Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

THE REMOVAL OF FURFURAL FROM WATER BY ADSORPTION WITH POLYMERIC RESINS

P. Gupta[a]; A. Nanoti[a]; M. O. Garg[a]; A. N. Goswami[a]
[a] Indian Institute of Petroleum, Dehradun, India

To cite this Article Gupta, P. , Nanoti, A. , Garg, M. O. and Goswami, A. N.(2001) 'THE REMOVAL OF FURFURAL FROM WATER BY ADSORPTION WITH POLYMERIC RESINS', Separation Science and Technology, 36: 13, 2835 — 2844
To link to this Article: DOI: 10.1081/SS-100107632
URL: http://dx.doi.org/10.1081/SS-100107632

SEPARATION SCIENCE AND TECHNOLOGY, 36(13), 2835–2844 (2001)

THE REMOVAL OF FURFURAL FROM WATER BY ADSORPTION WITH POLYMERIC RESINS

P. Gupta, A. Nanoti, M. O. Garg, and A. N. Goswami*

Indian Institute of Petroleum, Dehradun 248005, India

ABSTRACT

The removal of furfural from water by adsorption on a polymeric resin XAD-4 was studied. Equilibrium isotherm measurements were made and column dynamic data collected under various sets of operating conditions. The axial-dispersed plug-flow model was used to simulate the experimental data. The linear driving force parameters required in these simulations were determined independently of the column measurements, providing a more versatile simulation model. The model predicts the breakthrough curves with a fair degree of accuracy.

INTRODUCTION

Furfural is a polar solvent that is used extensively for extraction in lube-refining operations of the petroleum industry (1). Furfural preferentially extracts the undesirable aromatics from the raw lube distillates thereby improving the viscosity-temperature characteristics and oxidation stability of the base stock. Furfural extraction units experience furfural loss in the effluent water streams.

---

*Corresponding author. E-mail: goswami@iip.res.in

Apart from being an environmental pollution problem, this leakage also constitutes a sizable economic loss because the lost solvent must be replaced. This loss is especially significant in large lube units, which may lose up to 2% (wt) furfural in effluent water streams. The recovery of furfural from aqueous wastes is also of importance in the paper industry because furfural is a by-product of wood decomposition (2).

While solvent extraction may be used to recover furfural from wastewater, constraints affect the ease of solvent recovery and solvent solubility in the water stream. Adsorptive separations are ideally suited for recovery/removal of pollutants at low levels in wastewater streams. Polymeric resin adsorbents offer several advantages, including stability, adsorption capacity for organic materials, and ease of regeneration (3).

The present study is an investigation on the use of a polymeric resin adsorbent to remove furfural from water. The experiments covered collection of equilibrium and column dynamics data. The experimental data were simulated by a mathematical model.

EXPERIMENTAL

Materials Used

The polymeric resin XAD-4 from M/s Rohm and Haas Ltd (Lyon, France)was used in the experiments. The physical characteristics of this resin are given in Table 1.

The furfural was from M/s BDH (India) Ltd. The furfural was distilled under vacuum and the 154°–156° cut was collected for use. The physical properties are also given in Table 1.

Table 1. Properties of Materials Used

Adsorbent XAD-4	
Type	Polymeric Resin
Surface area (m^2/g)	700
Porosity	0.5
Pore envelope (nm)	5.5–8.0
Moisture (%)	44–50
Adsorbate, Furfural	
Boiling point (°C)	161.5
Density (kg/m^3)	1.160
Refractive index (20°C)	1.5260

Equilibrium Isotherm Measurements

The equilibrium isotherm measurements were made by standard shaker tests in which known weights of resin were agitated with aqueous furfural solutions of known composition in jacketed vessels for 8 hours at 30°C. The temperature was maintained with a thermostatic circulation bath. The samples were then filtered and the furfural content in the filtrate was determined through absorbance at λ_{max} 258.5 nm as determined by a Shimadzu UV Spectrophotometer. The analytical method used for furfural estimation was found to be accurate to within +/− 3% (wt). Furfural uptake by the resin was calculated by the difference of furfural found by spectroscopy in the feed and the filtrate.

Column Breakthrough Measurements

The column breakthrough measurements were also taken at 30°C in a jacketed glass column packed with XAD-4. A metering pump was used for feeding the aqueous furfural solution in an upflow mode. The column effluent from the top was sampled at regular intervals and was analyzed for furfural content as per the UV absorbance method.

