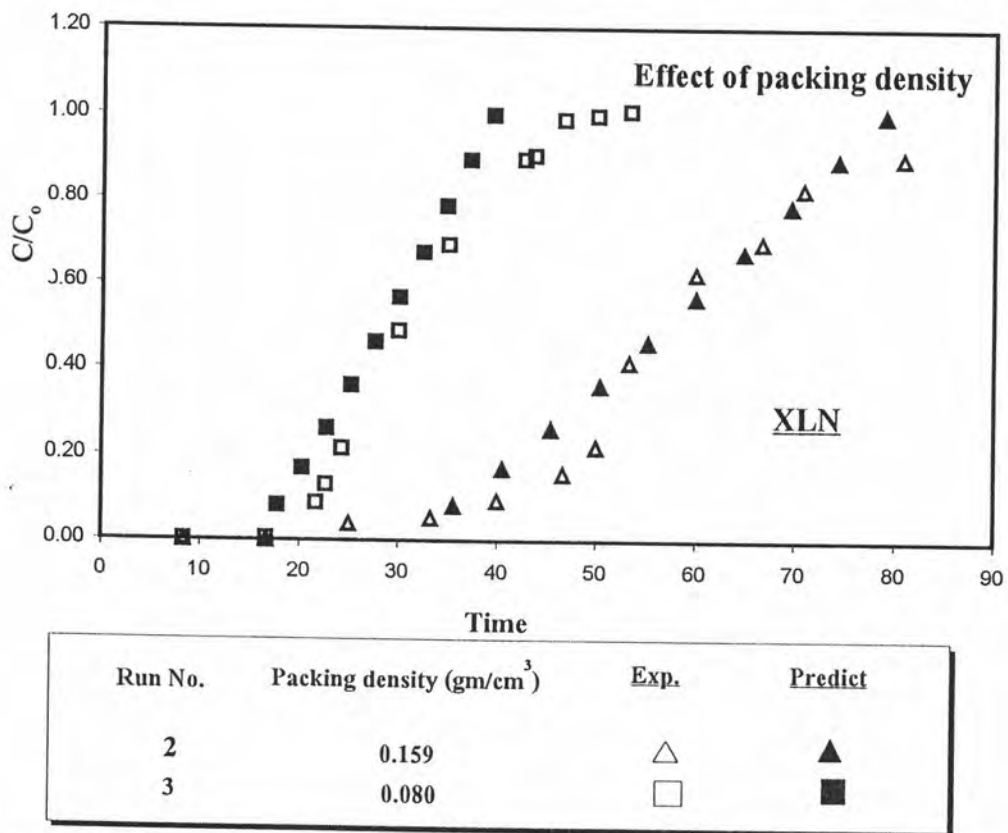


Figure 4-12 Breakthrough curves of XLN solution (Effect of packing density)

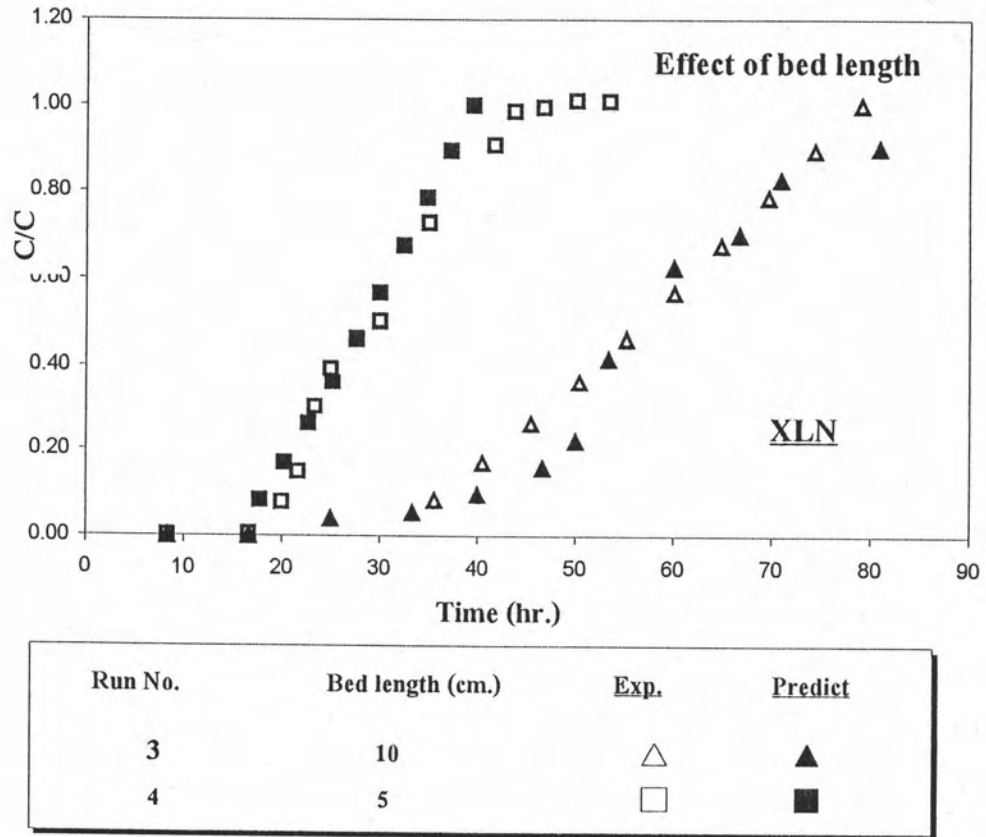
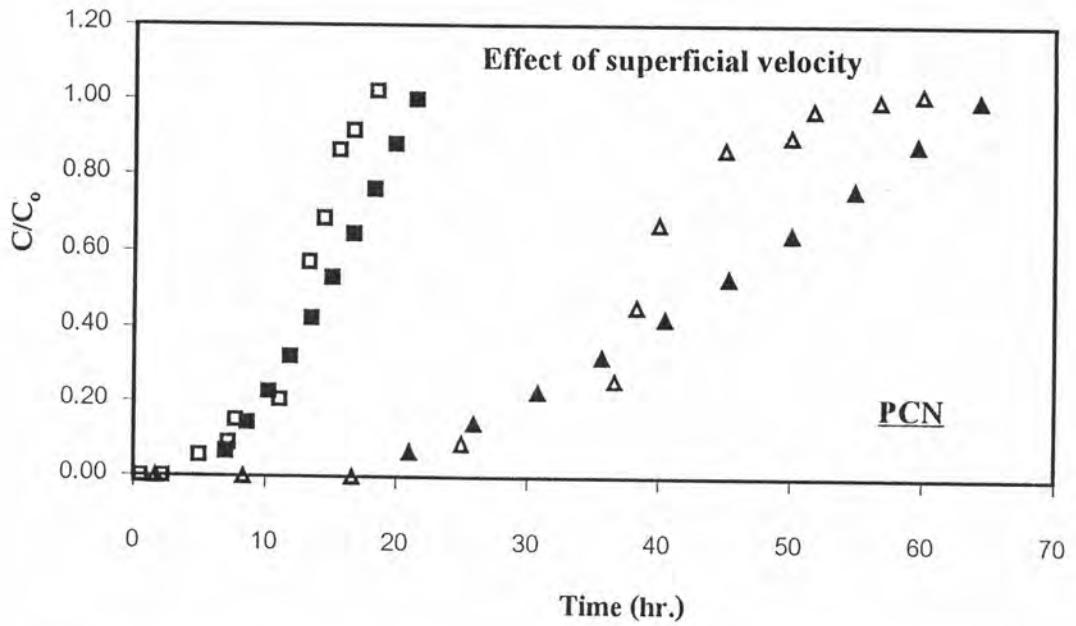
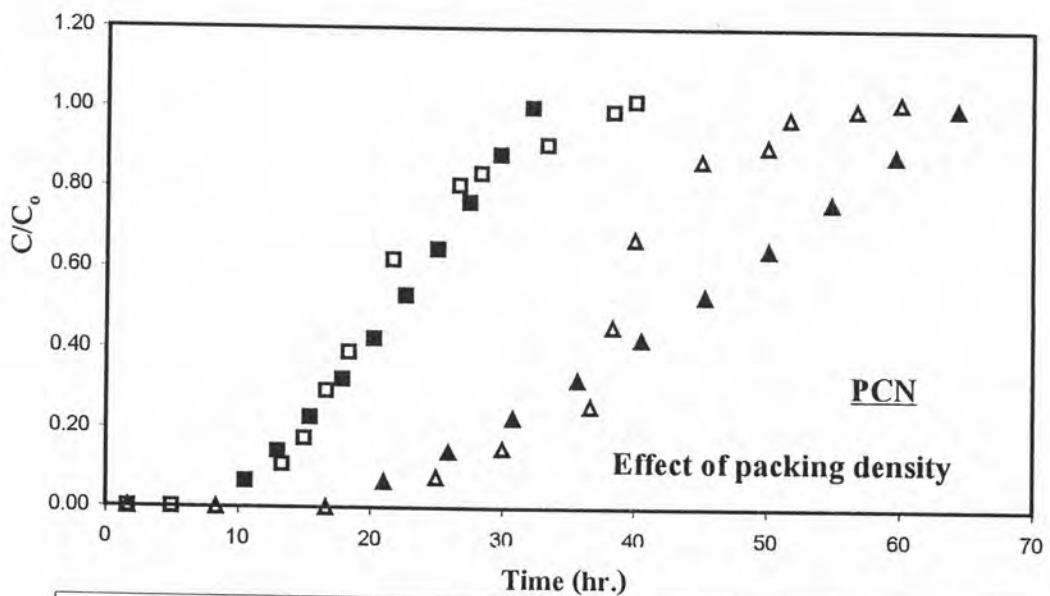


