

Diffusion kinetics of Furfural adsorption onto Activated Carbon

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Abstract

A range of batch experiments were carried out for the estimation of the key process parameters in adsorption of Furfural from aqueous solution onto activated carbon in fixed-bed adsorber. A batch adsorber model has been used to determine the external mass transfer coefficient (k_f) which equal to 6.24×10^{-5} m/s and diffusion coefficient (D_p) which equal to 9.875×10^{-10} m²/s for the Furfural system. The Langmuir model gave the best fit for the data at constant temperature (30°C). The pore diffusion mathematical model using nonlinear isotherm provides a good description of the adsorption of Furfural onto activated carbon.

Keywords: Adsorption, Batch adsorber, Furfural, Isotherm, pore diffusion, modelling

Introduction

Adsorption techniques are widely used in the field of removing small quantities of pollutant present in large volume of fluid, which can be carried out in batch wise or continuous manner of operation [1, 2, 3, and 4].

The design of single scale adsorption plants is still based on expensive experimental pilot-plant studies because a thorough understanding of process is lacking. The effective application of activated carbon adsorption requires a predictive model to facilitate the development of systematic design procedure [5, 6]. The key parameters for design of the adsorption system such as isotherm constants and mass transfer coefficients are the process parameters that are used for modeling the system for predicting the quality of effluent under a wide range of operating conditions [7].

The rates of adsorption of solute from aqueous and other liquid solutions by porous solid in batch-type system are greatly influenced by the mass transfer resistance outside the particles, diffusion resistance inside the particles, geometry of the pores, type of adsorption isotherm, operating conditions such as initial concentration, pH, temperature, phase ratio, agitation speed and vessels

geometry [8, 9].

Dedrick and Beckmann [10], represented a mathematical model described the amount adsorbed as a function of time for diffusion into sphere particles with a constant effective diffusivity.

Digiano [11], developed adsorption model included the effect of mass transfer both at the external carbon-solution interface and with the carbon pore structure.

Suzuki and Kawazoa [12], developed a simple technique to determine the intraparticle diffusivities of adsorbents from concentration change in an agitated tank. Pore diffusion and rectangular isotherm are assumed to derive the theoretical solution.

Ivars [13], solved numerically a mathematical model for finite bath adsorption of nonlinear isotherm described either by Langmuir or Freundlich type equations. The transport mechanism in the particles is assumed to be pore diffusion, solid diffusion or a combined. The effect of film resistance is included.

The objective of the present research is to estimate the equilibrium and kinetic data of the adsorption of Furfural (Fu) from aqueous solution onto activated carbon. These data are required to solve the mathematical model which includes axial dispersion, film mass transfer, pore diffusion resistance and non-linear isotherms of the

adsorption process in fixed-bed adsorber [7]. For accurate estimation of external mass transfer coefficient, and intraparticle diffusion coefficients for Furfural, the experimental results will be compared with that simulated by the numerical solution of the batch adsorber model.

Modeling of a Multicomponent Batch Adsorber

For batch adsorber, the mathematical model with pore diffusion model (8, 14) is:

- Mass balance in fluid-bulk phase:

$$V_L \frac{dC_b}{dt} + \frac{3W_A}{\rho_p R_p} k_f (C_b - C_{p,r=R_p}) = 0 \quad (1)$$

Where V_L = volume of fluid in the batch adsorber

W_A = mass of activated carbon in the batch adsorber

- Mass balance inside particle phase:

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \rho_p \frac{dq}{dt} = \varepsilon_p D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_p}{\partial r} \right) \quad (2)$$

- Initial and boundary conditions are:

$$t=0; \quad C_b=C_o; \quad C_p=0; \quad q=0 \quad (3)$$

$$r=0; \quad \left(\frac{\partial C_p}{\partial r} \right)_{r=0} = 0; \quad \left(\frac{dq}{dr} \right)_{r=0} = 0 \quad (4)$$

$$r=R_p; \quad \varepsilon_p D_p \left(\frac{\partial C_p}{\partial r} \right)_{r=R_p} = k_f [C_b - C_{p,r=R_p}] \quad (5)$$

In case of applying Langmuir isotherm model:

$$q = \frac{q_m b C_p}{1 + b C_p} \quad (6)$$

Where: C_b and C_p are the solute concentration in the fluid-bulk and particle phase, respectively. Mass transfer to particles suspended in a liquid in turbulent flow, particularly in agitated vessels, has been studied by several investigators [15, 16, 17, 18]. However, these studies have shown a variety of results and have not predicted reliable correlations that are universally applicable [19].

