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THE MODELLING AND DESIGN OF AN ACTIVATED CARBON ADSORBER FOR THE RECOVERY OF ORGANIC COMPONENTS FROM A CELLULOSE-PLANT EFFLUENT

Paul Anderson

Johannesburg 1986

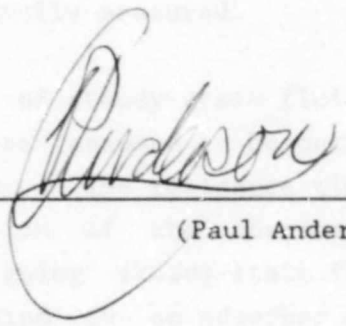
THE MODELLING AND DESIGN OF AN ACTIVATED CARBON ADSORBER FOR THE RECOVERY OF ORGANIC COMPONENTS FROM A CELLULOSE-PLANT EFFLUENT

Paul Anderson

A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the Degree of Master of Science in Engineering.

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted previously for any degree or examination in any other University.



(Paul Anderson)

20th day of March 1986

ABSTRACT

Adsorption of acetic acid and furfural from a simulated aqueous cellulose-plant effluent onto two commercially available activated carbons is investigated. A model of the adsorption/diffusion process is developed, where intraparticle diffusion is assumed to be controlled by diffusion along the pore surfaces. Adsorption equilibrium is calculated using a multicomponent adsorption isotherm, which is predicted from experimentally measured single-component isotherms. Model parameters are determined by fitting model predictions to stirred-tank batch-adsorber concentration histories, which are experimentally measured.

A model of steady-state fluidised-bed adsorption is developed. Solids are assumed to be perfectly mixed and liquid in perfect plug-flow. The residence-time distribution, fluidisation, and deactivation of the adsorbent are accounted for. A procedure for designing steady-state fluidised-bed adsorbers is proposed and applied to an adsorber for the simulated effluent stream. Experimental results indicate that decomposition of furfural would take place, preventing meaningful evaluation of design reliability. It is recommended that the complete effluent be investigated to quantify the effect of minor components on furfural decomposition, followed by modifications to the model and design procedure.

To Helen

Acknowledgements

I would like to thank :

Christopher Anderson, for many hours of assistance in the laboratory.

Dr. D. Baldwin of the Dept. of Chemistry, Wits Univ., for the loan and use of analytical equipment.

Prof. A. Bryson for assistance and advice on all aspects, from the laboratory investigation to the preparation of the dissertation.

CSIR for generous financial assistance during 1985 and 1986.

David Dortmundt, for assistance with processing of many data.

Messrs. J. Gaudard, A. Harris, L. Schwartz for manufacture and modification of laboratory equipment.

SAICCOR for a generous financial grant in 1985.

My wife and parents for their encouragement and support.

University of the Witwatersrand for financial assistance in the form of a Senior Bursary.

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NOMENCLATURE

a	specific surface-area	$m^2.kg^{-1}$
A	area	m^2
b_k	roots defining the concentration profile in an adsorbent particle - see eqn.(3/26)	-
B	capacity factor of adsorbent - see eqn.(3/24)	-
Bi	Biot number - see section 4.4	-
C	liquid-phase concentration	$kg.m^{-3}$
d	diameter	m
D	molecular diffusivity	$m^2.s^{-1}$
D_s	surface diffusivity	$m^2.s^{-1}$
$E(t)$	Exit age-density function	-
f	Langmuir adsorption-isotherm parameter distribution function - see eqn.(I/2)	-
F	multicomponent adsorption isotherm function (see eqn.(2/2))	
G	mass flowrate	$kg.s^{-1}$
h	height	m
$I(t)$	internal age-density function	-
J	flux	$kg.m^{-2}.s^{-1}$
k	Langmuir adsorption-isotherm parameter see eqn(I/1)	$m^3.kg^{-1}$
L	coefficient in boundary-layer theory solution	-
M	coefficient in boundary-layer theory solution	-
r	radius	m
r_o	outer radius of particles	m
S	multicomponent adsorption-isotherm parameter see section I.1	$kg.m^{-3}$
t	time	s
U	velocity	$m.s^{-1}$
W	mass	kg
x	general spatial coordinate	m
z	height measured up fluidised-bed	m

Subscripts

b	refers to bed properties or dimensions	
bulk	refers to bulk or average properties	
ex	refers to effluent properties	
feed	refers to feed-liquor properties	
i	refers to component i	
j	refers to component j	
l	refers to liquid	
p	refers to pore contents	
s	refers to solid (adsorbent)	
∞	refers to properties at large times (equilibrium)	

Superscripts

*	refers to a reference property	
o	refers to initial property	
^	refers to effective values	

Greek Characters

β	exponent in concentration dependent surface-diffusion coefficient - see eqn.(4/1)	-
δ	depth of boundary-layer	m
ϵ	voidage	-
φ	boundary-layer theory trial-function - see eqn.(7/10)	-
Φ	ratio of rates of adsorption for a two component system - see eqn.(7/16)	-
ϑ	specific adsorbance	-
Θ	reduced specific adsorbance	-
κ	parameter in multicomponent adsorption-isotherm theory - see eqn.(2/2)	-
λ	parameter correlating rate-ratio with concentration ratio - see Table 7.3	-
η	dimensionless spatial coordinate in boundary-layer theory	-
η_r	fractional regeneration efficiency	-
ρ	density	$kg.m^{-3}$
σ	time-scale parameter - see eqn.(4/7)	s
τ	dimensionless time	-

ν	parameter in effluent concentration prediction equation - see eqn.(7/18)	-
ξ	dimensionless radial coordinate	-
ψ, Ψ	rate-of-adsorption function - see eqn.(7/7)	
ζ	dimensionless liquid-phase concentration	-

1 INTRODUCTION

1.1 The Aims and Scope of the Research

This research has been undertaken for the purpose of the development and application of a design procedure for a continuous fluidised-bed, activated-carbon adsorber to treat an industrial aqueous effluent. The complete composition of the effluent is tabulated in Table 1.1 in order of decreasing concentration.

Effluent composition

Table 1.1

Solute	Concentration (g/l)
acetic acid	6.0
sulphur dioxide	5.8
furfural	3.0
ethanol	1.4
acetone	0.5
formic acid	0.5
methanol	0.2

Due to the relative magnitudes of the concentrations, the first three components, namely acetic acid, sulphur dioxide and furfural, have been selected as representative of the effluent. This was done to keep the mathematics and design procedure to manageable proportions.

The sulphur dioxide was not included in any modelling or design calculations, although it was included in all experimental runs. The motivation behind this simplification is discussed in section 2.2

The scope of this research includes the detailed testing of two different activated carbon types for their overall suitability with regard to adsorption capacity and rates. Elementary consideration was given to regenerability, re-usability and

fluidisation characteristics.

The physical characteristics of the two types of carbon, and the mass-transfer parameters for each combination of solute and carbon were determined since such information is essential to the design of adsorbers.

