Kinetic Studies on Biobutanol Recovery Process Using Adsorbent Resin


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Abstract: Adsorption of 1-butanol using adsorbent resin is considered as an energy-efficient method to recover 1-butanol from an acetone-butanol-ethanol (ABE) fermentation broth. To develop the adsorption process, kinetic studies were carried out on adsorption of fermentation products using poly-(styrene-co-divinylbenzene) adsorbent resin. The kinetics for the adsorption of each component were presented in the form of the Langmuir equation and the kinetic parameters were then estimated based on the experimental data. For the parameter estimation of the adsorption model, experiments have been carried out with a batch type slurry adsorption equipment and fermentation model broth, containing acetone, ethanol, 1-butanol, acetic acid, and butyric acid. It was found that the extended Langmuir model derived from single component adsorption can correctly predict the competitive adsorption of multi-component mixture. The developed kinetic models are validated by the experiment using the actual broth. This study is expected to contribute to designing a large-scale biobutanol recovery process.

1. INTRODUCTION

Recently, rising oil price and concern over the global warming have led to a widespread interest in bio-fuel. In particular, 1-butanol has received much attention, not only as a fuel but also as a chemical feedstock. 1-butanol is a considered as a more suitable form of fuel than ethanol for the existing fuel infrastructure due to its superior properties including the higher energy content, lower volatility and lower water solubility (Lee et al., 2008). Biologically, 1-butanol is generally produced by the fermentation of carbohydrates from renewable sources such as starch, sugar, and cellulosic sources. It is often referred as acetone-butanol-ethanol (ABE) fermentation since acetone, 1-butanol and ethanol are the major products of the fermentation by clostridia. The ABE fermentation process was first developed by Fernbach and Strange in 1911 and quickly spread around the world during World Wars I and II. However, the ABE fermentation process faded out in the mid-20th century as the production cost of the fermentation process was no longer competitive with the one of petrochemical processes (Dürre, 2008; Green, 2011; Lee et al., 2008). Although an industrial ABE fermentation process has been recently re-established in China (Chiao et al., 2007), the commercialization of ABE fermentation is still limited due to several technical challenges such as low volumetric productivity and high cost for recovery of the solvent (Green, 2011).

One of the critical technical challenges is a severe inhibition and toxicity by the solvent, mainly 1-butanol. The 1-butanol threshold of the wild-type clostridium is approximately 13 g/L (Jones and woods, 1986) and genetically modified clostridia have reached merely 17.6 g/L (Harris et al., 2001). To overcome the toxicity problem by 1-butanol, numerous new fermentation process designs have been suggested. For example, an in-situ or ex-situ auxiliary phase to separate and recover of 1-butanol from the fermentation broth is incorporated into the process (Groot et al., 1992) since cell mass and volumetric productivity can be increased significantly by simultaneously removing 1-butanol in fermentation broth. Reduction in the downtime and separation energy is also expected.

A number of 1-butanol recovery techniques, e.g., gas stripping, liquid-liquid extraction, pervaporation, adsorption, and perstraction (Ezeji TC, 2010; Vane LM 2008), have been investigated as candidate separation methods to be incorporated into the ABE fermentation. Among these techniques, adsorption has been identified as the most energy-efficient process (Qureshi et al., 2005; Oudshoorn et al., 2009). Numerous efforts have been made during the past two decades to find appropriate adsorbents with high selectivity and capacity for butanol recovery (Groot and Luyben, 1986; Nielson et al., 1988, Yang et al., 1994; Qureshi et al., 2005; Saravanan et al., 2009; Nielson and Prather, 2009). The polymeric resin, in particular, has been noted as having large adsorption capacity appropriate for industrial use.

To design a new fermentation process equipped with in-situ or ex-situ adsorption recovery method, a reliable adsorption model should be developed. In this study, we carried out adsorption kinetic studies using poly (styrene-co-divinylbenzene) adsorbent resin to develop an adsorption model. In the experiment, a batch type slurry adsorption process was used and the fermentation model broth, containing acetone, ethanol, 1-butanol, acetic acid, and butyric acid, was fed into the adsorption vessel. Based on the
experimental data we gathered, the adsorption kinetics for each component was assumed to be represented in the form of the Langmuir equation and the kinetic parameters were then estimated by an efficient optimization method.

2. THEORY

2.1 Adsorption Equilibrium: the Langmuir isotherm model

Among the available adsorption equilibrium isotherm models, the best known is the Langmuir isotherm model, shown below.

\[ q = \frac{q_m B C_i}{1 + \sum_{i=1}^{n} B_i C_i} \]  

(1)

where \( q_m \) is the maximum adsorption capacity, and \( B \) is the Langmuir constant.

