

## **Modeling and simulation of Dynamic Bio-Ethanol Adsorption**

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### **Abstract**

One of the limiting factors for the production of bio-ethanol from agricultural waste is its cost of recovery after fermentation. Adsorption has been proposed for this separation and an adsorbent screening study has been done previously (Jones et al., 2006). In this study, ethanol adsorption experiments were performed with selected activated carbon adsorbents in an adsorption packed column. A mass transfer model, solved by finite difference method, is proposed to simulate the adsorption of ethanol from solution. The model incorporates three rate controlling steps: external film mass transfer, intra-particle diffusion and adsorption site kinetics. The model is validated with experimental data at the lab-bench scale and used to simulate a large industrial adsorption process. Results indicate that particle size plays a major role in the ethanol mass transfer from the liquid to solid phase. For large particles the diffusion effects during adsorption are more pronounced. The model can be used to represent the experimental data at the lab-bench scale, and it is hypothesized that the model can be used as a useful tool to simulate adsorption mass transfer in large industrial scale operations.

### **Introduction**

The recovery of ethanol from fermentation broth is a major economic limiting step which prevents the wide-spread use of bio-ethanol as a gasoline additive or fuel alternative. While distillation is effective in separating the ethanol from the broth to about 85 %, it is not energy efficient (Pimentel, 2003).

An auxiliary adsorption system for the enhancement of bio-ethanol production is believed to have economic potential. The proposed external adsorption system would treat the bio-reactor effluent following fermentation. The goal of the system is to selectively adsorb ethanol from the solution as it flows through the column. The process is made cyclical by adding parallel columns and alternating between adsorption and desorption cycles. If the adsorbent is highly selective in its preference for ethanol, the desorbed solution could be highly concentrated and thus the downstream energy requirement could be reduced.

To implement the proposed system, it is important to first understand the ethanol mass transfer which takes place between the liquid and the solid phases in the column during the adsorption cycle. In this study, dynamic column

experiments were performed on binary ethanol-water solutions with selected activated carbon adsorbents in order to monitor the mass transfer occurring in the packed column. Adsorption simulation results were compared to the experimental ones.

## Materials and Methods

Solutions were prepared with anhydrous ethyl alcohol (Commercial Alcohols Inc.) and distilled de-ionized water. The adsorbents studied are presented in Table 1 along with some important properties of each adsorbent.

**Table 1.** Materials and Properties

Adsorbent	Company	Surface Area m <sup>2</sup> /g	Particle Size mm
XTRUSORB HP115 - Activated Carbon	Calgon, Mississauga, ON.	1333	6.7, 1.5 *
F 600 – Activated Carbon	Calgon, Mississauga, ON.	1053	1.05

\*Extrudes: (Length, Diameter)

## Breakthrough Experiments – Adsorption/Desorption

Dynamic breakthrough experiments were carried out in a fixed bed adsorption column. The adsorption was carried out at ambient conditions in a 26.5 cm column with a diameter of approximately 2.5 cm. The column was packed with fresh adsorbent of known mass. An aqueous ethanol solution of 60 g/L was used to mimic a typical industrial fermentation broth. The solution was pumped upwards through the column at a flow rate of approximately 2.5 mL/min. Timed samples were collected at the top exit of the column. The density of the samples were measured and recorded. Column saturation was attained when the sample density was equal to the feed density, at this time the flow was stopped and the column was drained of the interstitial fluid.

## Modeling

An unsteady-state mass transfer model based on finite difference method is used for the modeling of ethanol adsorption in a packed tower. A column of finite length L can be separated into n equal elements. By applying boundary conditions and conducting an ethanol mass balance on each of the n elements both on the liquid and the solid present, the mass transfer parameters can be estimated.