The inability to develop satisfactory correlations may stem from the fact that the flow fields around particles moving freely in the liquid are not only a function of the reactor and impeller geometries and power input, but also the particle shape and particle diameter distribution (20) Sano *et al.* [21] incorporated the effect of particle shape, by introducing the term Φ_c , the Garman's surface factor, and developed the following correlation:

$$Sh = \Phi_c \left(2 + 0.4 Re_m^{1/4} Sc^{1/3} \right) \quad (7)$$

Alexander and Zayas [20] developed the following equations for the particle size fractions with a Sauter mean diameter less than 923 μm (20/25 size).

$$Sh = 0.41 Re_m^{1/4} Sc^{1/3}, \quad \text{for } 10^2 < Re_m < 10^5 \quad (8)$$

$$Sh = 2 + 0.37 Re_m^{1/4} Sc^{1/3}, \quad \text{for } Re_m > 10^5 \quad (9)$$

For particles larger than 923 μm :

$$Sh = 1.60 Re_m^{1/8} Sc^{1/3}, \quad \text{for } 10^2 < Re_m < 10^5 \quad (10)$$

$$Sh = 2 + 1.58 Re_m^{1/8} Sc^{1/3}, \quad \text{for } Re_m > 10^5 \quad (11)$$

Alexander and Zayas found that the external mass transfer coefficient can be expected to vary with the three-fourth power of impeller speed, for particles in the 300 to 900 μm range. For larger particles, k_f is shown to be proportional to $d_p^{-0.5}$, this agrees well with the data and intuitive reasoning provided by Harriot and Vermeulen [22].

The external mass transfer coefficient for the solute adsorbed at certain particle size and optimum agitation speed, can be obtained by the analytical solution for equation 1, where at $t = 0$, $C_{p,r=R_p} = 0$ and $C_b = C_o$, hence:

$$k_f = - \frac{R_p \rho_p V_L}{3W_A t} \ln \left(\frac{C_t}{C_o} \right) \quad (12)$$

Where C_o , C_t are the solute concentration at time zero and time (t) and obtained from the typical concentration decay curve (20).

Experimental concentration-time data are compared to predicted concentration-time profiles for the above batch adsorber model and the best statistical description, used to determine the intraparticle pore diffusion coefficient.

If diffusion into particle is controlled by the surface concentration gradient, equation 2 is replaced by:

$$\frac{\partial q}{\partial t} = D_s \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (13)$$

With the same above procedure the surface coefficient can be obtained.

The bulk-fluid phase and particle equations for the batch adsorber model are first described using the finite element (FE) and the orthogonal collocation (OC) methods, respectively. The resulting ODE system is solved using an existing ODE solver provided by MATLAB v-6.5.

Experimental Work

The granulated activated carbon (GAC) used in the experiments was supplied by Unicarbon, Italian. Its physical properties are supplied by the company and listed in Table 1.

The GAC was sieved into 28/32 mesh with geometric mean diameter of 0.5mm. The GAC was boiled, washed

three times in distilled water, and dried at 110 °C for 24 h, before being used as adsorbent. The aqueous solution of Furfural was prepared using reagent grade. The properties of Furfural are listed in table 2.

Equilibrium Isotherm Experiment

Batch studies were used to obtain the majority of equilibrium data. Solution was prepared containing the desired solute concentration. The experiment was adjusted at the initial pH of 8.1 for Furfural with 0.01 mol/L NaOH and 0.01 mol/L HCl.

100 ml portions of the solution were placed in bottles of 250 ml in volume, containing accurately different weighted amount of activated carbon. The bottles were then placed on a shaker (type B. Baun, Karlkolb) and agitated continuously for 30 hours at 30 °C. The equilibrium concentrations were measured by means of UV-spectrophotometer. At this point the concentration is in equilibrium. The adsorbed amount is then calculated by the following equation:

$$q_e = \frac{V_L(C_o - C_e)}{W_A} \quad (14)$$

The adsorption isotherms were obtained by plotting the weight of the solute adsorbed per unit weight of activated carbon (q_e) against the equilibrium concentration of the solute in the solution (C_e) (23).