After each adsorption experiment, we regenerated the column by pumping acetone from the top and then pumping distilled water into the system to remove the acetone. Duplicate column breakthrough measurements made after several regeneration cycles established that no significant resin adsorption capacity for furfural was lost. The column breakthrough measurements were made at several different flow rates, resin bed heights, and at 2 different furfural-feed concentrations.

MODELING OF FURFURAL ADSORPTION

The axial-dispersed plug-flow model, as described by Raghavan, Hassan, and Ruthven (4) for isothermal trace systems was used in the present study to simulate the experimental data. The model equations that were modified for use with the Langmuir adsorption isotherm are subsequently described.

Adsorption Equilibrium Isotherm

The single-component Langmuir isotherm in dimensionless form is

$$\bar{q} = \frac{\beta\bar{C}}{1 + \beta\bar{C}} \tag{1}$$

where

$$\beta = bC_0 \tag{2}$$

Fluid-Phase Mass Balance

The dimensionless form of the fluid-phase mass balance equation is

$$\frac{\partial \overline{C}}{\partial \tau} = \frac{1}{\mathrm{P_e}} \cdot \frac{\partial^2 \overline{C}}{\partial x^2} - \frac{\partial \overline{C}}{\partial x} - \psi\alpha\left[\frac{\beta\overline{C}}{1 + \beta\overline{C}} - \overline{q}\right] \tag{3}$$

The parameters ψ and α are defined by the following relationships:

$$\psi = \frac{(1 - \varepsilon)}{\varepsilon} \cdot \frac{q_{\mathrm{m}}}{C_0} \tag{4}$$

$$\alpha = \frac{Lk}{u} \tag{5}$$

Resin Particle Mass Balance

The Linear Driving Force model (LDF) (5) was used to describe the uptake by the resin particle, and the dimensionless form of the mass balance for the resin particle is

$$\frac{\partial \overline{q}}{\partial t} = \alpha\left[\frac{\beta\overline{C}}{1 + \beta C} - \overline{q}\right] \tag{6}$$

NUMERICAL SOLUTION

The above equations have been discretized by the method of orthogonal collocation using 6 collocation points and shifted Legendre polynomials (6). The resulting system of ordinary differential equations was solved by a fourth-order Gear algorithm with a variable step-size control strategy (7).

Parameters Used in the Simulation

The relevant column dimensions, resin bed characteristics, and equilibrium isotherm parameters required in the simulations are given in Table 2. The molecular diffusivity of furfural in water was taken from experimental data reported in (8). The LDF mass-transfer parameter, *k*, was calculated by the

Table 2. Parameters Used in Simulation

Parameter	Value
Molecular diffusivity of furfural in water, m^2/s	1.05e–9
Adsorbent particle size, m	0.5e–3
Adsorbent density, kg/m^3	660
Adsorbent voidage	0.51
Fluid viscosity, kg/m·s	1e–3
Fluid density, kg/m^3	980
Bed voidage	0.31
Column lengths, m	0.19 and 0.35
Column diameter, m	0.021
Langmuir constant, b, l/mg	0.000702
Langmuir constant q_m, mg/L	74 549

Gleuckauf relationship (5):

$$k = \frac{15\varepsilon_p}{r^2} \cdot \frac{\overline{D}_m}{\tau_p} \cdot \frac{\overline{C}_0}{q_0} \tag{7}$$

$$\frac{E_Z\rho}{\mu} = \frac{Re}{0.20 + 0.011Re^{0.48}} \tag{8}$$

A tortuousity factor of 3.0 has been used for the resin particle. This value of tortuousity was taken from experimental data reported by Komiyama and Smith (9). The axial diffusivity E_z was calculated by the method of Chung and Wen (10). The column Peclet number was calculated from axial diffusivity as

$$Pe = L\frac{u}{E_z} \tag{9}$$

RESULTS AND DISCUSSION

The experimental equilibrium isotherm data from which the Langmuir constants were extracted are plotted in Fig. 1. The column breakthrough experiments were conducted at flow rates, bed heights, and furfural concentrations as reported in Table 3. The experimentally observed bed volumes of treated water containing < 50 ppm furfural per bed-volume resin are also given in Table 3.

In Figs. 2–4, we show a comparison of the experimental breakthrough curve data obtained under varying conditions with the predictions made with the model described above. The LDF mass-transfer parameter, k, used in these simulations was calculated from Eq. (7) and was found to be 0.0027 s^{-1} for the 5000-ppm furfural feed and 0.0015 s^{-1} for the 1000-ppm furfural feed.