The current model makes the following assumptions:

- Each of the column elements is perfectly mixed, that is, a uniform concentration throughout the liquid phase prevails at a given time. In addition, all adsorbent particles inside a column element have identical ethanol concentration profiles for both the mobile phase and the adsorbed phase.
- Liquid from the bulk is transferred through a thin film onto the surface of the pellet. The ethanol at the surface then diffuses within the liquid of the pellet pores. Finally, the ethanol in the pores adsorbs on the surface of the solid.
- Linear mass transfer driving force through the thin film.
- A single diffusion coefficient (effective diffusion coefficient) can be used to describe the ethanol diffusion into macro and micro pores.
- Applicability of Langmuir or Freundlich isotherm to determine the concentration gradient between liquid and adsorbed phase.
- Axial dispersion within the column is neglected

#### Ethanol mass balance for bulk liquid:

Ethanol In – Ethanol Out – Ethanol transferred to pellets = Ethanol Accumulation

$$\bar{v}_L \varepsilon A (C_L^{K-1} - C_L^K) - k_L a (C_L^K - C_L^*) A \Delta z = \varepsilon A \Delta z \frac{dC}{dt} \quad (4)$$

#### Ethanol mass balance on surface of solid:

Ethanol Transferred from Liquid Bulk = Ethanol Diffusing into Particles

$$k_L a (C_L^K - C_p^K) = \varepsilon_p D_{eff} \left. \frac{dC_p^K}{dr} \right|_{r=R} \quad (5)$$

#### Ethanol mass balance for liquid within the pores of the pellet:

Divergence of Ethanol Flux – Ethanol Adsorbed = Ethanol Accumulation

$$\varepsilon_p D_{eff} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_p}{\partial r} \right) - k_{ads} a_p (C_p^I - C_p^{I*}) = \varepsilon_p \frac{\partial C_p}{\partial t} \quad (6)$$

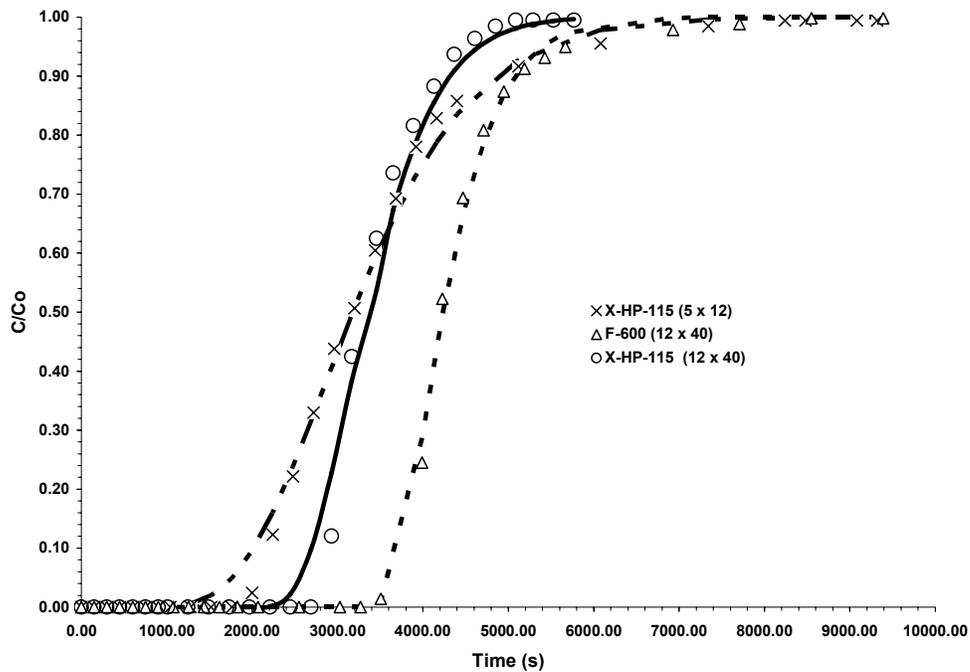
## Ethanol mass balance on adsorption sites within the solid:

Ethanol Appearance = Ethanol Accumulation

$$k_{ads} a_p (C_p - C_p) = (1 - \varepsilon_p) \rho_s \frac{dq}{dt} \quad (7)$$

## Results

Dynamic experiments were conducted in order to monitor the performance of the adsorbents in a packed adsorption tower. Of particular interest was modeling the mass transfer which takes place in order to validate the model. Figure 1 depicts the performance of the 2 adsorbents used in packed bed studies. Also depicted on the plot is the model prediction in each case.