Kinetic Experiments

The external mass transfer coefficient k_f and the intraparticle diffusion coefficients were obtained by using a well stirred batch contactor. In this method, a known amount of adsorbent is added to a constant volume of solution. The rate of adsorption of solute was measured by monitoring the solute concentration with time, using UV spectrophotometer.

A 2 liter Pyrex beaker was used fitted with a variable speed (0 – 1000 rpm) electrical mixer with 4-blade stainless steel impeller (Janke and Kunkel, IKA-WERK). The beaker was filled with 1.0 liter of known concentration solution and the agitation started before adding the activated carbon. At time zero, the accurate weight of activated carbon was added. Samples were taken every 10 minute during the experiment for analysis and these samples were returned back to the solution to achieve constant volume.

The necessary dosage of activated carbon to reach an equilibrium concentration of $C/C_o=0.05$ was calculated from isotherm equation and balance equation for Furfural as follow (in case of Langmuir model):

$$W_A = \frac{V_L(C_o - C_e)}{q_e} = \frac{V_L(C_o - C_e)}{\left(\frac{q_m b C_e}{1 + b C_e} \right)} \quad (15)$$

The optimum agitation speed was obtained by repeating the experiments for Furfural with variable speed (600, 700, 800, 900 and 1000 rpm). The optimum agitation speed is the speed needed to achieve $C_e/C_o = 0.05$. The batch experiments were achieved for Furfural at constant temperature (30 °C).

Results and Discussion

Adsorption Isotherm

The adsorption isotherm for Furfural onto activated carbon of size 0.5 mm at 30°C is shown in figures 1.

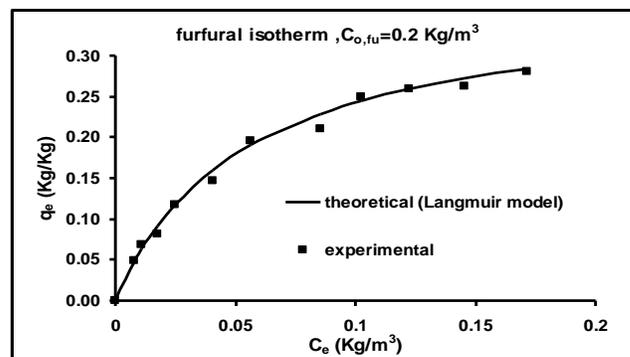


Figure (1) Adsorption isotherm for Furfural onto activated carbon at 303 K

The entire adsorption isotherm displays a nonlinear dependence on the equilibrium concentration. The adsorption data for Furfural fitted by Langmuir model (3), Freundlich model (3), Radke-Prausnitz model (24), Dubinin–Radushkevich model (25), Reddlich-Peterson model (3), and Combination of Langmuir-Freundlich (26). The parameters for each model were obtained from non-linear statistical fit of the equation to the experimental data. All parameters with correlation coefficients are summarized in table 3.

It is clear from figure 1 and table 3 that:

- The equilibrium isotherm for Furfural is of favourable type, for being somewhat convex upward and relatively high activated carbon loading were obtained at low concentration of solute in water.
- The Langmuir model gives the best fit of the experimental data of Furfural.
- The low adsorption capacity of Furfural may be explained by its higher solubility, low molecular weight and low octanol-water coefficient.
- Furfural is a polar solvent and activated carbon is generally regarded to favor the adsorption of non-

polar compounds rather than polar compounds, since pure carbon surface is considered to be non-polar, but in actual practice, some carbon-oxygen complexes are present which render the surface slightly polar (27).

Estimation of Intraparticle Diffusion Coefficient

The intraparticle diffusion coefficient for Fu can be estimated by matching the experimental concentration decay curves at optimum agitation speed with the predicting concentration decay curve, which can be generated by the numerical solution of the batch adsorber model.

First of all it must be tried to use the pore diffusion model for batch adsorber. If no matching between experimental and predicted results then the surface diffusion model must be used.

