Eng. & Technology, Vol.24, No.4, 2005

Dynamics Behavior Of Adsorption The Binary Pollutants By A Fixed Bed Column

Dr. Karima Marogy*, Intisar Hussain Khalaf*
Fatin Fahdeel Saffo*

Received on: 22/7/2004
Accepted on: 25/4/2005

Abstract

Adsorption of hydrocarbon pollutents (Ethanol and Butanol) by activated carbon had been investigated using a fixed bed column. A wide range of concentration ($25\times10^{-3} - 100\times10^{-3}$ kg/m^3) *were studied.*

The dynamic behavior of the bed adsorber was studied by created a step change in the feed concentration of (20%) and step change in the feed flow rate of (10%).

A frequency response analysis was carried out using bode diagram, the technique log modulus and the phase angle were used to analysis the process model. A matlab program was used to study the dynamic model of adsorber to predict the transient responses, it is also used to find the frequency response analysis using experimental data. The deviation between theoretical and experimental is agreement.

الخلاصة

المواد الممتزة هي مواد عضوية (الايثانول والبيوتانول) امتزت باستخدام الفحم المنشط في عمود ذات الحشوة الثابتة.
تراوح معدل التركيز المستخدم في التجارب ما بين ٢٥×١٠$^{-٣}$ – ١٠٠×١٠$^{-٣}$ كغم / م^{٣} لكل مادة.

اجريت دراسة السلوك الديناميكي لبرج الامتزاز الساكن من خلال اجراء تغير درجي step change بالتركيز الداخل بمقدار ٢٠% وتغير درجي بالجريان الداخل بمقدار ١٠%.

تم استخدام اسلوب مخطط بود (Bode diagram) لتحليل الاستجابة الترددية للـ (adsorber) للتغير الدرجي حيث استخدم (log modulus) وزاوية الطور (Phase angle).

---

* Dept. Of Chemical Eng., University of Technology.

https://doi.org/10.30684/etj.24.4.7
University of Technology-Iraq, Baghdad, Iraq/2412-0758
This is an open access article under the CC BY 4.0 license http://creativecommons.org/licenses/by/4.0

استخدم في هذه الدراسة (matlab program) لايجاد الاستجابة الانتقالية لتغير فجائي في التركيز الداخل ومعدل الجريان. كما تم ايجاد النموذج الخاص بديناميكية العمود من خلال (matlab program) الذي يقوم بحساب الاستجابة الترددية من النتائج العملية. ان نسبة الأنحراف بين النتائج العملية والنظرية مقبولة الى حد ما.

1. Introduction:

1.1 Fixed bed adsorption column

The efficient recovery of simple water soluble organics is complicated by several factors. The product is frequently intended for human consumption and is required in a high purity form without potentially toxic impurities. Such requirements place a heavy burdon on conventional separation such as distillation, ion exchange, activated carbon adsorption and solvent extraction.

Distillation proves energy inefficient because large quantities of water must be vaporized and is further complicated by the presence of other compounds of similar volatility and the heat sensitivity of the desired species.

Solvent extraction proves difficulties because solvent with a high selectivity for aqueous organics show a poor capacity where as high capacity solvent suffer from low selectivity. Such inherent difficulties have led to considerable interest in the development of separation process based on hydrophobic membranes and hydrophobic adsorbent by adsorption process[(1)].

Adsorption is the interaction between a fluid (adsorbate) and a solid surface (adsorbent) and it occurs on the surface of a solid because of the attractive force of the atoms or molecules in the surface of the solid[(2)]. Adsorption, was first observed by (Scheel in 1775) for gases and subsequently for solution by (Lowitz in 1785)[(3)].

Adsorption with a solid such as carbon is dependent on the surface area of the solid. Thus carbon treatment of water involve the liquid–solid interface[(4)]. Martin and Bahrani[(5)], found that the equilibrium data of adsorption for many organic pollutants were correlated well with the Langmuir and Frendlich equations. Stenzel[(6)], found that organic contaminants are more adsorbal that others.

The variables affecting adsorption are surface area and particle size of carbon, the solution condition (pH, temperature and adsorbate concentration), the adsorbate properties (functional group, molecular weight and solubility), contact time, linear velocity, flow rate and bed length, nature of adsorbent.

A theoretical analysis was made of the methods used for the purification of gas, containing impurities of small concentrations. A comparison is proposed between absorption and adsorption methods. It is shown that adsorption processes are more advantageous in these cases(7).

Jufang Wu, Zili Xie, Kunmin Guo and Ola describes a modified headspace method for measuring the adsorption equilibrium of mixtures of organic vapours. The advantage of the method relative to the ordinary headspace method is the shorter time needed to reach adsorption equilibrium. The adsorption isotherms of benzene, hexane and pentane on activated carbons were acquired quickly and easily using this method. The method has also been used to measure the binary equilibrium data of benzene- hexane, benzene-pentane and hexane-pentane mixtures on three types of activated carbon(8).

The adsorption of sodium dodecylsulfate (SDS) and the coadsorption of SDS and 1-butanol from aqueous electrolyte solutions and from microemulsions containing heptane on to acidic and basic aluminum oxide were measured. measurements were carried out just above the Krafft temperature at 26 degrees C. It is shown that the adsorption capacity of SDS and butanol onto the acidic alumina is slightly higher than that onto the basic, The adsorption of SDS decreases while butanol adsorption increases upon increasing alcohol concentration(9).

Adsorption of short chain alcohols in decane solutions onto kaolinite has been investigated by Fourier transform infrared spectroscopy (FTIR) for analysis of the alcohol content. The alcohols were methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol, The isotherms have been mathematically modeled by (i) a basic Langmuir equation, and (ii) a two-term Langmuir equation, In both cases, the equations were modified to take into account the self-association of alcohol molecules in the hydrocarbon solution, The methanol isotherm exhibits two plateaus of differing extent, in addition to a strongly increasing isotherm near the solubility limit. (10).