**Figure 1.** Dynamic ethanol adsorption on activated carbon adsorbents. Symbols represent experimental data and the lines are model predictions.

From Figure 1 it is evident that the larger adsorbent particles lead to a more gradual breakthrough profile, while the smaller particles lead to a sharper profile. Since the adsorption of ethanol will not be carried out to complete column saturation, a steep breakthrough profile indicates a greater amount of the total capacity being used up until the breakthrough point.

Based on a three-parameter model, the liquid mass transfer coefficient, the effective diffusion coefficient and the kinetics of adsorption were estimated. This model yielded reasonable results. The model prediction was slightly better for the small adsorbent particles. The estimated mass transfer parameters are presented in Table 2.

**Table 2.** Mass Transfer Parameters

Adsorbent	Mesh Size (Tyler mesh size)	$K_L$ m/s	$D_{eff}$ $m^2/s$	$K_{ads}$ $s^{-1}$	$R^2$ -
F-600	12 x 40	2.69E-04	8.95E-09	1.08E-01	0.9989
X-HP115	12 x 40	1.72E-05	9.94E-10	1.37E-01	0.9967
X-HP115	5 x 12	1.83E-05	6.94E-09	1.09E-01	0.9886

It was found from the dynamic experiments that the capacity of the adsorbent in the column was significantly below the capacity determined from the isotherm at the same ethanol concentration. This discrepancy can likely be explained by a slow diffusion of the ethanol into pores deep within the adsorbent. Some adsorption sites may be difficult to be accessed due to small pore size, or due to gas trapped within the pores creating a liquid-gas interface with high surface tension. These inaccessible sites require a much longer time to completely saturate. It should be noted that complete saturation was not attained in the experiment. As could be expected, the greatest loss in capacity was observed for the X-HP115 (5 x 12) which was the largest particle used and has the greatest potential amount of internal surface area. The diffusion effects were most pronounced for this system.

## Simulation

Having validated the adsorption mass transfer model, the program was used for simulation studies. In order to use the program based on lab-bench experiments for a simulation at the industrial level the following assumptions were made:

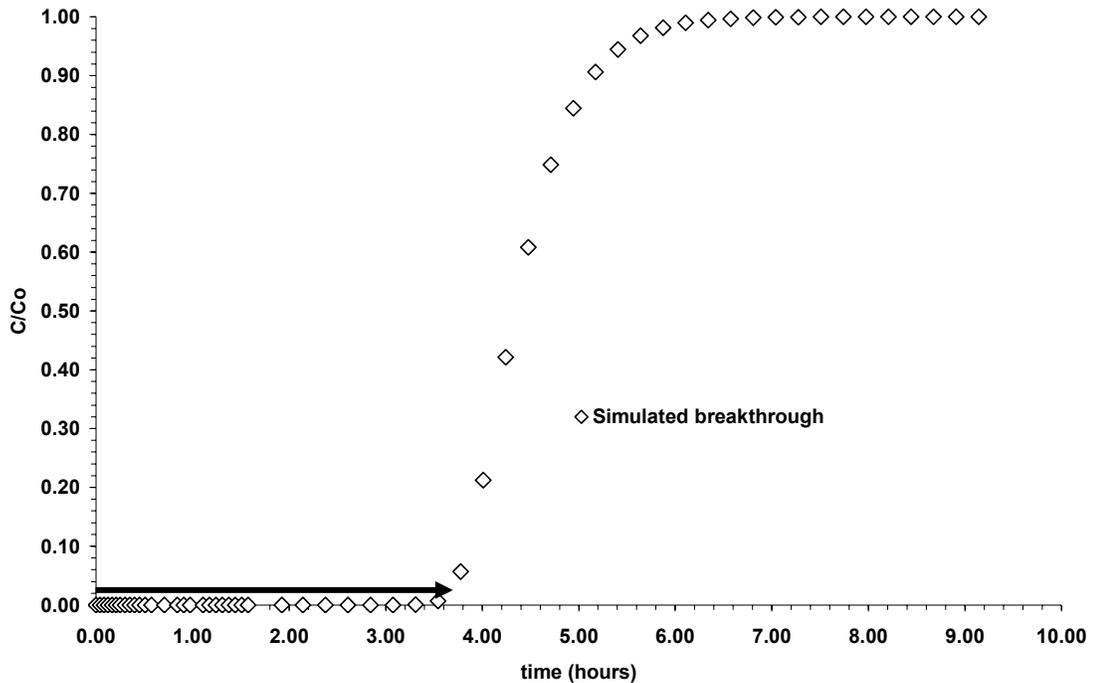
- The effective diffusion coefficient, and kinetics of adsorption calculated from the lab-bench experiment applies at the industrial level
- Packing density of the adsorbent and bed void fraction are unchanged
- Hypothetical broth with final concentration 60g/L ethanol is used as the feed to the adsorption column
- The feed volumetric flow-rate is 10 L/s