The estimation of intraparticle diffusion coefficient needs the following steps:

1. Estimation of optimum agitation speed for batch adsorber to reach the needed equilibrium concentration.
2. Estimation of mass transfer coefficient in batch process for Furfural at optimum agitation speed.
3. Numerical solution of batch adsorber model to obtain the intraparticle diffusion coefficient for Furfural.

Optimum Agitation Speed

The typical concentration decay curves of solute in batch experiments were carried on for Furfural at different agitation speeds.

The amounts of activated carbon used for Furfural was calculated for final equilibrium related concentration of $C_e/C_o = 0.05$. Using the Langmuir equation with mass balance in one liter of solution (equation 12), the dose of activated carbon for Furfural is 3.263×10^{-3} kg.

The agitation speeds (600, 700, 800, 900, 1000 rpm) were used as shown in figures 2.

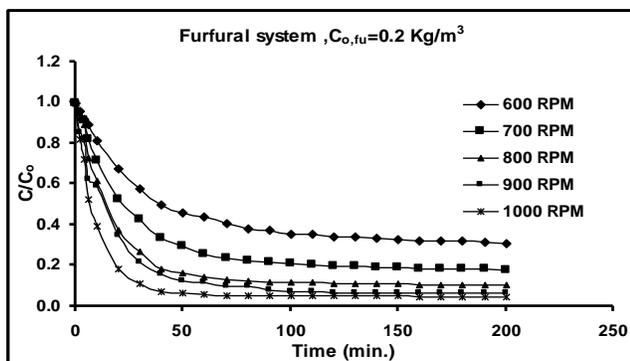


Figure (2) Concentration-time decay curves for Furfural adsorption Onto activated carbon in batch process at different agitation speed

The optimum agitation speed needed to achieve $C_e/C_o = 0.05$ was 900 rpm. It is clear that, if the speed is above 900 rpm, the equilibrium relative concentration is less than 0.05; this is due to pulverization of activated carbon at high speed of agitation.

External Mass Transfer Coefficient in Batch Adsorber

The external mass transfer coefficient in batch adsorber was computed from initial rate data, i.e. from the concentration decay curve of optimum speed and using equation 9.

For accurate estimation of k_f , samples were taken after 2, 4 and 6 minutes and analyzed immediately. The average calculated values k_f for Furfural is 0.624×10^{-4} m/s

Intraparticle Diffusion Coefficient

Intraparticle diffusion coefficients for Furfural was obtained from the numerical solution of equations 1 and 2 with the appropriate initial and boundary condition that describe the film and intraparticle transport mechanisms in batch-wise experiments, using the external mass transfer coefficient estimated in previous section.

The pore diffusion coefficient was derived from the typical concentration decay curve for Furfural by an iterative search technique predicted on the minimization of the difference between experimental and predicted data from pore diffusion model as shown in Figure 3.

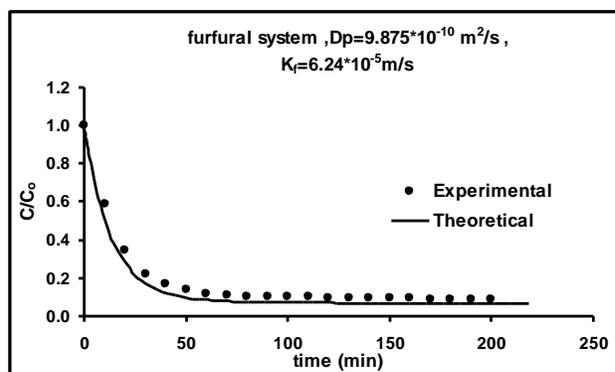


Figure (3) Comparison of the measured concentration-time data with that predicted by pore diffusion model in batch adsorber for Furfural.

It is clear from Figure 3; there was a good matching between experimental and predicted data by using pore diffusion model.

The pore diffusion coefficient for Furfural was 9.875×10^{-10} m²/s with a correlation coefficient of 0.9921.

It is clear from above data that there was a good matching between experimental and predicted data in batch experiment by using pore diffusion model for Furfural. Hence the transfer of Furfural within the activated carbon is controlled by pore diffusion.

The estimated values of isotherm constants, external mass transfer coefficients k_f , and pore diffusion coefficients D_p , were used to solve the mathematical model which describes the adsorption process in fixed-bed adsorber [7].