1.2 The Adsorption Process

Adsorption is the name given to the process whereby the molecules of gas or liquid attach themselves to, and for the most part remain confined to, the surface of a solid adsorbent. In contrast, **absorption** occurs when there is intimate mixing on a molecular level of a liquid or gas with the **absorbent**, which may itself be a liquid or a solid.

There are two types of adsorption which commonly occur, namely **physisorption** and **chemisorption**. These terms refer to whether the nature of surface attachment is physical, as in van der Waal's forces (see Atkins, 1978), or chemical, in which case a reaction is responsible for 'joining' the molecule to the adsorbent surface. Chemisorption may or may not be reversible, depending on the adsorbent type and adsorbed chemical, and can thus contribute largely to deterioration of the capacity of the adsorbent when re-used. A basic discussion of the two types of adsorption and their relative contribution to the overall adsorption and their relative contribution to the overall adsorption process is given by Coulson and Richardson (1979).

Due to the nature of adsorption as discussed above, it is not suprising to note that adsorbents have differing capacities and 'preferences' for different chemical species. For example, medium to high molecular weight species with a low degree of ionisation adsorb better onto activated carbon than do other species. It is this ability for differentiating between chemicals that is exploited in classical adsorption operations, such as water purification, dye recovery,gas cleaning and so on.

In the practical application of adsorption, it is common to ignore the distinction between the different types of adsorption, and to concentrate rather on the overall effect of treatment by adsorption. A very practical consequence of chemisorption, however, is that which is mentioned above, namely the question of deterioration or exhaustion of adsorbent, which gives rise to a very important consideration regarding the **regeneration** and re-use of adsorbent. The ability of the adsorbent to retain its activity despite repeated cycles of adsorption, regeneration and re-use seriously affects the economics of the process. This question of regeneration is discussed in more depth at a later stage, with reference to a particular type of adsorbent.

1.3 Types of Adsorbent

There are many different adsorbents currently in use. These can be divdided into the obvious groups of natural and synthetic adsorbents.

1.3.1 Natural Adsorbents

The most common, purely natural adsorbent is charcoal, though it is rarely used in industrial or commercial context due to its relatively low adsorption capacity. Thus charcoal of wood, coconut-shell, bone or coal origins is usually activated at high temperature in an oxygen-lean atmosphere to make it suitable for industrial use, hence the name **activated carbon**. The activation process results in a highly porous material with a large surface-area to weight ratio, composed mainly of carbon interfaced with aromatic structures. Activated carbon typically has a surface-area of about $2000 m^2 g^{-1}$ (McDougall,1982). The large surface-area to weight ratio is important since adsorption is a surface phenomenon, as discussed in section 1.2 above.

The major advantage of activated carbon is its relatively low cost. Although not as specific as molecular sieves or synthetic organic adsorbents - see section 1.3.2 - there are different

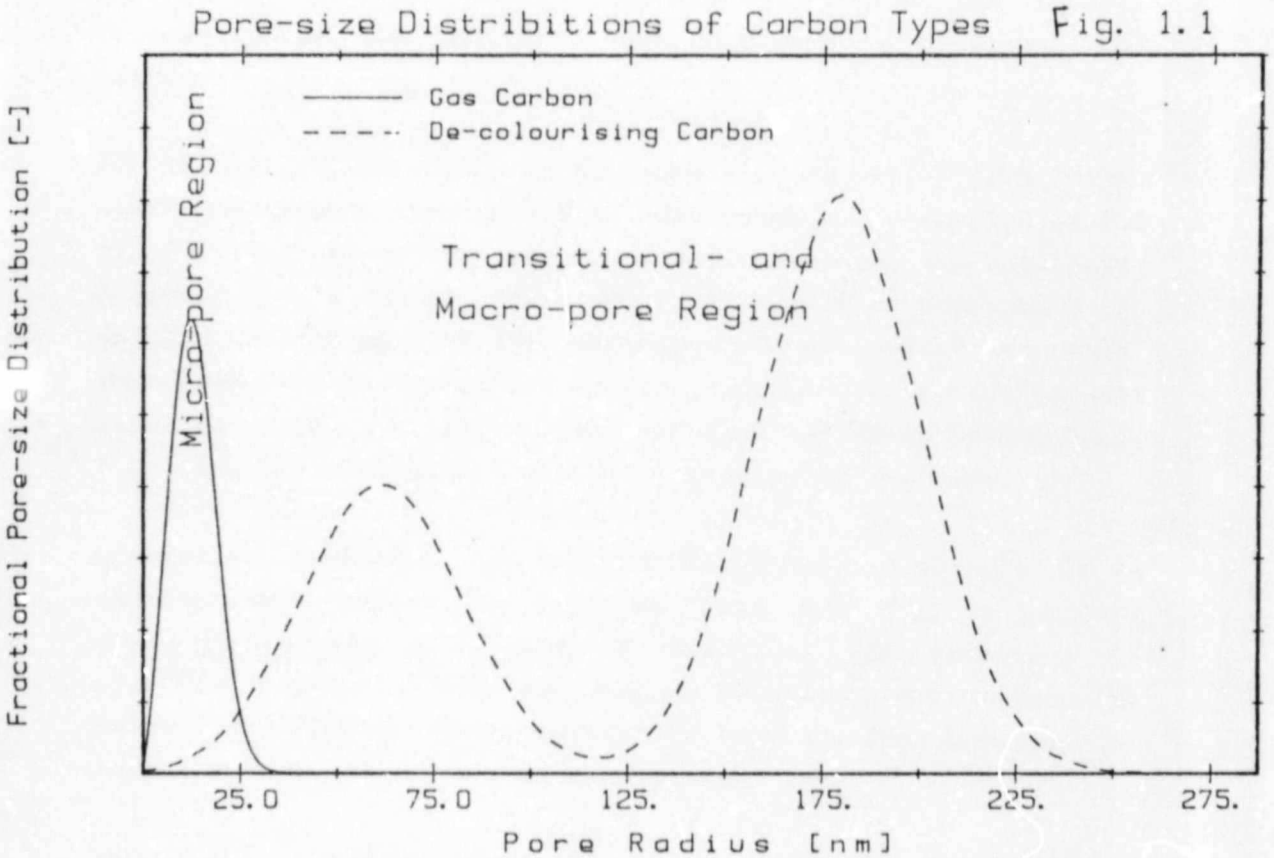
types of activated carbon which can give a degree of selectivity based on size. For example there are the so-called 'gas carbons', made from coconut shells, which have a narrow distribution of relatively small pores. This type of carbon is normally used for gas-cleaning or for treatment of low molecular weight, low-viscosity liquids containing low molecular weight solutes.

The other basic type of activated carbon is made of coal or wood, and has a comparatively wide pore-size distribution, which may be bi- or even tri-disperse in nature. This grade is used mainly for effluent treatment where pollutants are heavy organics, and in de-colourising of liquids (as in dye-recovery). **Fig.1.1** shows the idealised pore-size distributions in the two carbon types. The pore-size distribution of the de-colourising carbon is usually bi-disperse.