For the purpose of the simulation study, a single adsorption column with a height of 5 meters and a radius of 2.5 meters is considered. It is known that the adsorption of ethanol is diffusion limited and thus the interstitial velocity is a key design parameter. Table 1 summarizes conditions of the simulation:

**Table 3: Simulation conditions for industrial scale adsorption system.**

Bed height (m)	5
Bed diameter (m)	5
Bed porosity (-)	0.35
Packing density of adsorbent (kg adsorbent/m <sup>3</sup> bed)	548
Total adsorbent mass (kg)	52199
Breakthrough concentration (kg EtOH/m <sup>3</sup> )	2.5
Ethanol concentration in broth inlet (kg EtOH/m <sup>3</sup> )	60
Inlet volumetric flow-rate (m <sup>3</sup> /s)	0.01

Figure 2 shows the simulated data for an industrial size adsorption unit. The estimated breakthrough time (at a set breakthrough concentration of 2.5g EtOH/L) is indicated in this figure. It is thought that the simulated data may be a conservative estimate. From working experience with the model simulation, the general trend is that the simulation under-estimates the useable capacity of the column (capacity up until breakthrough point).



**Figure 2.** Simulated Breakthrough Performance for an industrial size adsorption column.

## Simulation Details

- From the simulation, a breakthrough time of approximately 3.6 hours is attained. After this time, the feed to the column would be stopped and desorption-recovery would be used to recover the purified ethanol from the porous solid
- A useable capacity (up until breakthrough time) of approximately 0.11 kg EtOH/kg Adsorbent was calculated
- The ratio of useable capacity to total capacity was approximately 0.79
- Complete column saturation is achieved after approximately 7 hours
- A total of 5690 kg of ethanol adsorbed in a single cycle (up until breakthrough point)

The results of the modeling and simulations will be used in the future to perform rigorous economic analysis.

## Conclusions

The mechanistic model developed is a useful tool for fitting experimental breakthrough data, and determining mass transfer parameters. The model can also be used as a prediction tool to simulate adsorption mass transfer in large scale operations. The ability to predict mass transfer allows one to simulate a system and estimate many important adsorption characteristics such as the breakthrough profile, the breakthrough time, quantity of ethanol which can be adsorbed and bed useable capacity. The simulation data also provides the basis for performing economic case studies which will be used in the future to explore the technical and economic feasibility of adsorption technology in the field of bio-ethanol production.

## References

1. Geankoplis, C. J. 2003. *Transport Processes and Separation Process Principles*. New Jersey: Prentice Hall
2. Pimentel, D. 2003. Ethanol Fuels: Energy Balance, Economics and Environmental Impacts are Negative. *Natural Resources*. 12. No.2.
3. Jones, R., Tezel, F. H., Thibault, J., Tolan, J., 2006. Selective ethanol separation from water using silicalite, activated carbon and ZSM-5 adsorbents: Adsorption isotherms and kinetics. *International Journal of Energy Research (accepted, but not yet published)*.