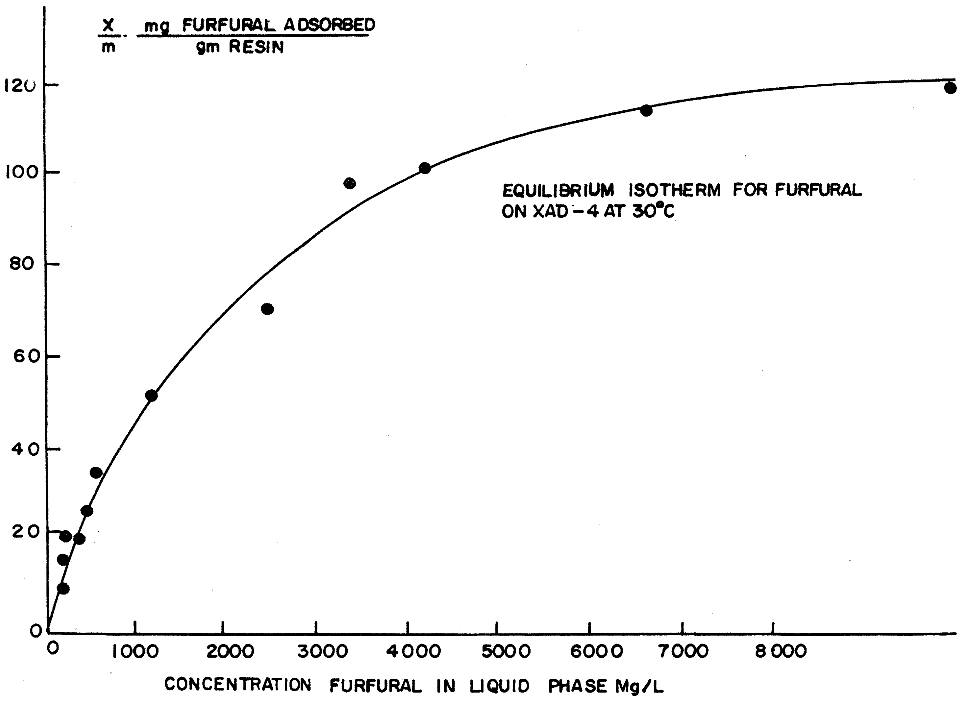

Figure 1. Equilibrium isotherm for furfural adsorption on XAD-4 resin.

The figures show that the model is able to predict the breakthrough curves under varying experimental conditions with a fair degree of accuracy. While the curve-fit of experimental breakthrough data has been used to estimate the LDF parameter (11), in the present study the simulations were carried out with an LDF parameter that had been estimated independently. This improves the versatility of the model.

Table 3. Experimental Data on Furfural Adsorption in Continuous Column

Run No.	Feed Furfural Concentration (ppm)	Flow Rate (mL/min)	Bed Height (cm)	Average Residence Time (min)	Bed Volume Treated
1	5000	10.0	35	12.1	7.1
2	5000	14.0	35	8.6	6.4
3	5000	22.0	35	5.5	5.8
4	5000	25.0	35	4.8	5.5
5	1000	26.0	35	4.7	14.3
6	5000	7.5	19	8.6	6.7

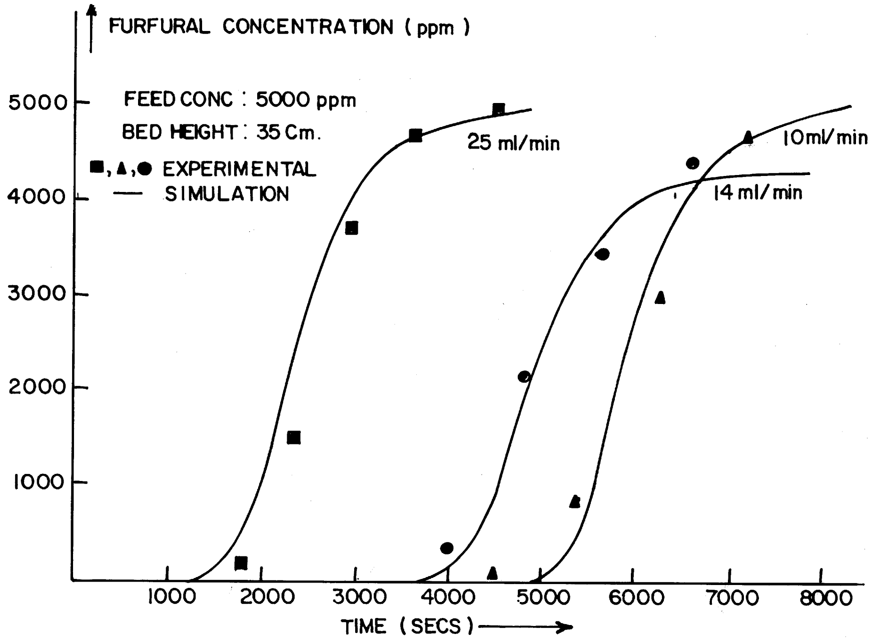

Figure 2. Comparison of experimental and predicted furfural breakthrough data at different feed flow rates.