1.2 Dynamic Behavior of fixed bed Adsorption Column

Dynamic adsorption experiments have been carried out with the help of an FT-IR (Fourier-Transform infrared) spectrometer. Fixed bed adsorption breakthrough curves were obtained for n-butane, SO2 and NO2 gases as well as for the reaction products NO, N2O and CO2. The adsorption of SO2 and NO2 on activated carbon was studied both during single- and co-adsorption experiments at 30°C. The activated carbon used exhibited a disadvantage towards NO2 adsorption in that it was partly converted to NO and immediately desorbed as NO. A further reaction to N2O could also be observed. The activated carbon was rapidly altered and lost a notable part of its loading capacity as a result of the presence of water and oxygen(11).

The adsorption characteristics of volatile organic compounds (VOCs) on viscose rayon-based activated carbon fibres (ACFs) were investigated. ACFs with specific surface areas of 640 m2/g and 1460 m2/g were used to adsorb trace volatile organic compounds in nitrogen streams at atmospheric pressure at or near room temperature (25°C and 30°C). The experimental results showed that ACFs with different surface areas exhibited different dynamic adsorption behaviours at or near room temperature(12).

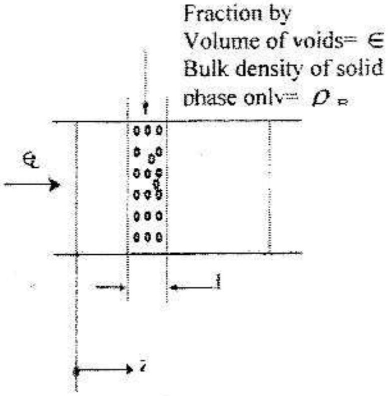
A two-dimensional model that includes radial thermal conduction has been developed to investigate the dispersive effect of heat, including the effect of radial temperature gradient, on adsorption column dynamics. Such effects can be much greater than axial dispersion. The form of the breakthrough curves can well be represented by the isothermal dispersed plug flow model using an appropriately modified dispersion coefficient. When the natural velocity of the temperature wave is lower than that of the concentration wave, leading to an combined wave front, a simple one-dimensional model with heat transfer to the column wall provides a good prediction of the dynamical behaviour. However, when the thermal front leads the concentration wave (pure thermal wave formation), the one-dimensional model over-predicts the dispersion. To obtain an accurate prediction of the dynamic behaviour under these conditions requires the use of the two-dimensional model(13).

The effect of thermal gradients on the dynamic response of an adsorption column has been investigated experimentally by measuring adsorption and desorption break through curves and corresponding temperature profiles (both radial and axial) in a series of adsorption columns with internal diameters ranging from 0.77 to 7.9 cm. The departure from isothermal conditions becomes more pronounced as the column diameter is increased, and this leads to the corresponding broadening of the experimental breakthrough curves(14).

1.3 Dynamic process

1.3.1 The equations of Transport

Referring to Fig below:



A material balance on the fluid and solid phases contained within the section dx shows that

$$\varepsilon \frac{\partial c}{\partial t} + \rho B \frac{\partial q}{\partial t} + \varepsilon v \frac{\partial c}{\partial x} = 0$$

Where *c* and *q* are fluid and solid concentrations, respectively, ε is the fraction of fluid-filled space outside the particles, and ρ_B is the bulk density of solid particles in the tube, including any fluid which the particles may contain in their pores. Note that v is the average fluid velocity in the interstices between the particles; εv is the superficial velocity based on an empty tube. Longitudinal diffusion along the axis of the tube is neglected and "piston flow" of the fluid is assumed.

Equation above must be coupled with another equation representing the behavior of the solid phase alone:

$$\rho_B \frac{\partial q}{\partial t} = kaF(c,q)$$

this equation expresses the rate of addition of solute to the solid phase in terms of the interphase mass-transfer coefficient, *ka*, and a driving force, *F(q,c)*, to be selected. Following the procedure used for packed columns operating at steady state, *k* is based on a unit of exterior particle surface and *a* is the total surface in a unit volume of packed space.

1.3.2 Dynamic model

Process dynamics may be simply defined as the time dependent behavior of a process. The dynamic response of a process is the way in which one or more of the variables associated with a processing a unit changes during the period of time following a change in one of the conditions affecting the process .A plant operator makes changes from time to in various input variables such as feed – flow rate and feed concentration, from one operating level to a new level. These change can be either instantaneous or gradual, the result is a step response data which are often easily obtained be merely recording the variable of interest for a few hours or days during plant operation.

To analysis the frequency response from which the dynamics characteristics of the process were established as, transfer function, gain, time delay….etc. In general, the transfer function can be represented into laplace domain as follows:

$$G(S) = \frac{\text{Output variable change}}{\text{input variable change}}$$

or

$$G(S) = \frac{X(S)}{Q(S)} \qquad \text{...........(1)}$$

Where Q: input variable change, X: output variable change

Referring to laplace transfer = $\int_{0}^{t} f(t)e^{-st}dt$

So that, $X(S) = \int_{0}^{t} X(t)e^{-st}dt$

$$Q(S) = \int_{0}^{t} Q(t)e^{-st}dt$$

From studying and establishing the dynamics characteristics of the adsorber one can design an accurate automatic (on-line) control to operate the process in desired conditions.

2. Experimental arrangement and procedure:

2.1 Materials

2.1.1 Adsorbate

Butanol ($CH_3CH_2CH_2CH_2OH$) Ethanol (CH_3CH_2OH) were used as adsorbate because of their industrial importance and harmful effect in water, it's properties are listed in table (1).

Table (1)
Properties of adsorbates

Properties	Ethanol	Butanol
Solubility at 293 K (g/100 gH_2O)	∞	7.7
Molecular weight	46.07	74.12
Boiling point (K)	324.6	390

2.1.2 Adsorbent

Activated carbon (supplied by the Northen oil company) was used as adsorbent, it's. properties are listed in table (2).