Figure 4-13 Breakthrough curves of XLN solution (Effect of bed length)



Run No.	Superficial Vel. (m./hr.)	Exp.	Predict
5	14.32	□	■
6	4.77	△	▲

Figure 4-14 Breakthrough curves of PCN solution (Effect of superficial velocity)



Run No.	Packing density (gm/cm ³)	Exp.	Predict
6	0.159	△	▲
7	0.080	□	■

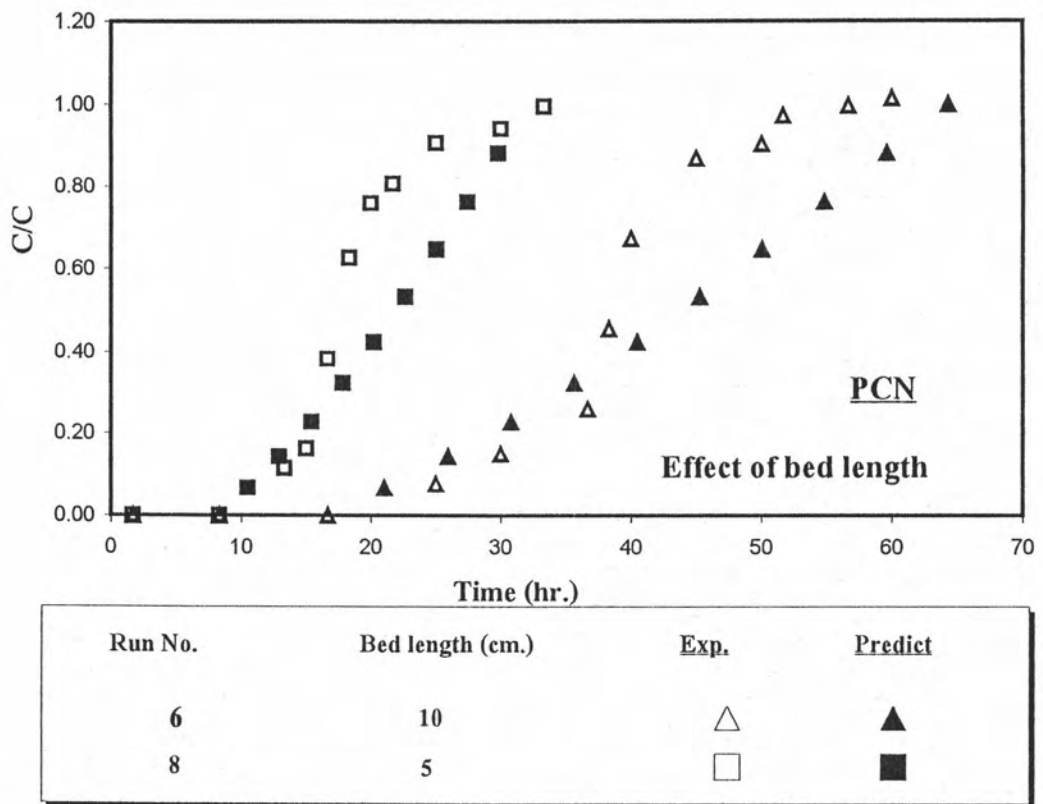


Figure 4-16 Breakthrough curves of PCN solution (Effect of bed length)