1.3.2 Synthetic Adsorbents

Examples of well-known inorganic synthetic adsorbents are aluminosilicate and alumina. These adsorbents share the advantage with other synthetic adsorbents that their characterisics can be closely controlled, so that they may be used to perform highly specific tasks. In the case of aluminas, the control can take the form of incorporating different metal ions into the structure. This is so effective that these adsorbents separate components based on molecular size or shape, hence the term 'molecular sieve'.

Other synthetic adsorbents include cross-linked polystyrenes, acrylic esters, and phenolic resins. These have been widely used in effluent treatment for organic solute removal and de-colourising, though it has been shown by Weber and van Vliet (1981) that the use of such synthetic adsorbents is only economically competitive when solute concentrations are high. A major disadvantage of synthetic adsorbents is their relatively high cost.


Pore-size Distribitions of Carbon Types Fig. 1.1
Gas Carbon
De-colourising Carbon
Micro-pore Region
Transitional- and
Macro-pore Region
Fractional Pore-size Distribution [-]
25.0
75.0
125.
175.
225.
275.
Pore Radius [nm]

1.4 Conclusions

The reasons for designing an adsorber which uses activated carbon are now clear: activated carbon is cheap, easily available and can be regenerated and re-used.

2 ADSORPTION ISOTHERMS AND ADSORBENT REGENERATION

2.1 Introduction

The proper design of any unit operation requires knowledge of the equilibrium and kinetics of the process occurring. Simply put, the following questions must be answered: 'how much can this process achieve?', and 'how quickly does it happen?'. The **adsorption isotherm** answers the first question, and the rate of adsorption the second - see section 3 for details of the latter.

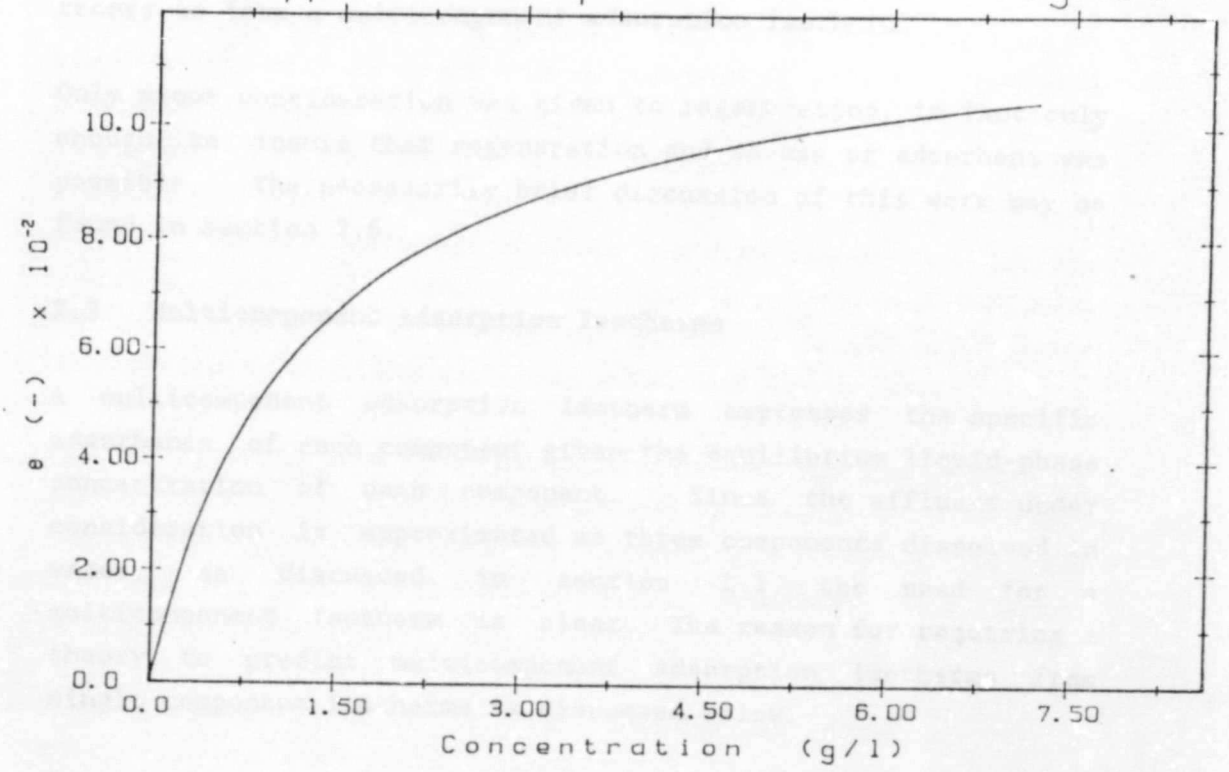
An adsorption isotherm is an expression or set of data points which expresses the specific adsorbance as a function of the liquid-phase concentration in equilibrium with the adsorbent, measured at a fixed temperature. **Specific adsorbance** is defined as the mass of adsorbed material per mass of adsorbent. Thus one would expect the specific adsorbance, θ, to increase with increasing equilibrium concentration, which it indeed does. **Fig. 2.1** shows a plot of a typical adsorption isotherm.

Adsorption isotherms can be obtained by experiment only. It is to the data points so obtained that one fits an isotherm expression that satisfactorily describes the variation of specific adsorption with equilibrium solute concentration. The method of calculating the adsorption isotherm from experimental measurements is discussed in section 2.4 below.