Table (2) Physical properties of activated carbon

Pellet Diameter	1.5 mm
Bulk density	0.45×10^3 Kg/m^3
Particle density	1.4×10^3 Kg/m^3
Internal porosity	0.46
Surface area	1150×10^3 m^2/Kg

2.2 Experimental work column system.

Nine runs were conducted with activated carbon. Three runs were carried out at various initial concentration, three runs were carried out in the unsteady state step change in the initial concentration for various condition. Three run were carried out in the unsteady state step change in flow rate for various condition.

Table (3) shows the column system experimental data.

Tables (4a, 4b, 4c) show the layout of the experiment.

2.3 Equipments

A small scale pilot plant of adsorber was constructed to determine the column characteristic of the adsorption system. A schematic representation of the experimental arrangement is shown in fig (1). A glass Q.V.F. column was used (1.5×10^{-2} m) internal diameter. The activated carbon bed was confined in the column by perforated plate. Three thermocouples were located at different positions along the central axis of the adsorption column. Heating tape is used and a thick glass – wool tape was used as an insulator. Two Q.V.F. spherical containers were used as storage reservoirs.

Flow rate were measured by one rotameter. The type of rotameter (Lab – crest Q.V.F. and PCO meter tube) range (0 – 0.54 m^3 / hr) and (0-1 m^3 / hr) of water. The solution was pumped from the feed container through the carbon bed by means of a centrifugal pump.

The specification of the pump are:

1. maximum flow rate = 17600 L/hr.
2. power = 80, 110, 125 watt.
3. Rotational speed was used to reduced the flow rate to the desired quantities. A three way valves was used for air vent before the inlet of the column.

2.4 Experimental procedure.

The solution with the desired concentration of solutes (Ethanol, Butanol) was prepared by using distilled water in the feed container, the three way valve was opened the vent direction (not to the column). The solution was pumped through the rotameter to vent opening for two minutes to allow all bubbles to be moved out. The desired value of the flow rate was controlled by the needle valve, the direction of the three way value was converted to the column which contained the bed of activated carbon.

For the unsteady state step change runs, the container (A) was filled with aqueous solution of solute concentration (50 Kg/m^3 for each component). The container (B) was filled with the aqueous solution of solute concentration (60 Kg/m^3) for each component, after 10 min the three – way valve was turned to change the feed concentration from 50 Kg/m^3 to 60 Kg/m^3.

For the unsteady state step change in flow rate runs, after 10 min the flow rate was changed by the needle valve.

Every 20 minutes, (25 ml) of the sample was taken from the outlet of the column until the equilibrium state was reached.

Gas liquid chromatography (G.L.C.) with flame ionization detector system using the direct injection of the aqueous solution used to analyze the samples.

2.5 Analysis system.

The equilibrium concentration of each of the studied solution was determind by gas liquid chromatography (Pye unicam Ltd) equipped with a flame ionization detector (F.I.D.) and glass column 1.5 m in length and 4 mm O.d.

The column was packed with chromosorb WHP (100 – 120) mesh coated with 3% ov – 101 stationary phase.

Hydrogen was applied by means of hydrogen generator (by Unicam Cambrige England) to be used in (F.I.D.) detector to create the flam by burning with air. Dried compressed air was supplied from a cylinder. Nitrogen with 99.9% purity was used as a carrier gas. The column temperature was held at 70 ˚C.

The detector and injector temperature were maintained at 180 ˚C. flow rates of N2, H2 and air were 20,20 and 300 l/min., respectively.

A suitable amount of the aqueous solution (2l) was injected into GLC unit.

The signal generated by the detector was presented from the area under the curve by minigrator (Ar 5 I series recorders) calibration of (G.L.C.) was made by the injection of a known concentration sample in (G.L.C.), the area under the curve of the known sample was recorded.

From the comparison of the area under the curve of the known sample with the area under the curve of the unknown sample, the concentration of the unknown sample was determined.

3. Results and Discussions:

3.1 Effect of solute concentration

a- Three experiments (Table (4a)) were carried out at different Ethanol and Butanol concentration $(25,50,100) \times 10^{-3}$ kg / m^3 respectively,it shows that the amount adsorbed of Ethanol and Butanol increased with the increasing of influent concentration because at low concentration only external mass transfer resistance was rate limiting.

b- The total quantity of Butanol removed from solution is greater than that of the total quantity of Ethanol because the solubility of Butanol is less than the solubility of Ethanol and the molecular weight of Butanol is more than molecular weight of Ethanol.

c- The dynamics behavior of the fixed bed adsorber is shown by set of experiments. The experiments results of the responses in the outlet concentration of aqueous to a step change in feed concentration of (Ethanol and Butanol) and step change in feed flow rate used at different initial conditions (concentration flow rate). The system responses were studied in both time and frequency domains. A Matlab program used to analyze the experimental data from adsorber and to predict the transient response. A computer program is given in appendix (A).

3.2 Effect of concentration.

Time Domain

The system responses to a step change (20%) in feed concentration for both Ethanol and Butanol at different flow rate shown in figs (2&3). It can be seen that as the flow rate increases the rate of adsorption and capacity of the activated carbon decreases.

To represent the dynamic process model, two transfer function can be drawn using:-

a- Bode diagram method.

b- Process Reaction Curve (PRC) method.

The best transfer function represents the adsorber for Ethanol is first order (lead and lag) system.

$$G(s)=\frac{K_p(\tau_2 S+1)}{(\tau_1 S+1)}$$

The numerical values of Kp, τ_1 and τ_2 at different flow rates are shown in Table (5).