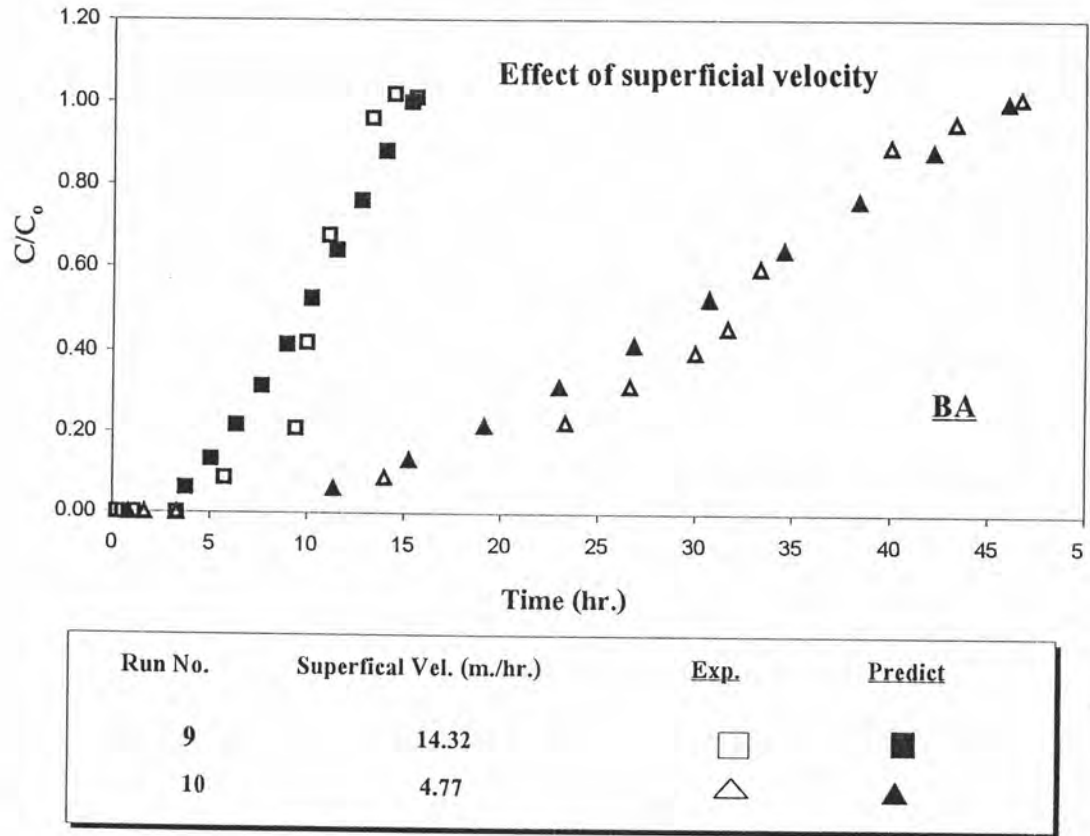


Figure 4-17 Breakthrough curves of BA solution (Effect of superficial velocity)

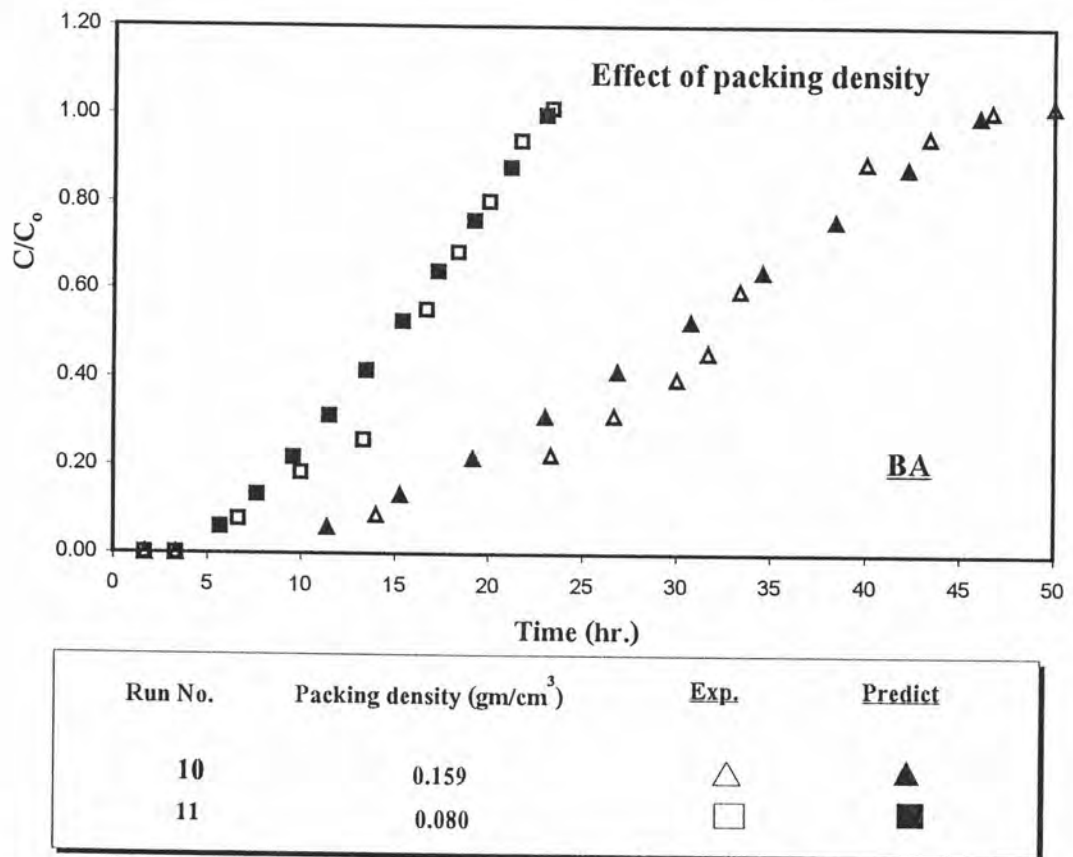


Figure 4-18 Breakthrough curves of BA solution (Effect of packing density)