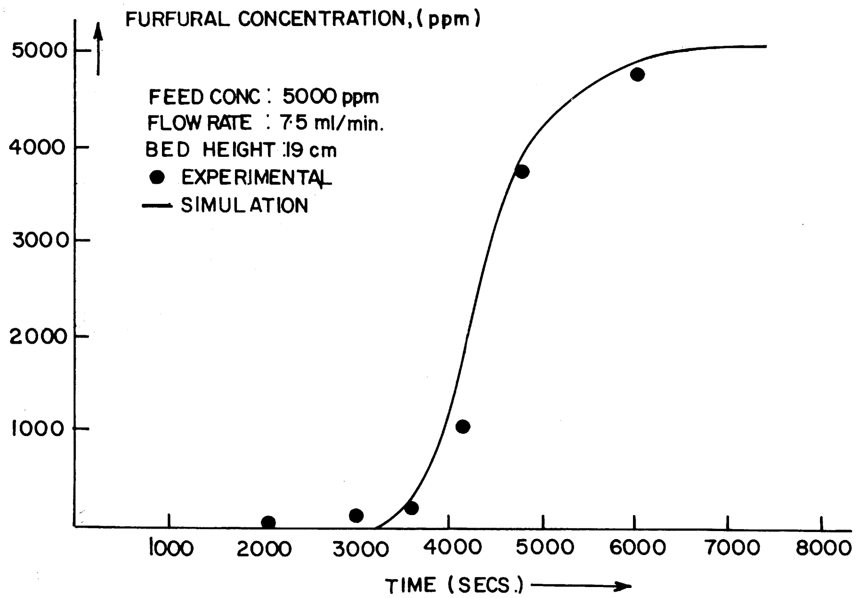

Figure 3. Comparison of experimental and predicted furfural breakthrough data for a 19-cm tall bed.

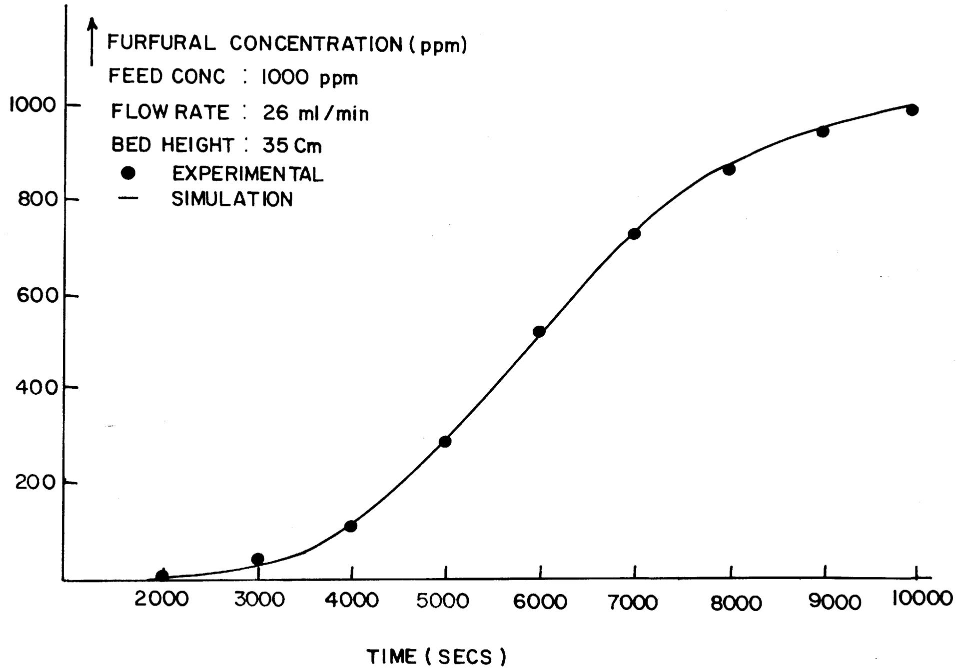

Figure 4. Comparison of experimental and predicted furfural breakthrough data for experiment with a feed furfural concentration of 1000 ppm.