The best transfer function represents the adsorber for Butanol is second order (lead and two lags) system

$$G(s)=\frac{K_p(\tau_3 S+1)}{(\tau_1 S+1)(\tau_2 S+1)}$$

The numerical values of Kp, τ_1, τ_2 and τ_3 at different flow rates are shown in Table (5), where the transfer function obtained by PRC.method is first order with dead time.

$$G(s)=\frac{K_p e^{\tau_d S}}{(\tau_p S+1)}$$

The values of Kp, τ_d and td are calculated from the process reaction curve and shown in Table (5). A tangent is drawn to the curve at the point of maximum inflection then:-

td: the intercept of this tangent on the abscissa to the original steady state value

$$K_p = \frac{B}{A} = \frac{\text{Output (at steady state)}}{\text{Input (at steady state)}}$$

Where

Kp: is a static gain.

$$\text{and } \tau_p = \frac{B}{S}$$

where S is the slop of the tangent.

Frequency Domain

To study the behavior of the adsorber, frequency analysis technique was used namely bode diagram.

Figures (6 & 7) show bode plot for experimental data positive step change in feed concentration.

By analysis of bode plot, first order lead with lag transfer function were obtained to represent the adsorber for Ethanol and second order (lead and two lags) transfer function were obtained for Butanol.

The numerical values of Kp, τ_1 and τ_2 are shown in Table (5).

3.3 Effect of flow rate

Time Domain

The system responses to a step change in flow rate (10%)for both Ethanol and Butanol are shown in figs(4&5).

The best transfer function represents the adsorber for Ethanol is first order and for Butanol the transfer function is second order (lead &two lags).

The numerical values Kp, τ_1, τ_2 and τ_3 for positive step change are shown in Table (6).

Frequency Domain

Figures (8,9) show bode plot for experimental data at positive step change (10%) in flow rates.

From these figures the transfer function obtained is first order (lead and lag) for Ethanol. But for Butanol, the transfer function is second order (lead & two lags).

4. Conclusion

The present work involves studying of dynamic behavior of adsorber from experimental work using Matlab Program.

The following conclusion have been made from the result obtained:

1. There is a general tendency of increase in adsorption capacity with increase in

moleculer weight, low solubilities and low polarity so adsorption was found to proceed in order Butanol > Ethanol.

2. The capacity of activated carbon increased with increasing influent concentration and increases with decreasing the flow rate.
3. The transfer function represents the adsorber for step change in feed concentration and flow rate for Ethanol is first order (lead and lag) system which is

$$G(s) = \frac{K_p(\tau_2 S + 1)}{(\tau_1 S + 1)}$$

4. The transfer function represents the adsorber for step change in feed concentration and flow rate for Butanol is second order (lead and two lag), which is

$$G(s) = \frac{K_p(\tau_3 S + 1)}{(\tau_1 S + 1)(\tau_2 S + 1)}$$

References

1. Farhadpour, F. A. and Awang Bono, Chemical Engineering and processing Vol. 35 (1996) p. 141-155.
2. Thurner, F. and Stetz, M., International chemical Engineering, Vol. 30, No. 1, p. 36, 1990.
3. Weber W. J., Physicochemical processing for water quantity control, by John Wiley & Sons, 1972.
4. Cheremisionoff, P. N. and Ellerbusch, F., "Carbon Adsorption hand book", by Ann Arbor science publisher, Inc, 1978.
5. Martin, R. J. and Al-Bahrani, K. S., water research, Vol. 11, p.991, 1977.
6. Stenzel, M. H., Chemical Engineering progress, p. 36, April 1993.
7. C. Boyadjiev , "The Purification of Gases Containing Impurities of Small Concentration " Hung. J. Ind. Chem., Vol. 30, 81-160, 2002
8. Jufang Wu, Zili Xie, Kunmin Guo and Ola, "Measurement and Prediction of the Adsorption of Binary Mixtures of Organic Vapours on Activated Carbon " Adsorption Science and Technology.
9. G. M. Førland, T. Rahman and H. Høiland, "Adsorption of Sodium Dodecyl Sulfate and Butanol onto Acidic and Basic Alumina "J. Colloid Interface Sci..

10. G. M. Førland, K. J. Børve, H. Høiland and A. Skauge, "Adsorption of Short Chain Alcohols from Decane Solutions onto Kaolinite " J. Colloid Interface Sci.,171,261-269,1995.
11. Falk Ahnert and Wolfgang Heschel, "Multicomponent Adsorption of Butane, NO2 and SO2 on Activated Carbon ",Adsorption Science and Technology, Vol. 20 No.4
12. Zheng-Hong Huang, Feiyu Kang, Yong-Ping Zheng, Jun-Bing Yang and Kai-Ming Liang "Asorption Characteristics of Trace Volatile Organic Compounds on Activated Carbon Fibres at Room Temperature", Vol. 20 No.5.
13. S. Farooq, D.M. Ruthven "Heat Effects of the Adsorption Column Dynamics. 1. Comparision of One and two–dimensional models", Ind. Eng. Chem. Res. 29, 1076-1084, 1990.
14. S. Farooq, D.M. Ruthven "Heat Effects of the Adsorption Column Dynamics. 2. Experimental validation of the one-dimensional model", Ind. Eng. Chem. Res. 29, 1084-1090", 1990.

Table (3) column system experimental data

Exp. No.	Co × 10^3 Kg/m^3	Temp. K.	Flow rate Q×10^6 m^3/s	Bed depth m×10^2	M×10^3 Kg	Observation
1	25	318	2.0	6	4.01	Variable concentration
2	50	318	2.0	6	4.02	
3	100	318	2.0	6	4.0	
4	50	318	1.5	6	4.0	Multicomponent variable step change in feed conc. 20%
5	50	318	2.0	6	4.01	
6	50	318	2.5	6	4.01	
7	50	318	2.5	6	4.01	Multicomponent variable flow rate step change in flow rate 10%
8	50	318	2.0	6	4.0	
9	50	318	1.5	6	4.0	