For multi-component mixtures containing \( n \) species, the Langmuir model for adsorption of component \( i \) is represented as follows:

\[ q_i = \frac{q_{i,m} B C_i}{1 + \sum_{i=1}^{n} B_i C_i} \]  

(2)

The amount of the adsorbed components, \( q_i \), in the experiments, is calculated by means of mass conservation as shown in eq (3). Thus, the values of eq (3) are used as the experimental data to estimate the parameters, \( q_{i,m} \) and \( B_i \), in eq (2).

\[ q_i^{\text{experiment}} = \frac{(C_{i,0} - C_i) V_{aq}}{m} \]  

(3)

where \( C_{i,0} \) and \( C_i \) represent the concentration of the components in aqueous phase, \( V_{aq} \) is the volume of the aqueous solution, \( m \) is the mass of the polymer resin.

2.2 Adsorption Kinetics

When the adsorption isotherm is highly favourable, adsorption rate between the liquid and solid phases can be represented as follows (Hashim et al., 2007):

\[ \frac{d q_i}{dt} = k_i (q_i^* - q_i) \]  

(4)

where \( k \) is the rate constant, \( q_i^* \) is the solid phase adsorbates concentration which is in equilibrium with bulk liquid concentration.

Eq (4) can also be represented as the function of the concentration of the component \( i \) following mass conservation equation (see eq (5)).

\[ \frac{d q_i}{dt} = -\frac{V_{aq}}{m} \frac{d C_i}{dt} \]  

(5)

Rearranging eqs (3), (4) and (5), we can obtain the following mass balance equation which is the function of the concentration of the component \( i \). Using an optimization algorithm, the rate constant, \( k_i \), in eq (6) is estimated with the experimental data.

\[ -\frac{V_{aq}}{m} \frac{d C_i}{dt} = k_i \left( q_{i,0} - \frac{(C_{i,0} - C_i) V_{aq}}{m} \right) \]  

(6)

2.3 Optimization method: Combination of Genetic Algorithm and Levenberg-Marquardt Method

To estimate the parameters in (1)-(6), an optimization scheme that combines the genetic algorithm (GA) and the Levenberg-Marquardt algorithm (LMA) is used. The GA is a heuristic algorithm based on the theory of evolution in a natural system. The algorithm works with a set of solutions called a population, of which each solution is called an individual. After an initial population is created, the objective function value for each individual is computed. Subsequently, individuals with superior objective function values are selected to generate the next generation of the population through genetic operators: crossover and mutation of the selected individuals. In general applications of the GA, this regeneration procedure is repeated until the solution satisfies the termination criteria (Holland, 1975; Goldberg, 1989). Although the GA has been applied to kinetic parameter estimation for highly non-linear and multidimensional optimization problems, it suffers from the drawback that the computational load dramatically increases for more complex problems. When handling multi-dimensional problems, a significantly larger population is required, and the overall number of calculations grows exponentially with the size of the population. In the proposed approach, this issue is resolved by locally employing a fast deterministic optimization method, the LMA (Venugopal et al., 2009; Kim et al., 2011). The LMA is mathematically derived by a linear approximation and the searching method is based on calculation of a gradient (Levenberg, 1944; Marquardt, 1963).

The overall procedure of the combined method is described in Fig. 1 (Kim et al., 2011). A large solution space is searched by the GA without concern over the initial points. After a given number of generations, the GA provides the
LMA with the best solution found thus far. Since the initial point so provided by the GA is thought to be already close to the optimum, the LMA converges rapidly to find the optimal solution.

\[
K_{opt} = \begin{bmatrix} k_{0,opt} & k_{1,opt} & k_{2,opt} & A_{opt} & E_{a,opt} \end{bmatrix}
\]

population

Fig. 1. Application of a novel optimization technique combining a genetic algorithm and the Levenberg-Marquardt algorithm (Kim et al., 2011)

3. MATERIAL AND METHOD

3.1 Polymer resin

Poly (styrene-co-DVB) polymer resin used in this research is Dowex optipore L-493 purchased from Dow Korea. This polymer resin has high surface area and porosity. It was evaluated as the proper resin from the previous study because it has a high surface area (1100 m²/g) and high adsorption capacity for 1-butanol, about 4,100 mmol/kg at a fixed aqueous 1-butanol concentration of 1% (w/v). (Nielson and Prather, 2009)

3.2 Chemicals

Acetone (99.9%, Sigma-Aldrich), 1-butanol (99.8%, Sigma-Aldrich), ethanol (anhydrous, 99.5%, Sigma-Aldrich), acetic acid (99.7%, Sigma-Aldrich), and butyric acid (99%, Sigma-Aldrich) were used.