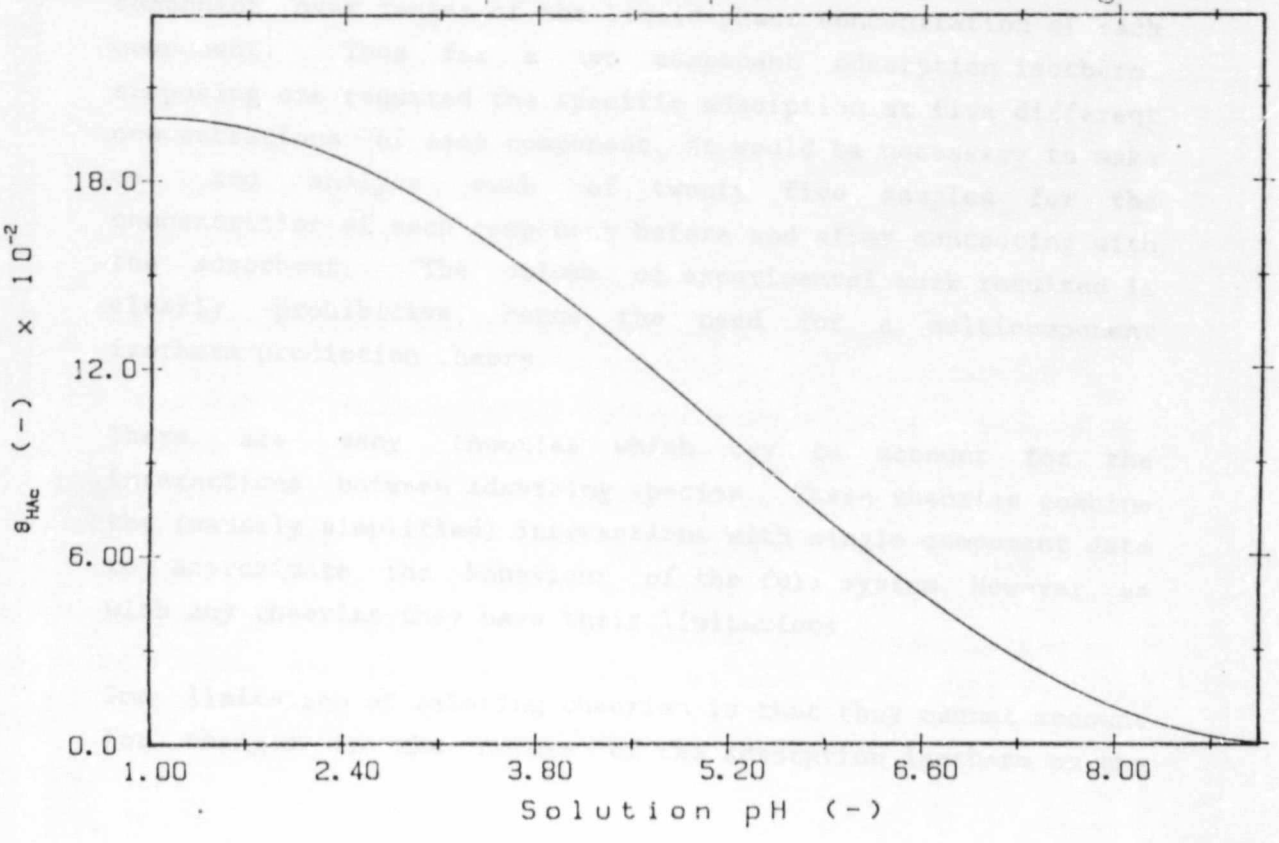
Among the simplest adsorption isotherm equations are those of Langmuir and Freundlich, which may be applied to single component systems; see Perry and Chilton (1973) for a general review of common isotherms. However, since the ultimate object of this research is the practical application of multicomponent adsorption, a more sophisticated isotherm capable of predicting and correlating multicomponent adsorption isotherms is required.

In fact what is desirable is the combination of **single component isotherm** data by means of a **sound, consistent**

A Typical Adsorption Isotherm Fig. 2.1



The effect of pH on adsorption of Acetate Fig. 2.2



theory to form a multicomponent adsorption isotherm.

Only minor consideration was given to regeneration, in fact only enough to ensure that regeneration and re-use of adsorbent was possible. The necessarily brief discussion of this work may be found in section 2.6.

2.2 Multicomponent Adsorption Isotherms

A multicomponent adsorption isotherm expresses the specific adsorbance of each component given the equilibrium liquid-phase concentration of each component. Since the effluent under consideration is approximated as three components dissolved in water, as discussed in section 1.1, the need for a multicomponent isotherm is clear. The reason for requiring a theory to predict multicomponent adsorption isotherms from single component isotherms is discussed below.

Proper characterisation of multicomponent adsorption isotherms requires measurement of the specific adsorption of each component over ranges of the liquid-phase concentration of each component. Thus for a two component adsorption isotherm, supposing one required the specific adsorption at five different concentrations of each component, it would be necessary to make up, and analyse each of twenty five samples for the concentration of each component before and after contacting with the adsorbent. The volume of experimental work required is clearly prohibitive, hence the need for a multicomponent isotherm prediction theory.

There are many theories which try to account for the interactions between adsorbing species. These theories combine the (usually simplified) interactions with single component data to approximate the behaviour of the full system. However, as with any theories they have their limitations.

One limitation of existing theories is that they cannot account for changes in the nature of the adsorption isotherm on the

addition of an extra component. This is exactly what happens when an acidifying agent such as sulphur dioxide is added to a solution already containing acetic acid: the extent of adsorption of the acetic acid changes dramatically - see McDougall (1982), and Fig. 2.2 for the results of this effect. The best that any of these theories can do is allow for specific types of effects - for example, Radke and Prausnitz (1972) refer to publications on systems where the solutes are only partially miscible with each other and the solvent.

It was reasoned that it would be best to include the acidifying effect of dissolved sulphur dioxide on each adsorption isotherm explicitly. This was done by measuring the single component isotherm of each of the two remaining components in a sulphur dioxide solution.

The effluent system has two degrees of freedom, and a multicomponent adsorption isotherm is still necessary.

2.3 Theories of Combination

A combination theory is one which combines single-component adsorption isotherms on a rational basis to form a multicomponent adsorption isotherm. This section describes the requirements made on such a theory, and outlines the basis of a particular combination theory.

2.3.1 Requirements imposed on combination isotherms

Since the multicomponent adsorption isotherm in this case is to be used in an extensive model of the overall process, the combination theory must be simple, with a minimum of fitted parameters and computational complexity. At the same time, however, the selected theory must give reasonable results, the simplest test being that in the limit as all concentrations but one vanish, the resultant isotherm must tend toward that for the nonvanishing component.

The multicomponent adsorption isotherm must be continuous with respect to all concentrations. A combination theory satisfying the above requirements is that of Okazaki, Kage and Toei (1980). The complete theory is extensive, so only the basics are discussed here.

2.3.2 The Combination Theory of Okazaki et al

The theory of Okazaki et al (1980) comprises a single component adsorption isotherm which is based on the Langmuir isotherm - APPENDIX II gives details of assumptions made, and of the derivation of the single and multicomponent adsorption isotherms. The resulting single-component adsorption isotherm is an equation with three parameters, one of which has a physical interpretation.

$$\theta = \frac{Q_s}{\ln(k_{max}/k_{min})} \ln\left(\frac{1 + k_{max}C}{1 + k_{min}C}\right) \qquad \ldots(2/1)$$

Where θ = specific adsorbance [-]
Q_s = specific adsorbance at saturation [-]
k_{min}, k_{max} = fitted parameters [$m^3.kg^{-1}$]
C = liquid-phase concentration [$kg.m^{-3}$]

Note that although Q_s has a physical interpretation, there is no loss of generality by fitting it as an extra parameter. In the case where adsorption isotherm measurements extend well into the region of saturation, the fitted parameter Q_s and the actual saturation adsorbance will coincide. In the case where isotherm measurements do not extend to saturation, the parameter Q_s is varied so as to get the best fit over the low concentration range, a fact which must be remembered when applying the equation.

Eqn.(2/1) is fitted to each of the experimentally measured, single component adsorption isotherms by choice of the

parameters Q_s, k_{min} and k_{max}, before proceeding to the next step.