Conclusions

The concentration decay curves obtained during batch kinetic studies on the adsorption of Furfural on activated carbon were simulated by a combined external film transfer-pore diffusion model. It is clear from above data that there was a good matching between experimental and predicted data in batch experiment by using pore diffusion model for Furfural. Hence the transfer of Furfural within the activated carbon is controlled by pore diffusion.

The estimated values of isotherm constants, external mass transfer coefficients k_f , and pore diffusion coefficients D_p , were used to solve the mathematical model which describes the adsorption process in fixed-bed adsorber [7].

Nomenclature

Symbols	
A_R	Reddlich-Peterson model parameter
B_R	Reddlich-Peterson model parameter
b	Langmuir constant, m ³ /kg
C	Concentration in fluid, kg/m ³
C_o	Initial concentration, kg/m ³
D_p	Pore diffusion coefficient, m ² /s
D_m	Molecular diffusion coefficient, m ² /s
D_s	Surface diffusion coefficient, m ² /s
d_p	Particle diameter, m
Fu	Furfural
F_{RP}	Radk-Prausnitz model parameter
g	Gravitational force (=9.81 m/s ²)
K	Freundlich model parameter
K_{ow}	Partition coefficient for actanol-water, -
K_{RP}	Radk-Prausnitz model parameter

Symbols	
k_f	Fluid to particle mass transfer coefficient, m/s
m_R	Reddlich-Peterson model parameter
N_{RP}	Radk-Prausnitz model parameter
N	Freundlich model parameter
P	Agitation power per unit mass of fluid, W/kg
q_{DR}	Maximum adsorption capacity in the micropore volume (kmole/kg)
q	Internal concentration of solute in particle , kg/kg
q_m	Adsorption equilibrium constant defined by Langmuir equation, kg./kg
Re	Reynolds number $\left(\frac{\rho_w v d_p}{\mu_w} \right), -$
Re_m	Modified Reynolds number $\left(\frac{P d_p^4}{\mu_c^3} \right),$
R_p	Radius of particle, m
R	Radial direction, m
S	Surface area, m ²
Sc	Schmidt number $\left(\frac{\mu_w}{\rho_w D_{m,i}} \right),$
Sh	Sherwood number $\left(\frac{k_{f,i} d_p}{D_{m,i}} \right),$
S_w	Specific surface area, m ² /kg
t	Time, s
V_L	Volume of solution, m ³
W_A	Mass of activated carbon, kg

Greek symbols	
ε_p	Porosity of adsorbent, -
B	Characteristic parameter related to adsorption energy
ϵ	Polanyi adsorption potential
μ_c	Kinematics viscosity, m ² /s
μ_w	Viscosity of water (=0.8937×10 ⁻³ Pa.s)
ρ_p	Particle density, kg/m ³
ρ_s	Solid density, kg/m ³
ρ_w	Density of water, kg/m ³
Φ_c	Carman's surface factor $\left(\frac{6}{\rho_s S_w d_{gm}} \right)$

Subscript	
b	Bulk fluid phase
e	Equilibrium
Fu	Furfural
L	Liquid phase
o	Initial
p	Particle phase

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عباس حميد سليمان، كوثر وعدالله وعمار وعد الله

تم إجراء تجارب من النوع النمطي لإيجاد القيم اللازمة في تصميم عمود ذو الحشوة الثابتة لادمصاص الفورفورال بواسطة الكربون المنشط. تم اقتراح موديل رياضي لمنظومة الامدصاص من النوع النمطي لاحتساب معامل انتقال الكتلة الخارجي (k_f) و معامل الانتشار (D_p) للفورفورال في الكربون المنشط. تبين أن استخدام موديل لانكماير هو الأنسب في وصف عملية الامدصاص عند درجة حرارة ثابتة 30 مئوي حيث وجد ان معامل انتقال الكتلة الخارجي (k_f) يساوي 6.24×10^{-5} m/s و معامل الانتشار للفورفورال في الكربون المنشط (D_p) يساوي 9.875×10^{-10} m²/s، وان استخدام الموديل الرياضي لمنظومة الامدصاص من النوع النمطي والذي يعتمد على وصف الانتشار داخل الكربون المنشط من النوع الفجوي يعطي وصفاً صحيحاً و دقيقاً لعملية ادمصاص الفورفورال على الكربون المنشط.