Table (4a) the layout of initial variable concentration

Time$\times10^{-3}$ sec.	25×10^{-3} Kg/m^3		50×10^{-3} Kg/m^3		100×10^{-3} Kg/m^3	
	CE	CB	CE	CB	CE	CB
0.6	2	1.0	6	4	19	16
1.2	3	1.2	7	5	22	17
2.4	4	1.5	8	6	28	18
3.6	5	2.0	10	7	35	30
4.8	6	2.2	15	10	43	38
6.0	7	2.5	24	18	58	50
7.2	8	4.0	33	28	78	65
8.4	16	12.0	40	35	88	76
9.6	20	16.0	44	38	94	82
10.8	23	17.0	45	41	95	84
12	23.1	17.0	45.5	41	95	84.1

	CoE$\times10^3$	CoB$\times10^3$	d$\times10^2$ m	Q$\times10^6$ m^3/s	Z$\times10^2$ m	T K	M$\times10^2$	qE$\times10^3$	qB$\times10^3$
1	25	25	1.5	2	6	318	4.01	11.4	47.9
2	50	50	1.5	2	6	318	4.02	26.9	53.7
3	100	100	1.5	2	6	318	4.0	30.0	95.4

Table (4b) the layout of component variable concentration step change

Time$\times10^{-3}$ sec.	Q=2.5×10^{-6} m^3/sec		Q=2×10^{-6} m^3/sec		Q=1.5×10^{-6} m^3/sec	
	CE	CB	CE	CB	CE	CB
0.6	11	3.5	7	2	5	1
1.2	20	5	15	3	10	2
1.8	29	7	22	5	15	2.3
2.4	35	11	27	6	19.5	2.6
3.0	38	17	30	7.5	22.5	3
3.6	42	22	34	10.5	27	4
4.2	45	26	36	12	29	6
4.8	47.5	34	37	17	30	9
5.4	50	39	40	20	31.5	12.5
6.0	52	43	41.5	24	32.6	16

7.2	54	47	43.5	32	35	26
7.8	55	50	44.5	36.5	35.5	28
8.4	56	51	45.6	38	36	30
9.0	56.5	52	46	40	36.5	32
9.6	57	53	46.5	41	37	32
10.2	57.6	54	47.2	42	37.5	32.5
10.8	58	54.5	47.5	42	38	33
11.4	58	54.5	47.5	42	38	33
12.0	58	54.5	47.5	42	38	33

	$CoE \times 10^3$	$CoB \times 10^3$	$d \times 10^2$ m	$Q \times 10^6$ m^3/s	$Z \times 10^2$ m	Temp K	$M \times 10^3$	$qE \times 10^3$	$qB \times 10^3$
1	60	60	1.5	1.5	6	318	4	14.9	41.1
2	60	60	1.5	2	6	318	4.01	74.8	107.7
3	60	60	1.5	2.5	6	318	4.01	99	121.5

Table (4c) the layout of component variable flow rate step change

$Time \times 10^{-3}$ sec.	$Q=2.5 \times 10^{-4}$ m^3/sec		$Q=2 \times 10^{-4}$ m^3/sec		$Q=1.5 \times 10^{-4}$ m^3/sec	
	CE	CB	CE	CB	CE	CB
0.6	7	6	4	2.2	3	1
1.2	18.1	13.8	10.1	4	7.2	2
1.8	24.5	16.4	15.5	9.5	10.1	4
2.4	29.2	17.0	20.5	13.0	14.5	4.5
3.0	33	21	23.5	16	17.0	5.0
3.6	36.5	24	26	20	20	7
4.2	39.5	28	28.5	22	22	9
4.8	41	32	31	24	23	13

5.4	42	35	33	26	24	15
6.0	43	37	34	29	26	18.5
7.2	45	41	37	32	27	22
7.8	45.5	43	37	33	28	23
8.4	46.0	44	37	34	28	24
9.0	46.1	44	37.5	34.5	29	24.2
9.6	46.1	44.2	38	34.7	29.5	24.5
10.2	46.2	44.3	38.5	35	29.5	24.7
10.8	46.2	44.5	39.0	35	30	25
11.4	46.2	44.5	39.0	35	30	25
12.0	46.2	44.5	39.0	35	30	25

	$CoE\times10^3$	$CoB\times10^3$	$d\times10^2$ m	$Q\times10^6$ m^3/s	$Z\times10^2$ m	Temp K	$M\times10^3$	$qE\times10^3$	$qB\times10^3$
1	50	50	1.5	2.5	6	318	4.01	28.4	41.1
2	50	50	1.5	2	6	318	4.0	66	90
3	50	50	1.5	1.5	6	318	4.0	90	112.5

Table (5) parameters of transfer function for step change (20%) in feed concentration