The multicomponent adsorption isotherm is then derived using assumptions regarding the relation between corresponding parameters as fitted above, for the different components, and the above functional form of eqn.(2/1) - details of the fitting procedure are discussed in **APPENDIX II**. The multicomponent adsorption isotherm equation takes the following form:

$$\theta_i(\underset{\sim}{C}) = \frac{Q_{s,i}C_i}{\ln\left(\frac{k_{i,max}}{k_{i,min}}\right)} \int_{k_{i,min}}^{k_{i,max}} \frac{dx}{F_i(x)} \qquad \ldots(2/2)$$

$$\text{where } F_i = 1 + \sum_{j=1}^{N} \left(\frac{x}{k_{i,max}}\right)^{\kappa_{i,j}} k_{j,max}C_j$$

N = total number of components in the mixture
and $\underset{\sim}{C}$ is the vector of liquid-phase concentrations

$$\text{and } \kappa_{i,j} = \frac{\ln\left(\frac{k_{j,max}}{k_{j,min}}\right)}{\ln\left(\frac{k_{i,max}}{k_{i,min}}\right)}$$

Although the above expressions may appear a little too involved to have any real significance, recall that they are only a means

of combining single-component experimental data on a rational basis to predict the behaviour of a multicomponent system, and that all the various parameters are fitted before these equations are used. Note also that apparent complexity of F_i in eqn.(2/2) is considerably reduced once substitutions are made for the κ, k_{min} and k_{max}. The resulting expression for F_i is as follows:

$$F_i = 1 + \alpha_1 x^u C_1 + \alpha_2 x^v C_2 + \alpha_3 x^w C_3 + \ldots\ldots$$

where the u, v, w, α_1, α_2.... for any given set of components are constants depending only on the value of the subscript i.

The method for predicting multicomponent adsorption isotherms from single component isotherms may be summarised as follows:

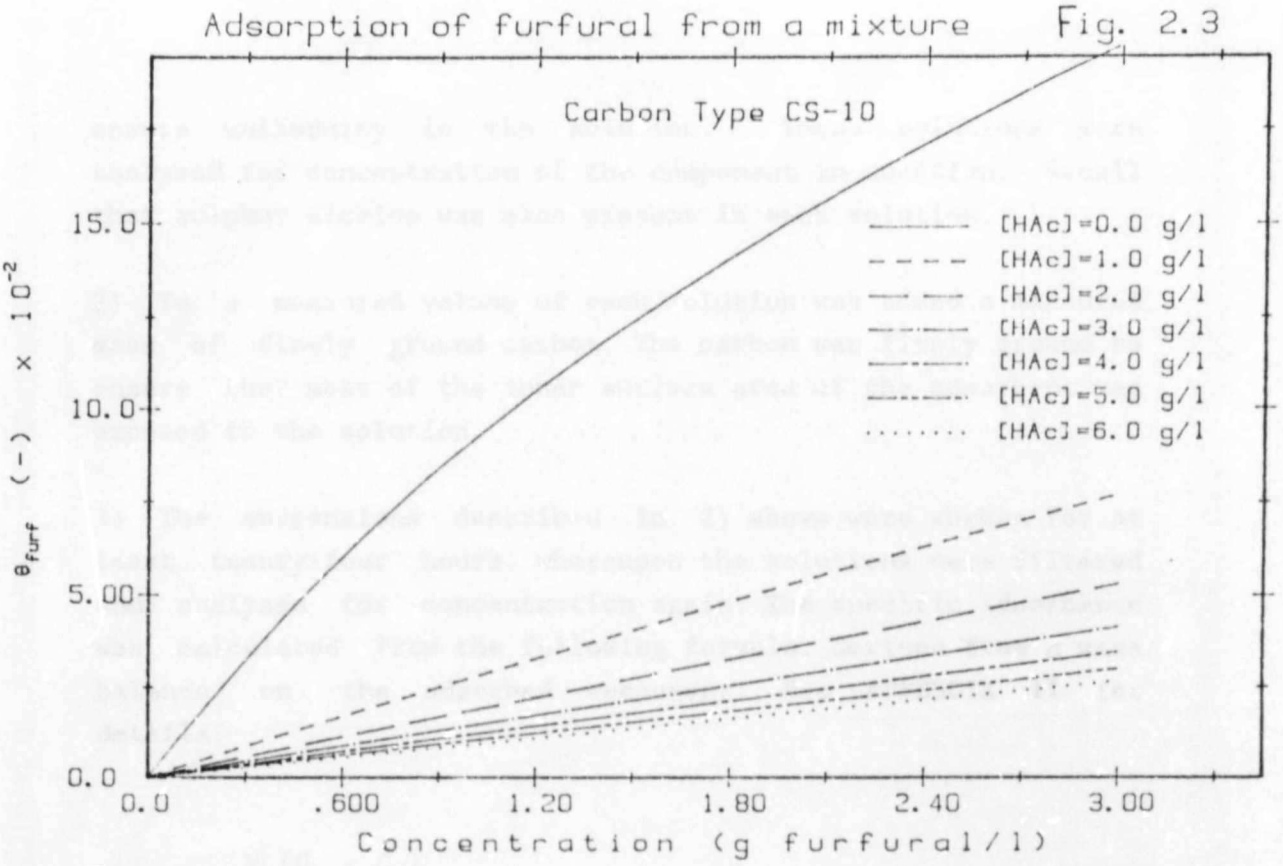
1) find the parameters k_{min}, k_{max}, Q_s which make eqn.(2/1) fit the single component isotherm data in some 'best sense', by minimising the sum of squares of errors, for example. Do this for each component in the mixture.