An examination of the data reported in Table 3 indicates that the residence time in the column is more important than fluid velocity in improving furfural removal efficiency. Thus, as the average residence time was decreased (runs 1 to 5), the efficiency dropped; the number of bed volumes of treated water obtained per bed-volume resin decreased. However a comparison of runs 2 and 6 (where bed heights are different but residence time was kept constant by changing the flow rate) shows that increase of fluid velocity had no significant effect; the bed volumes of treated water obtained remained the same. Thus, the uptake of furfural by the resin appears to be controlled by particle diffusion, and the simulations indicate that the particle diffusion process can be satisfactorily modeled by the LDF approach. The same phenomena have been observed in various other applications of resins used for removing trace amounts of substances (12).

CONCLUSION

Furfural can be removed from water by adsorption on polymeric resins. The adsorption isotherm data of furfural on these resins can be represented by the

Langmuir adsorption isotherm. Column breakthrough experiments can be simulated by an axial-dispersed plug-flow model with mass transfer in the resin described by an LDF approximation. The mass transfer and axial dispersion parameters were determined independently of the column measurements. The experimental data indicate that residence time in the adsorption column is more important than fluid velocity in improving adsorption. This result indicates that furfural adsorption in polymeric resins is controlled by particle diffusion rather than by film diffusion.

NOMENCLATURE

b	Langmuir constant (l/mg)
C	fluid phase concentration (mg/L)
$\overline{C}$	dimensionless fluid phase concentration, (C/C_0)
d_p	particle diameter (m)
E_z	axial diffusivity (m^2/s)
k	mass transfer parameter (s^{-1})
L	column length (m)
Pe	Peclet number
q	adsorbed phase concentration (mg/L)
$\overline{q}$	dimensionless adsorbed phase concentration ($= q/q_m$)
q_m	Langmuir constant (mg/L)
Re	Reynolds Number ($=d_p u[\rho/\mu]$)
T	time (s)
u	interstitial velocity (m/s)
x	dimensionless length ($=z/L$)
z	axial distance along column (m)

Greek Symbols

α	parameter defined in Eq. (5)
β	parameter defined in Eq. (2)
ε	bed voidage
ε_p	particle voidage
μ	fluid viscosity ($kg/m \cdot s$)
ρ	fluid density (kg/m^3)
τ	dimensionless time ($= u[t / l]$)
τ_p	particle tortuousity factor
ψ	parameter defined in Eq. (4)

ACKNOWLEDGMENT

The authors would like to express their sincere thanks to Shri S. Mohan for his assistance in the experimental program.

REFERENCES

1. Sankey, B.M.; Gudelis, D.A. Chapter 18.3. In *Handbook of Solvent Extraction*; Lo, T.C., Baird, M.H.I., Hanson, C., Eds.; John Wiley and Sons: New York, 1983; 549.
2. Gamse, T.; Marr, R. The Extraction of Furfural with Carbon Dioxide. Sep. Sci. Technol. **1997,** *32*(1–4), 355.
3. Slejko, Frank L., Ed. Chapter 4. *Adsorption Technology;* Marcel Dekker, Inc: New York and Basel, 1985; 167.
4. Raghavan, N.S.; Hassan, M.M.; Ruthven, D.M. Numerical Simulation of a PSA System. AIChE J. **1985,** *31* (3) 385.
5. Tien, C. *Adsorption Calculations and Modelling;* Butterworth-Heinemann: Boston, 1994; 82.
6. Finlayson, B.A. *Nonlinear Analysis in Chemical Engineering;* McGraw-Hill: New York, 1980; 73.
7. Villadsen, J.; Michelsen, M.L. *The Solution of Differential Equation Models by Polynomial Approximation.* Prentice-Hall: Englewood Cliffs, NJ, 1978; 314.
8. Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. *The Properties of Gases and Liquids;* McGraw-Hill: New York, 1977; 567.
9. Komiyama, H.; Smith, J.M. Intraparticle Mass Transport in Liquid Filled Pores. AIChE J. **1974,** *20* (7), 728.
10. Chung, C.F.; Wen, C.Y. Longitudinal Dispersion of Liquid Flowing Through Fixed and Fluidised Beds.AIChE J. **1968,** *14* (6), 857.
11. Run-Tun, H.; Chen, L.; Shan. H.W. Binary Adsorption in a Fixed Bed Column Packed with Ion Exchange Resin. Sep. Sci. Technol. **1995,** *30* (13) 2731.
12. Studies for Design of Resin Based Process for Sulpholane Clean-Up. IIP DOC No. SPA 5:98. Indian Institute of Petroleum: Dehra Dun, 1998.

Received May 2000
Revised November 2000

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 10:42 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS100107632