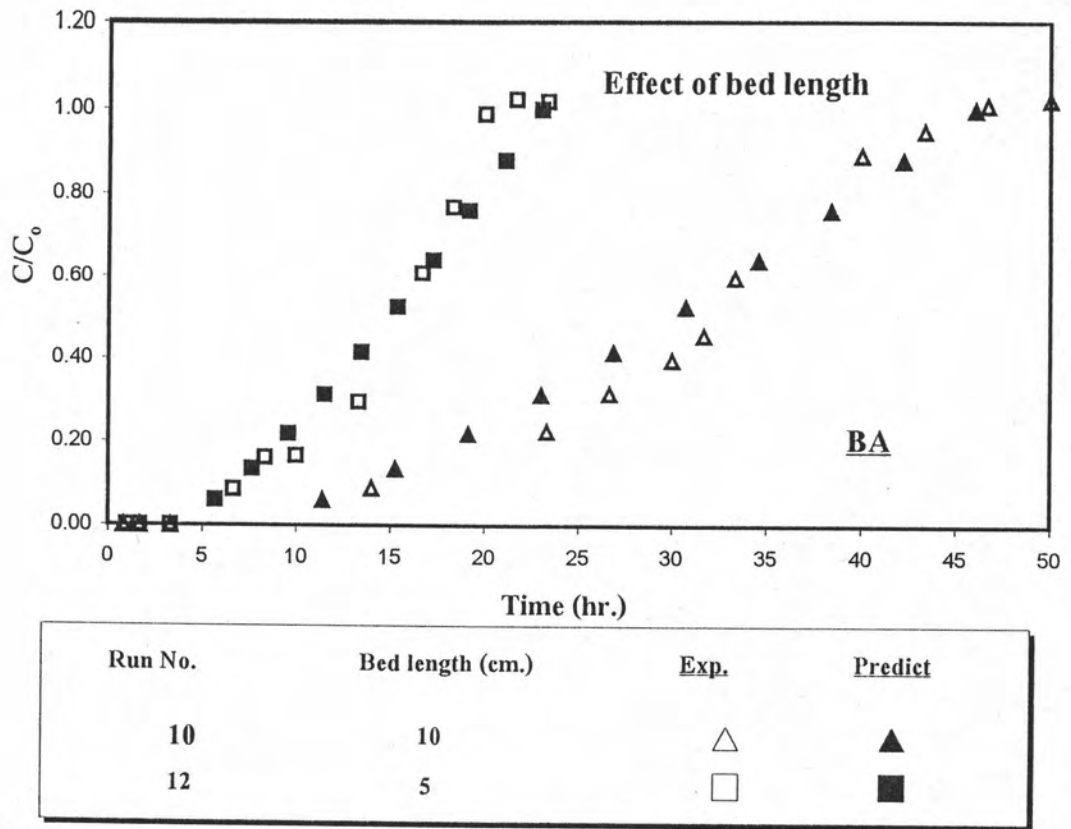


Figure 4-19 Breakthrough curves of BA solution (Effect of bed length)

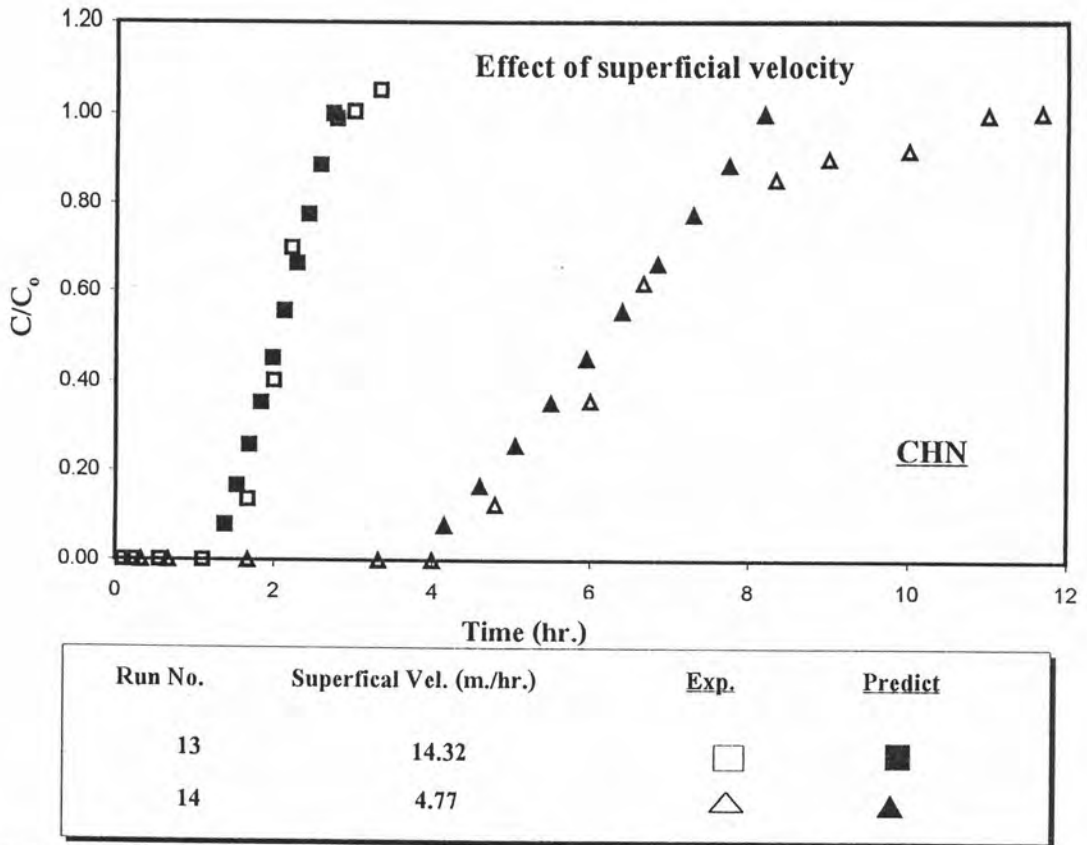
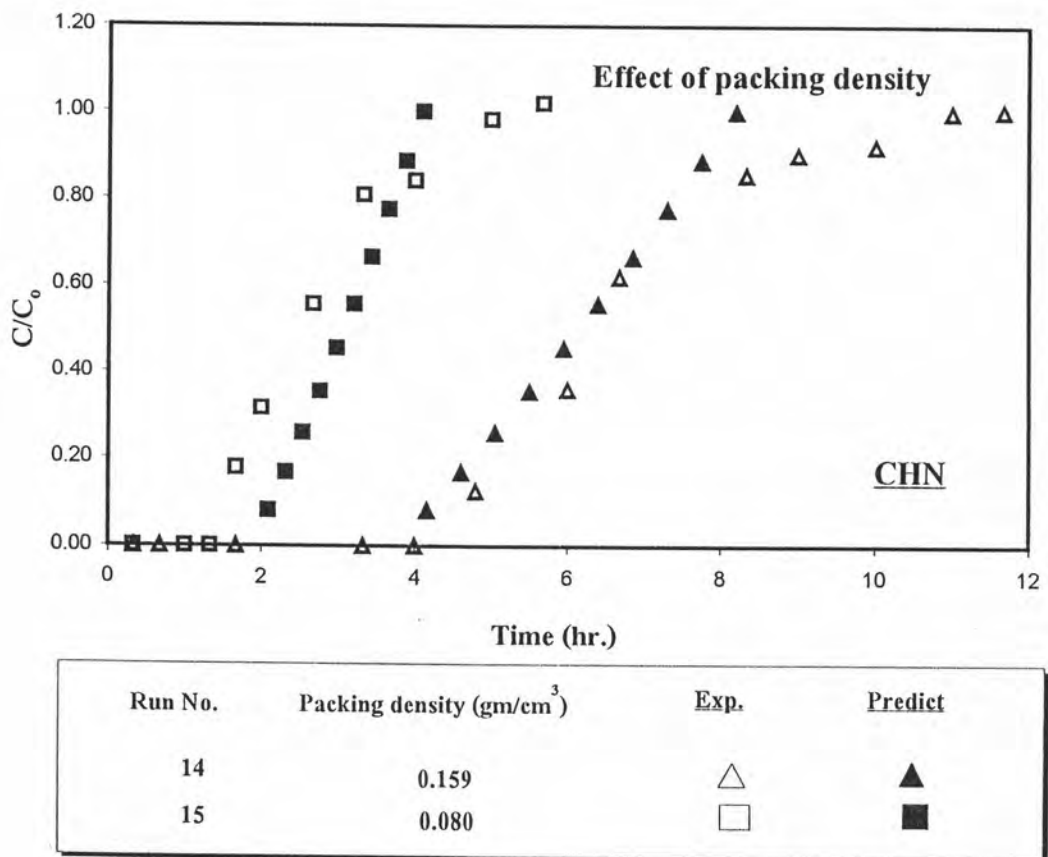