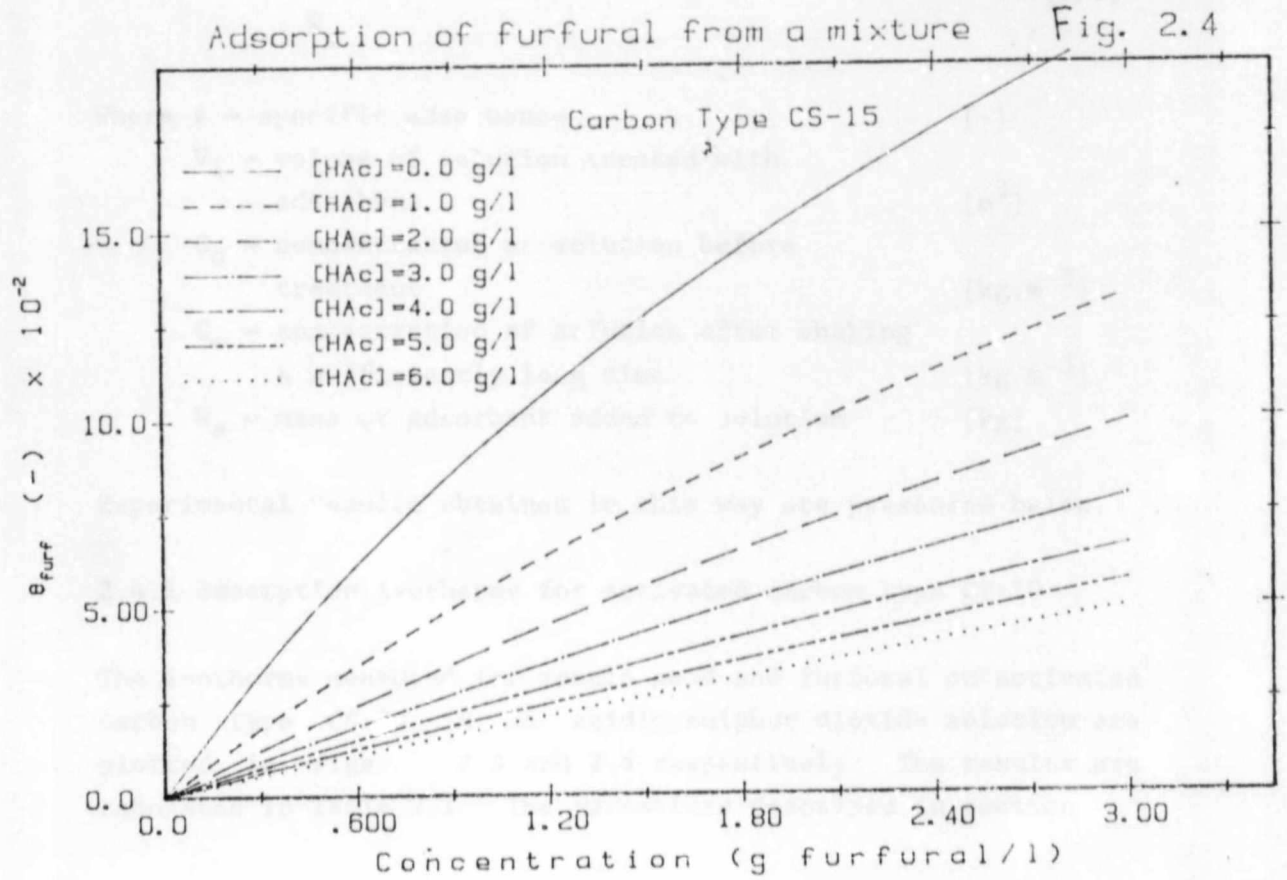
2) Eqn.(2/2) gives the theoretical prediction of the adsorbance of each component given the equilibrium liquid-phase concentration of each component. Multicomponent adsorption isotherms derived from single-component data (see below) are plotted in Figs. 2.3 and 2.4 for carbon types CS-10 and CS-15 respectively.

2.4 Experimental Results

The measurement of adsorption isotherms is simple, and the procedure is summarised below.

1) Several solutions of the component in question, of increasing concentration, were made. The containers were shaken well to


Adsorption of furfural from a mixture
Fig. 2.3
Carbon Type CS-10
[HAc]=0.0 g/l
[HAc]=1.0 g/l
[HAc]=2.0 g/l
[HAc]=3.0 g/l
[HAc]=4.0 g/l
[HAc]=5.0 g/l
[HAc]=6.0 g/l
θfurf (-) x 10-2
15.0
10.0
5.00
0.0
0.0
.600
1.20
1.80
2.40
3.00
Concentration (g furfural/l)


Adsorption of furfural from a mixture
Fig. 2.4
Carbon Type CS-15
[HAc]=0.0 g/l
[HAc]=1.0 g/l
[HAc]=2.0 g/l
[HAc]=3.0 g/l
[HAc]=4.0 g/l
[HAc]=5.0 g/l
[HAc]=6.0 g/l
θfurf (-) x 10-2
15.0
10.0
5.00
0.0
0.0
.600
1.20
1.80
2.40
3.00
Concentration (g furfural/l)

ensure uniformity in the solution. These solutions were analysed for concentration of the component in question. Recall that sulphur dioxide was also present in each solution.

2) To a measured volume of each solution was added a measured mass of finely ground carbon. The carbon was finely ground to ensure that most of the inner surface area of the adsorbent was exposed to the solution.

3) The suspensions described in 2) above were shaken for at least twenty-four hours, whereupon the solutions were filtered and analysed for concentration again. The specific adsorbance was calculated from the following formula, derived from a mass balance on the adsorbed component. See **APPENDIX II** for details.

$$\theta = \frac{V_1(C_o - C_\infty)}{W_s} \qquad \ldots(2/3)$$

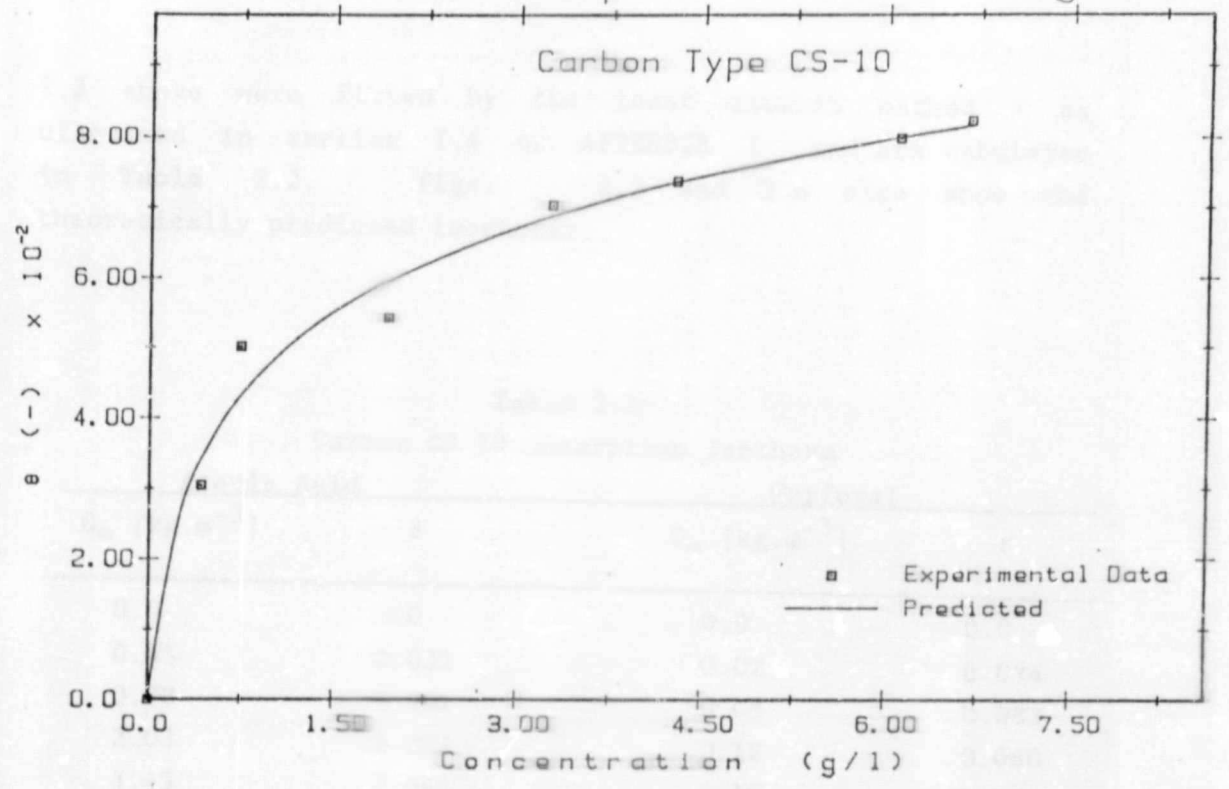
Where θ = specific adsorbance [-]
V_1 = volume of solution treated with adsorbent [m^3]
C_o = concentration of solution before treatment [$kg.m^{-3}$]
C_∞ = concentration of solution after shaking a sufficiently long time [$kg.m^{-3}$]
W_s = mass of adsorbent added to solution [kg]

Experimental results obtained in this way are presented below.