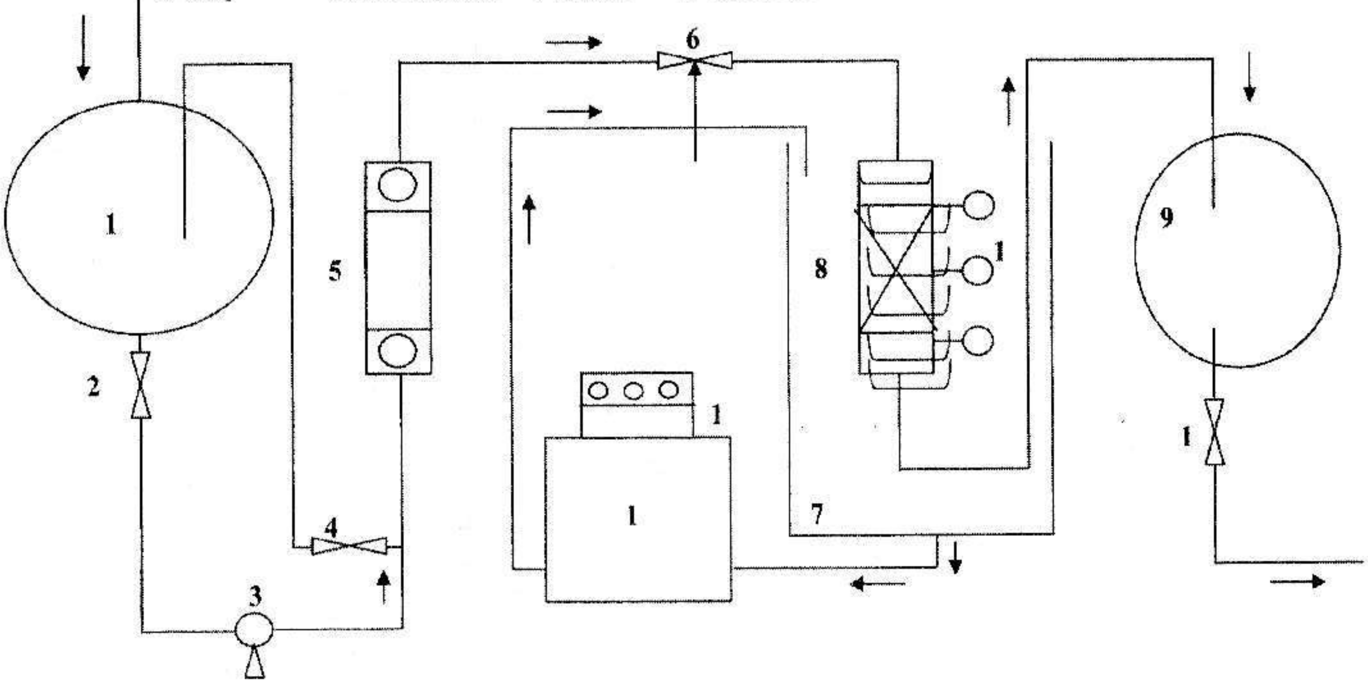
Experiments		Bode method				PRC method		
Parameters		Kp	τ_1	τ_2	τ_3	Kp	τ_p	td
Ethanol	2.5	13.7	1032.8	2042.1		4.8	1066.6	10
	2.0	10.2	1021.9	2032		4.1	1025.0	7.0
	1.5	8.2	999.5	1869.7		3.4	994.73	5.0
Butanol	2.5	20.6	369.2	720.4	705.8	5.2	371.42	10.0
	2.0	17.3	420.7	850.1	820.4	4.0	475.61	60.0
	1.5	9.2	780.12	1600.5	1570.5	3.4	822.56	100.0

Table (6) parameters of transfer function for step change (10%) in flow rate

Experiments		Bode method				PRC method		
Parameters		Kp	τ_1	τ_2	τ_3	Kp	τ_p	td
Ethanol	9.5	45	1046.8	2200.6		38	1085.71	12
	9.0	40	1058.9	2120.3		35	1060.60	8
	1.5	36	331.4	680.4		27	337.5	6
Butanol	2.5	44	1129.3	2300.2	2150	37	1233.33	20
	2.0	41	1121.8	2000.9	1860.6	33	1178.57	75
	1.5	30	289.2	620.1	602.4	18	300.6	115

Fig (1) Schematic Diagram of Experimental Apparatus

1- Feeder
2- Needle valve
3- Pump
4- Valve
5- Rotameter
6- Three way valve
7- Container
8- Column
9- Receiver
10- Valve
11- Water bath
12- Thermostate
13- Temperature Gage



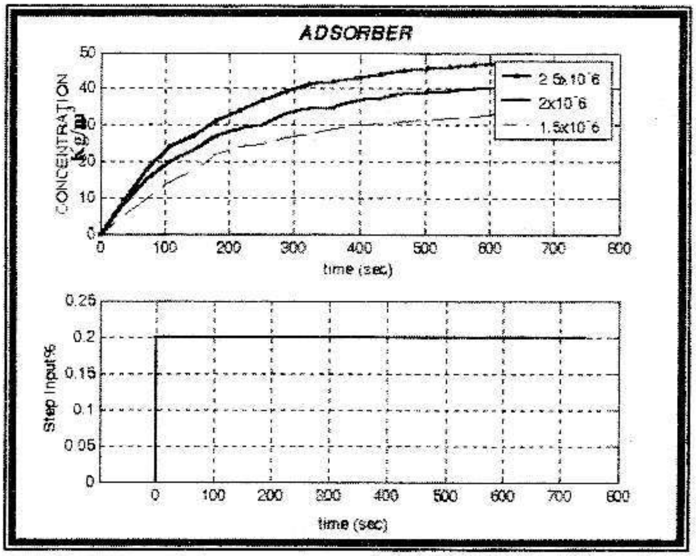


Fig (2) outlet concentration responses of Ethanol to step change in feed concentration (20%) for different flow rate

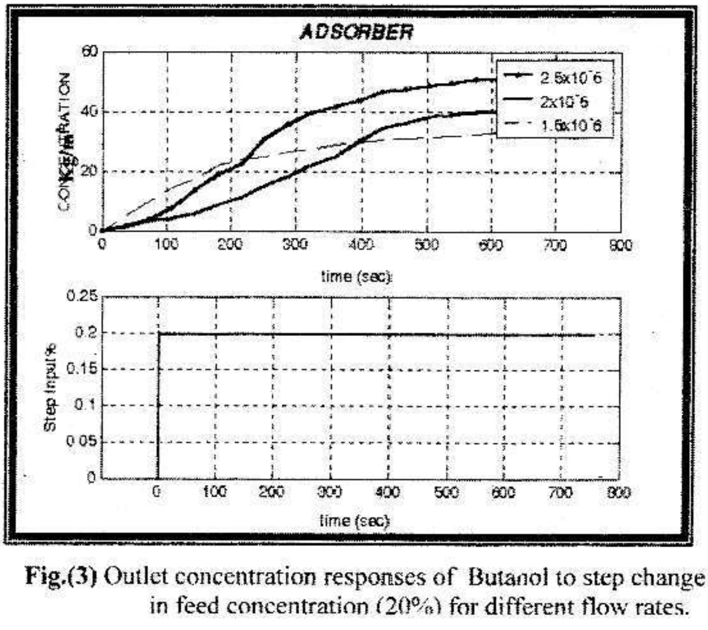


Fig.(3) Outlet concentration responses of Butanol to step change in feed concentration (20%) for different flow rates.