Figure 4-20 Breakthrough curves of CHN solution (Effect of superficial velocity)



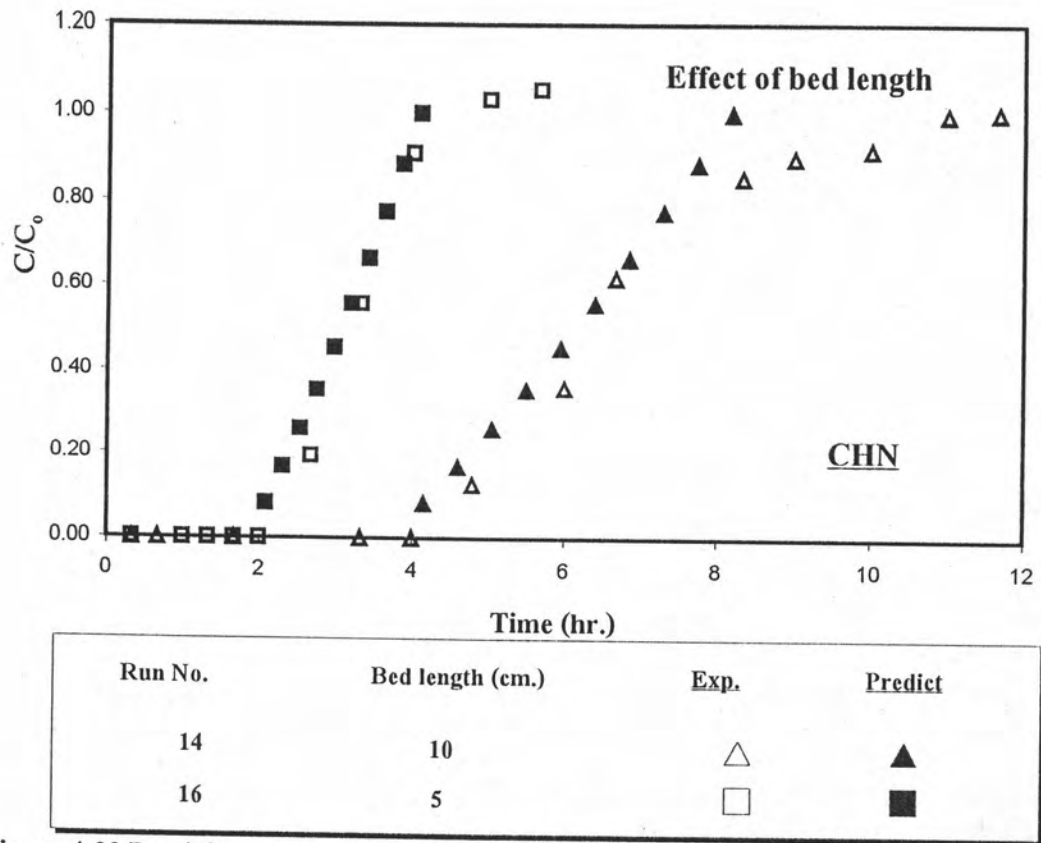
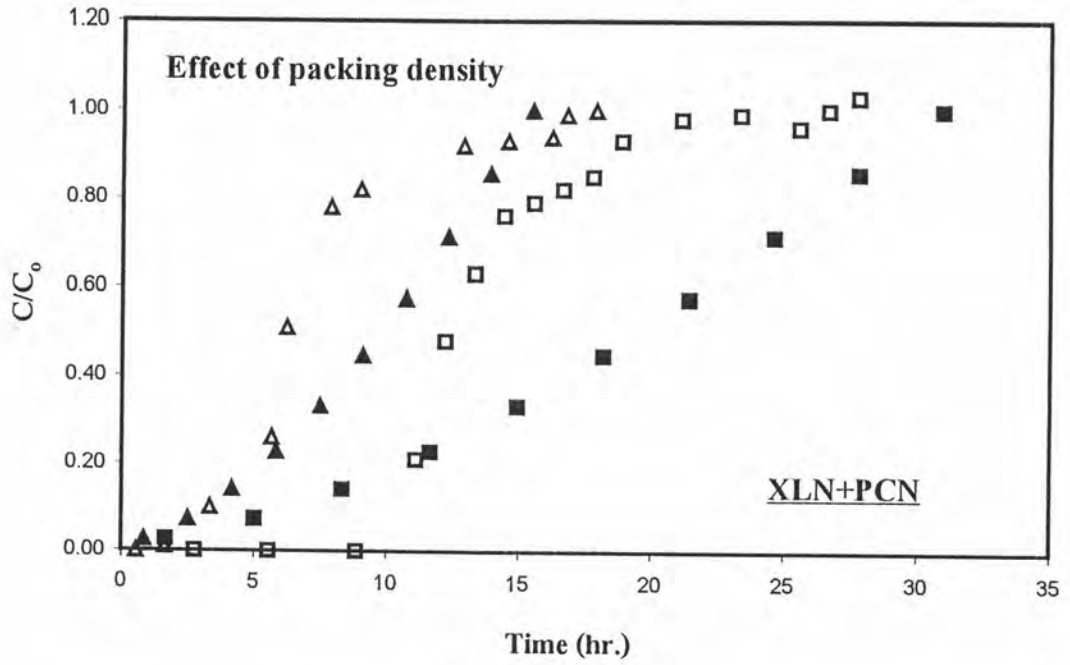
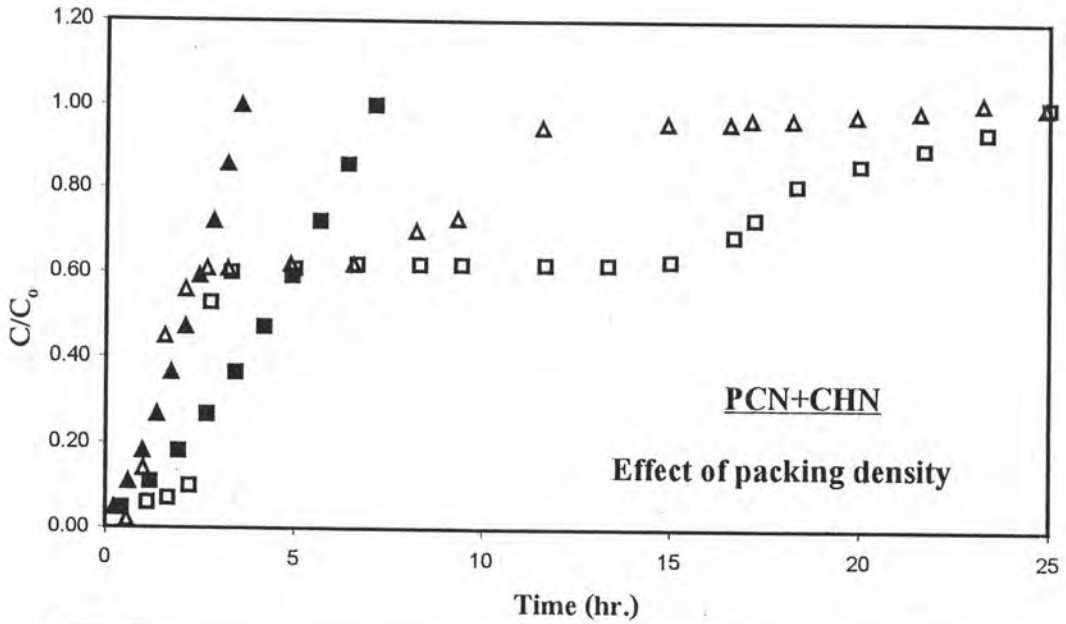