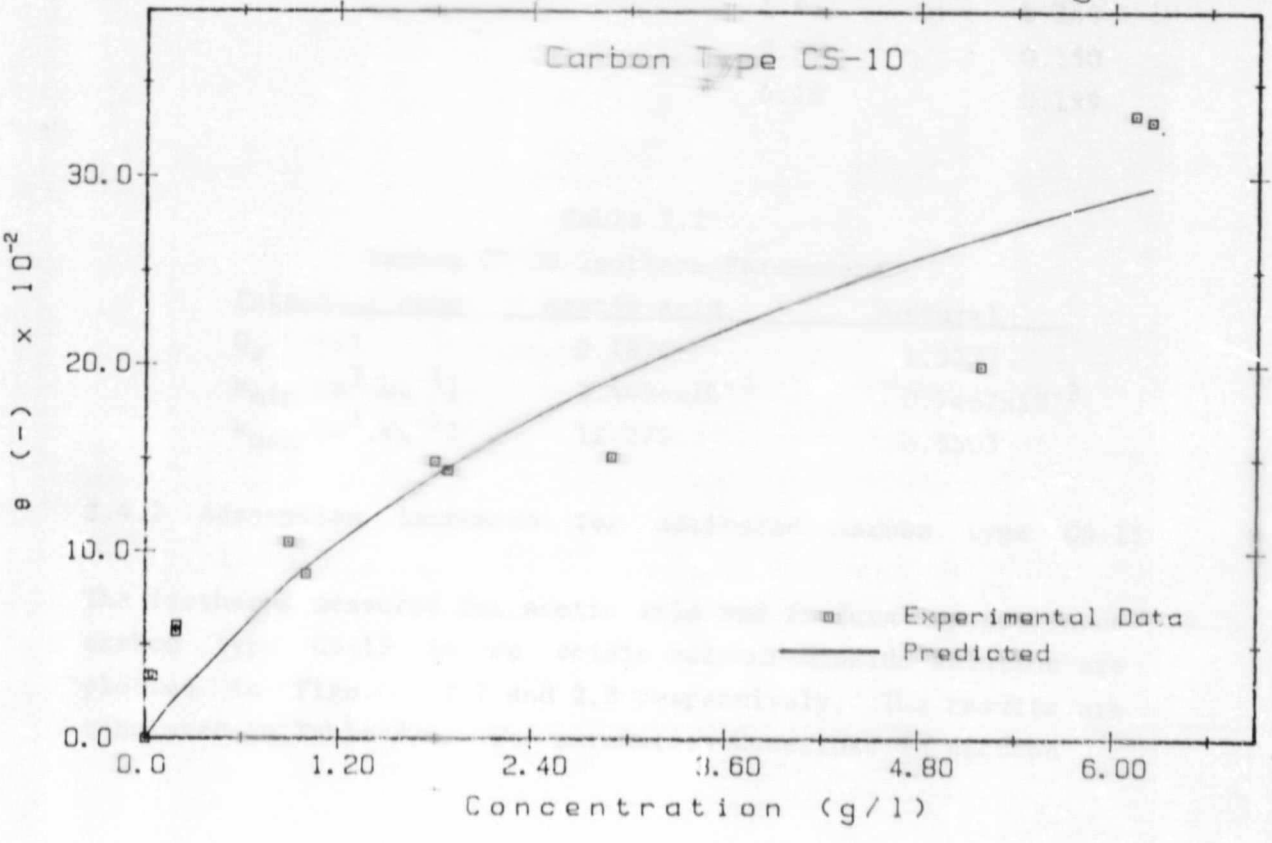
2.4.1 Adsorption isotherms for activated carbon type CS-10

The isotherms measured for acetic acid and furfural on activated carbon type CS-10 in an acidic sulphur dioxide solution are plotted in **Figs.** 2.5 and 2.6 respectively. The results are tabulated in **Table** 2.1. The parameters described in section

Acetic Acid Adsorption Isotherm Fig. 2.5



Furfural Adsorption Isotherm Fig. 2.6



2.3 above were fitted by the least squares method · as discussed in section I.4 o APPENDIX I - and are tabulated in Table 2.2. Figs. 2.5 and 2.6 also show the theoretically predicted isotherms.

Table 2.1

Carbon CS-10 Adsorption Isotherm

Acetic Acid		Furfural	
C_∞ [kg.m^{-3}]	θ	C_∞ [kg.m^{-3}]	θ
0.0	0.0	0.0	0.0
0.45	0.031	0.02	0.034
0.78	0.052	0.05	0.033
2.03	0.057	0.18	0.060
3.43	0.062	0.19	0.057
4.49	0.078	0.89	0.105
6.24	0.097	1.00	0.088
6.77	0.092	1.80	0.148
		1.88	0.143
		2.90	0.150
		5.18	0.199