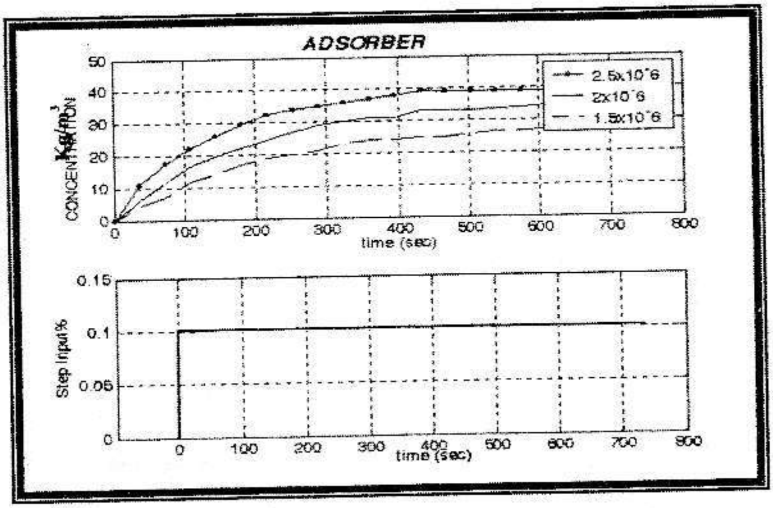


Fig.(4) Outlet concentration responses of Ethanol to step change in flow rate

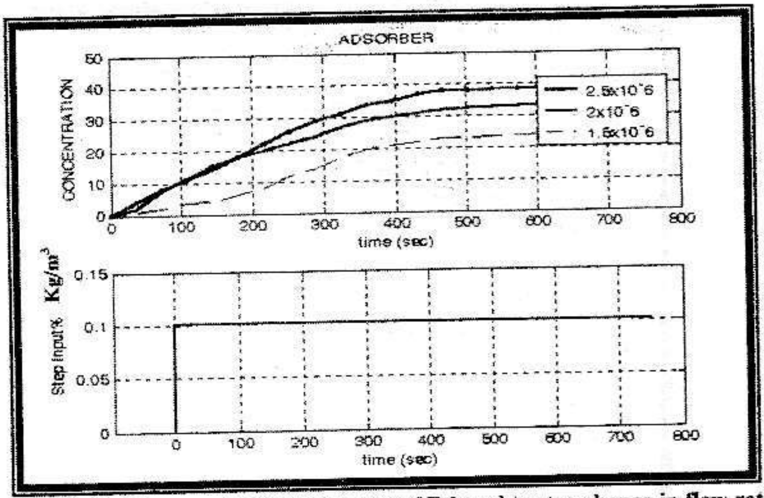


Fig.(5) Outlet concentration responses of Ethanol to step change in flow rate

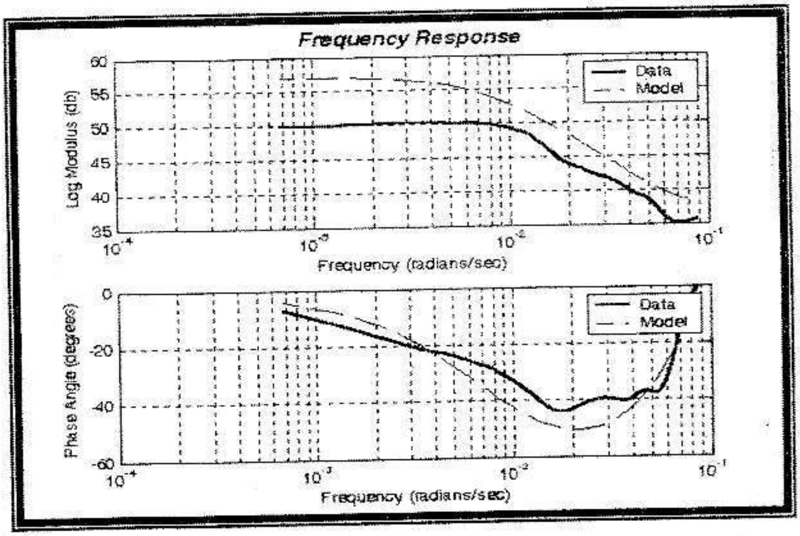


Fig.(6) Bode diagram of outlet concentration responses of Ethanol to step change in feed concentration (20%) for different flow rates.

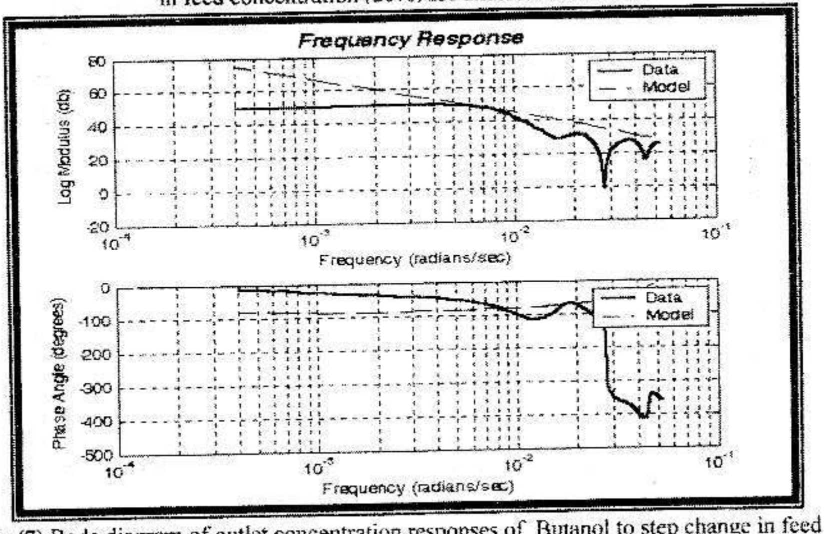


Fig.(7) Bode diagram of outlet concentration responses of Butanol to step change in feed concentration (20%) for different flow rates.