Figure 4-22 Breakthrough curves of CHN solution (Effect of bed length)

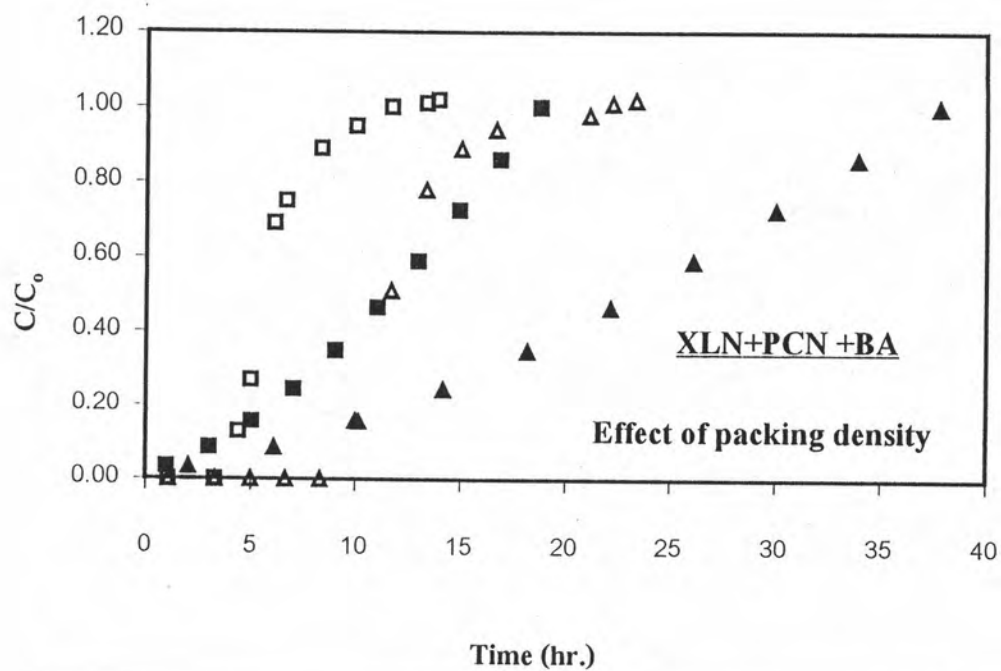


Run No.	Packing density (gm/cm ³)	Exp.	Predict
17	0.159	△	▲
18	0.080	□	■

Figure 4-23 Breakthrough curves of XLN+PCN solution (Effect of packing density)



Run No.	Packing density (gm/cm ³)	Exp.	Predict
19	0.159	△	▲
20	0.080	□	■



Run No.	Packing density (gm/cm ³)	Exp.	Predict
21	0.159	△	▲
22	0.080	□	■

Figure 4.25 Breakthrough curve of XLN+PCN+BA solution (Effect of packing density)