Table 2.2

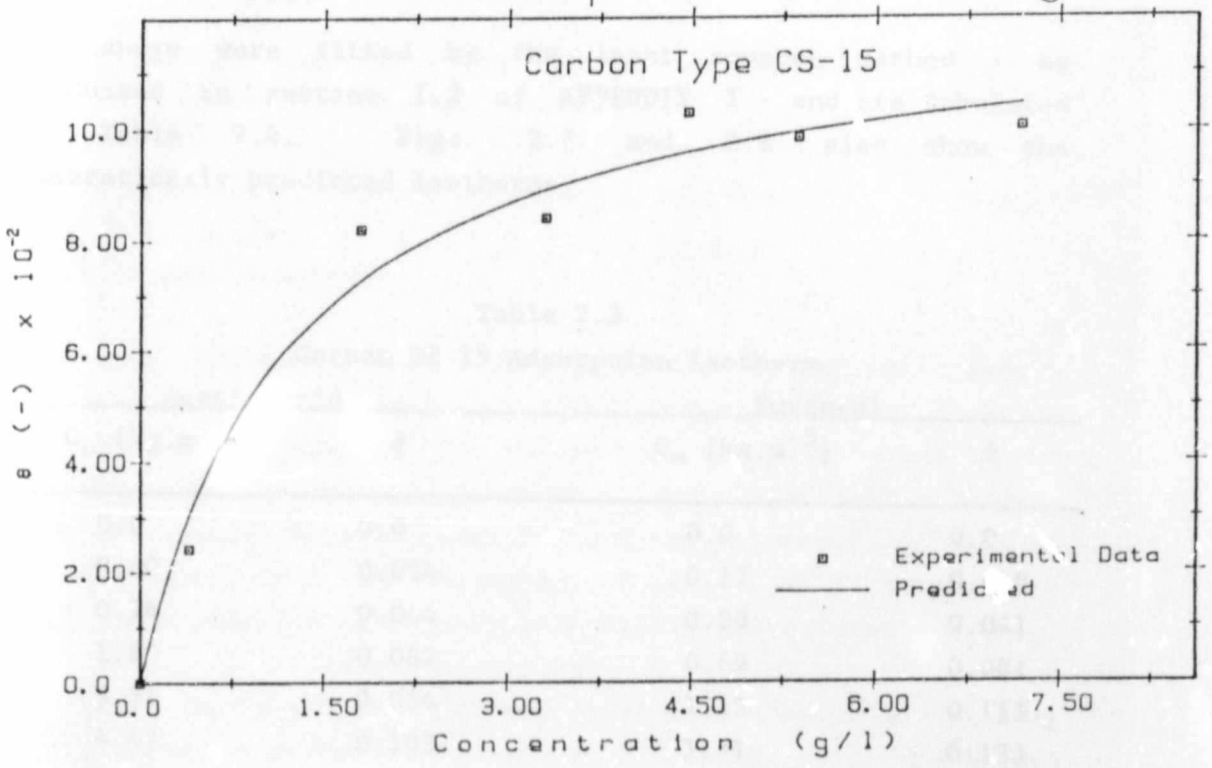
Carbon CS-10 Isotherm Parameters

Parameter name	Acetic Acid	Furfural
Q_s [-]	0.1876	1.5277
k_{min} [m^3.kg^{-1}]	0.4494×10^{-3}	0.1457×10^{-3}
k_{max} [m^3.kg^{-1}]	12.276	0.6503

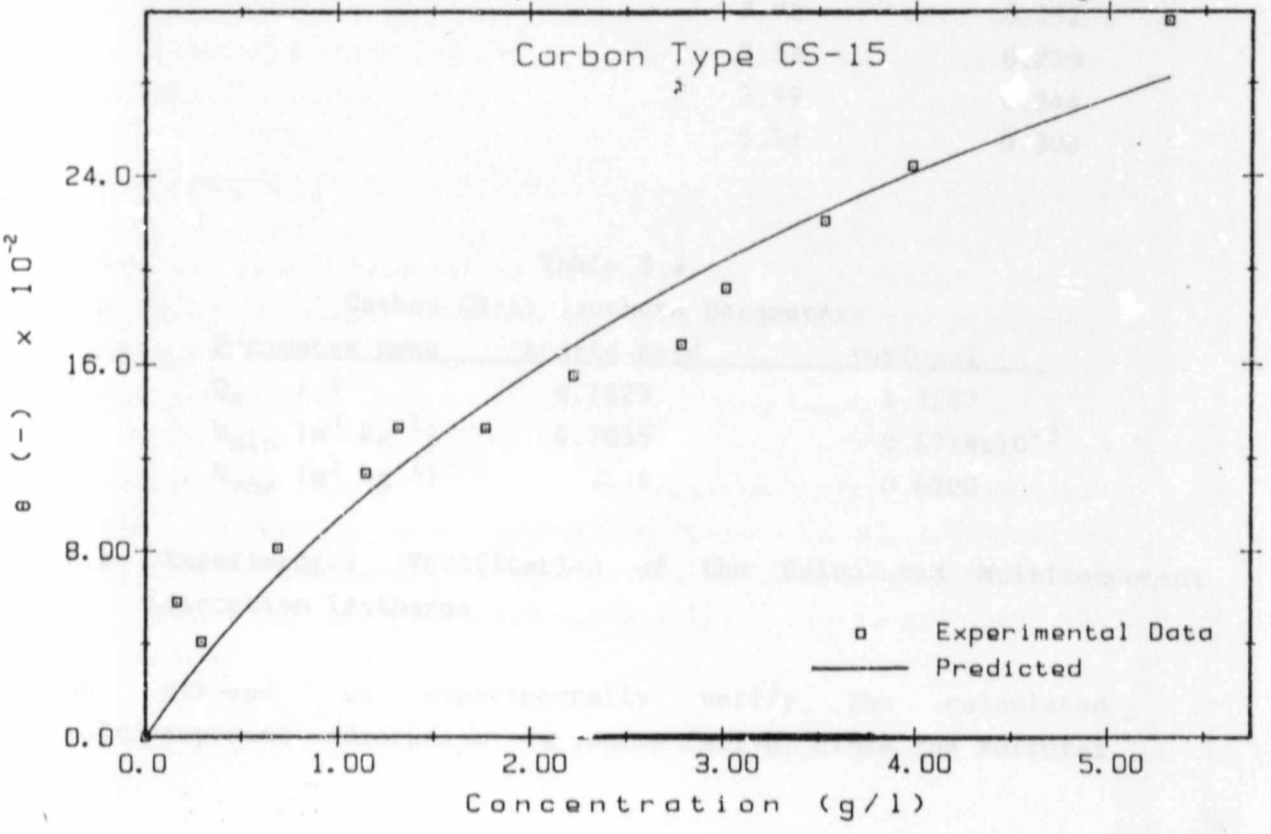
2.4.2 Adsorption isotherms for activated carbon type CS-15

The isotherms measured for acetic acid and furfural on activated carbon type CS-15 in an acidic sulphur dioxide solution are plotted in Figs. 2.7 and 2.8 respectively. The results are tabulated in Table 2.3. The parameters described in section

Acetic Acid Adsorption Isotherm Fig. 2.7



Furfural Adsorption Isotherm Fig. 2.8



2.3 above were fitted by the least squares method - as discussed in section I.2 of APPENDIX I - and are tabulated in Table 2.4. Figs. 2.7 and 2.8 also show the theoretically predicted isotherms.

Table 2.3

Carbon CS-15 Adsorption Isotherm

Acetic Acid		Furfural	
C_∞ [kg.m^{-3}]	θ	C_∞ [kg.m^{-3}]	θ
0.0	0.0	0.0	0.0
0.40	0.024	0.17	0.058
0.74	0.044	0.29	0.041
1.80	0.082	0.69	0.081
3.31	0.084	1.15	0.113
4.47	0.103	1.71	0.133
5.37	0.098	1.77	0.133
7.20	0.100	2.22	0.155
		2.78	0.168
		3.02	0.192
		3.53	0.220
		3.99	0.244
		5.32	0.306

Table 2.4

Carbon CS-15 Isotherm Parameters

Parameter name	Acetic Acid	Furfural
Q_s [-]	0.1223	1.3247
k_{min} [m^3.kg^{-1}]	0.7035	0.6718×10^{-3}
k_{max} [m^3.kg^{-1}]	0.9436	0.6200

2.5 Experimental Verification of the Calculated Multicomponent Adsorption Isotherms

An attempt to experimentally verify the calculated multicomponent adsorption isotherms failed, since the furfural

Author Anderson Paul
Name of thesis The Modelling And Design Of An Activated Carbon Adsorber For The Recovery Of Organic Components From A Cellulose-plant Effluent. 1986

PUBLISHER:
University of the Witwatersrand, Johannesburg
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