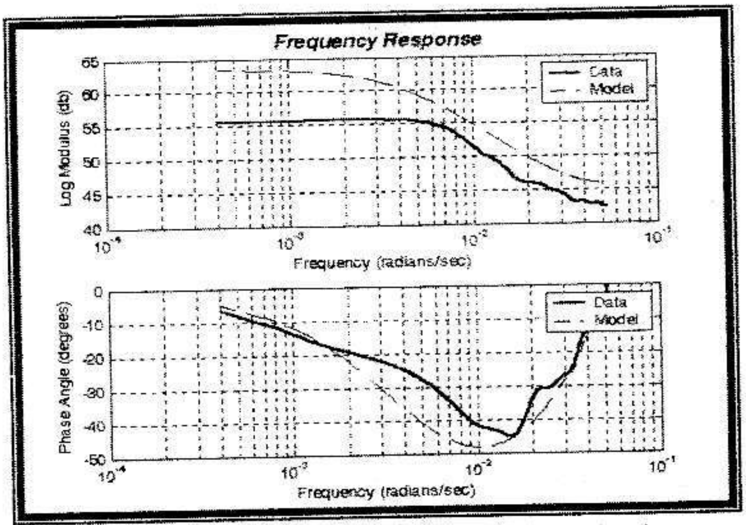


Fig.(8) Bode diagram of outlet concentration responses of Ethanol to step change in flow rate (10%).

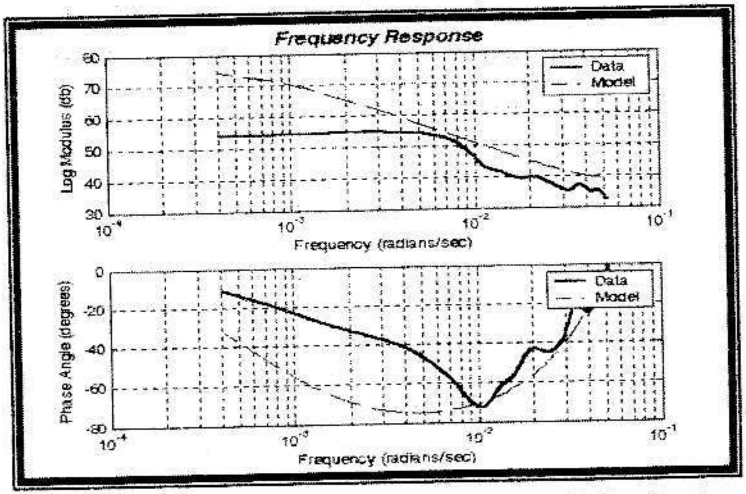


Fig.(9) Bode diagram of outlet concentration responses of Ethanol to step change in flow rate (10%).

Appendix A
Frequency Response Program

```
t=[0;.60;1.20;1.80;2.40;3.00:3.60;4.20;4.80;5.40;6.00;6.60:7.20;7.80;8.40;9.00;9.60;10.20;
10.80;11.40;12];
CONC1=[7;18.1;24.5;29.2;33;36.5;39.5;41;42:43;44;45;46.5;46;46.1;46.1;46.2;46.2;46.2;
46.2;46.2];
CONC2=[4;10.1;15.5;20.5;23.5;26;28.5;31;33;34;35;35;37;37;37;37.5;38;38.5;39;39;39];
CONC3=[3;7.2;10.1;14.5:17;20;22;23;24;26;27;27;28;28;29;29.5;29.5;30;30;30;30];
s=[0;.1;.1;.1;.1;.1;.1;.1;.1;.1;.1;.1;.1;.1:.1;.1;.1;.1;.1;.1;.1];
CONC1=(CONC1-7);
CONC2=(CONC2-4);
CONC3=(CONC3-3);
t=t*60;
t=t-t(1);
clf
subplot(211)
plot(t,CONC1,'.-',t.CONC2,'-'.t,CONC3,'--')
grid
legend ('2.5x10^-6','2x10^-6','1.5x10^-6')
title('ADDSORBER  ')
xlabel('time (sec)')
ylabel('CONCENTRATION')
subplot(212)
plot(t,s)
grid
xlabel('time (sec)')
ylabel('Step Input%')
pause
y=detrend(CONC1);
u=detrend(s);
z=[y u];
nu=length(u);
w=[];
ts=60;
g=spa(z,20,w,[],ts)
[w,mag,phase]=getff(g);
db=20*log10(mag);
na=1;
nb=2;
nk=0;
z=[y u];
th=arx(z,[na nb nk]);
```

```
ts=60;
th=sett(th.ts);
gmodel=trf(th,1,w);
[w,magmodel,phasemodel]=getff(gmodel);
db=20*log10(mag);
dbmodel=21*log10(magmodel);
clf
subplot(211)
semilogx(w,db,'-',w,dbmodel,'--')
title('Frequency Response')
grid
legend('Data','Model')
xlabel('Frequency (radians/sec)')
ylabel('Log Modulus (db)')
subplot(212)
semilogx(w,phase,'-',w,phasemodel,'--')
grid
legend('Data','Model')
xlabel('Frequency (radians/sec)')
ylabel('Phase Angle (degrees)')
pause
variance=th(1,1)
fpe=th(2,1)
a1=th(3,1)
b1=th(3,na+1)
pause
tauo=-ts/log(-a1)
kp=b1/(1+a1);
pause
ycalc=idsim(u,th);
clf
plot(t,y,'-',t,ycalc,'-.')
legend('Data','Model')
title ('Data versus First-Order Model Predictions (d=16 sec. )')
xlabel ('Time (seconds)')
ylabel ('Output')
grid
```