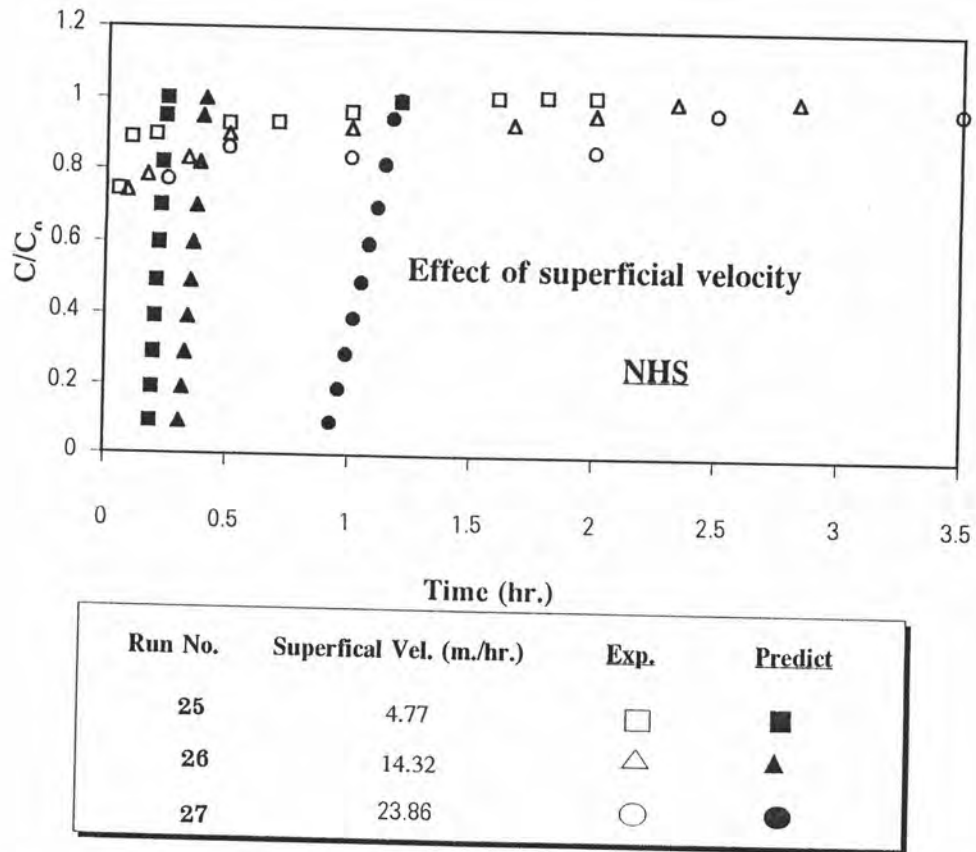


Figure 4-26 Breakthrough curves of NHS solution : ACFs-15 (Effect of superficial velocity)

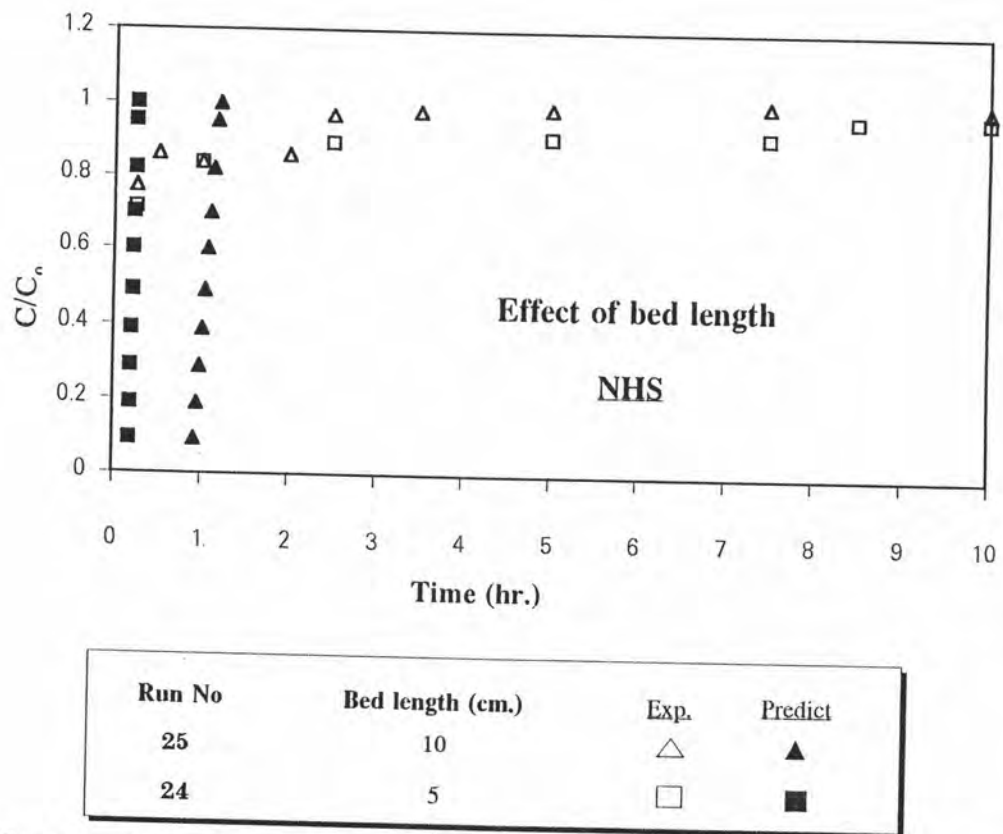
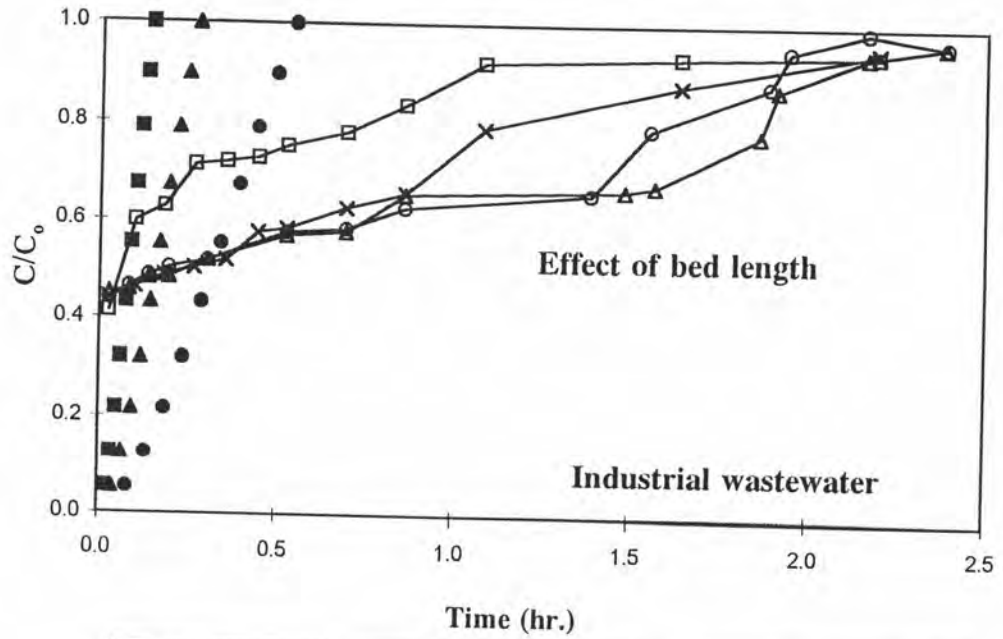
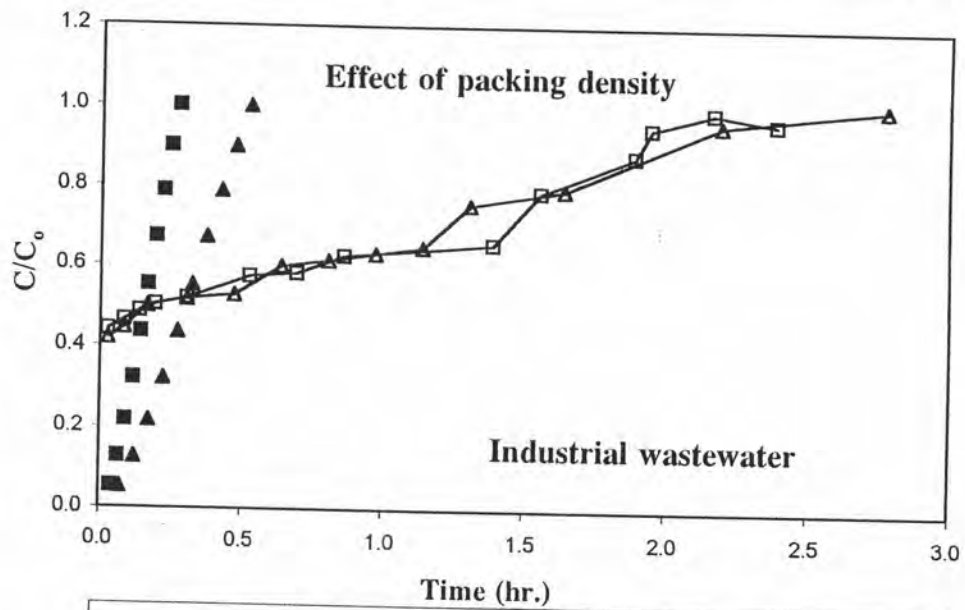


Figure 4-27 Breakthrough curves of NHS solution : ACFs-15 (Effect of bed length)



Run No.	Bed length (cm.)	Exp.	Predict
30	5	□	■
31	10	△	▲
33	20	○	●

Figure 4-28 Breakthrough curves of an industrial wastewater (Effect of bed length)



Run No.	Packing density (gm/cm ³)	Exp.	Predict
31	0.312	△	▲
32	0.160	□	■

Figure 4-29 Breakthrough curves of an industrial wastewater (Effect of packing density)

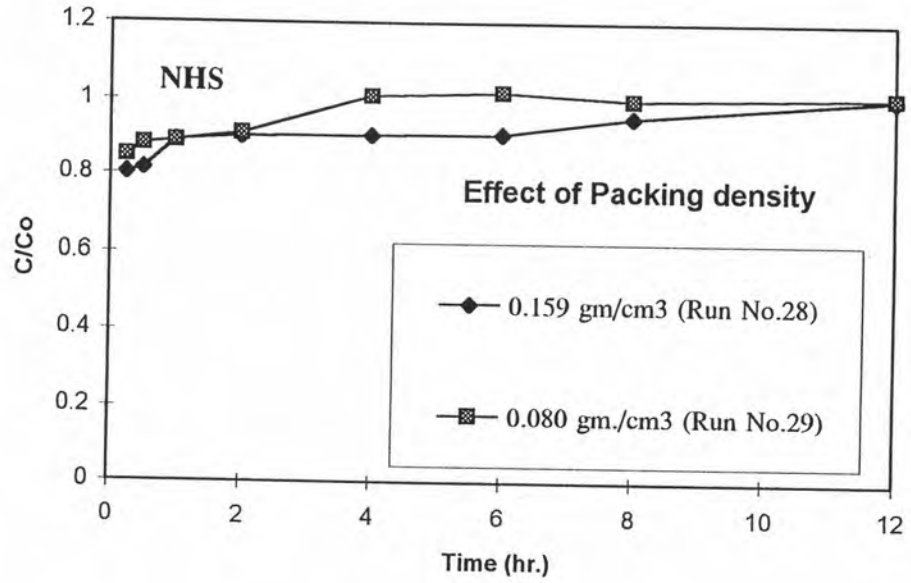


Figure 4-30 Breakthrough curves of NHS solution: ACFs-20 (Effect of packing density)

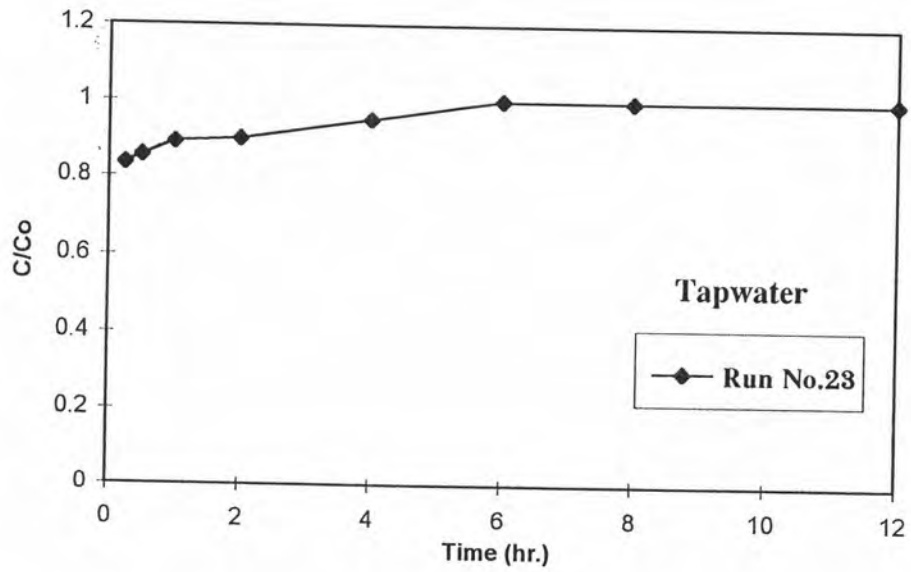


Figure 4-31 Breakthrough curves of Tapwater