3.3 Analytical Method

Concentrations of ABE solvents and acids (acetic and butyric acid) in the aqueous solution were determined by gas chromatograph (GC) using Agilent 6890N Series/5873 Network (Agilent Technologies, Palo Alto, CA, USA). A GC was equipped with a flame ionization detector (FID) and a 300 mm x 7.8 m glass 80/120 Carbopack BAW packed column (Supelco Inc., Bellefonte, PA). Helium as carrier gas operated at flow rate of 3 mL/min. Inlet heater and FID temperature operated at 220 °C and 280 °C. The following conditions were used: oven temperature of 100 °C for 30 s, ramping to 135 °C at 10 °C/min, ramping to 170 °C at 30 °C/min, and then programmed at 170 °C for 9 min final hold.

4. EXPERIMENTAL

4.1 Adsorption Equilibrium Isotherm

Equilibrium adsorption experiments of single components were performed in a sterile, 50 mL flask containing 25 mL of the aqueous solution and desired mass of polymer resin. The initial concentration of 1-butanol and other adsorbates in the aqueous solution was about 10 g/L. Between 1 and 25 g of a polymer resin was added to the solution in the experiments. Flasks were agitated at 150 rpm in a water bath at 37 °C. After 24 hr equilibration, the liquid phase concentrations of 1-butanol and other adsorbates were analyzed by GC-FID.

Equilibrium adsorption experiments of multi-components mixture were carried out in the same manner as the single component experiments with 50ml of 8g/L of Acetone, 8g/L of Ethanol, 20g/L of 1-butanol, 5g/L of Acetic acid, and 2g/L of Butyric acid solution and 1 ~ 15 g of polymer resin.

4.2 Adsorption Kinetics

Experiments for studying the adsorption kinetics are also performed in the batch type slurry reactor. About 20 g of the polymer resin is added to 500 mL flask containing about 250 mL of the model broth solution. Flasks were stirred in a water bath maintained at 37 °C. After adding the polymer resin, 10 liquid samples were taken from the flask at every single minute for 10 mins. and then seven additional samples are taken with five and ten minute intervals by 60 min. The concentration of adsorbates were analyzed and recorded as concentration versus time data. The kinetic experiment using the actual fermentation broth is carried out in the same way as the model broth experiment.

5. RESULT AND DISCUSSION

5.1 Single component equilibrium isotherm

The adsorption isotherm of 1-butanol, acetone, ethanol, butyric acid, and acetic acid with polymer resin are shown in Fig. 2. In case of acid adsorption isotherm, only the undissociated form of acids is assumed to be adsorbed preferentially onto the polymer resin.
A comparison of adsorption isotherms of each component shows polymer resin adsorbs highly preferentially 1-butanol and butyric acid, then acetone followed by acetic acid and ethanol. This result is in line with the hydrophobicity of the components. This means that hydrophobic components are adsorbed preferentially on this resin.

A Langmuir equation was fitted to the single component isotherms data using the non-linear Marquardt method to estimate the two parameters, $q_{i,m}$ and $B_i$, of the Langmuir isotherm. Fig. 2 shows that acceptable fits were obtained.

### 5.2 Multi-components mixture equilibrium isotherm

An equilibrium experiments with aqueous mixtures of 1-butanol, acetone, ethanol, butyric acid, and acetic acid was also performed in order to describe competitive adsorption (see Fig. 3). Acetone, ethanol, and acetic acid adsorption were obviously decreased compared to the case of single component adsorption. This is clearly caused by the competition with 1-butanol adsorption.

The predicted data by the extended Langmuir isotherm model derived from the single component Langmuir isotherm matched the experimental data very closely so this model can describe the competitive adsorption of multi-components.

### 5.3 Adsorption kinetics

The kinetic adsorption profile of each component in the model broth experiment is shown in Fig. 4. The parameter of the kinetic model, $k_i$, is calculated by fitting the concentration curves as represented in Fig. 4. All the components have reached to equilibrium state in about 10 min. 1-butanol and butyric acid which have higher affinity to the adsorbent had a lower kinetic parameter than other components.

The kinetic model for the model broth experiment is verified with the actual fermentation broth. The experimental results and the prediction data of the developed kinetic model are plotted in Fig. 5. It is shown that the kinetic model estimated with the experimental data of the model broth effectively predicts the adsorption phenomena in the real broth. This result proves that the cells, the nutrients, and unknown compounds in the real broth do not disturb the adsorption phenomena of the 1-butanol. This means that 1-butanol has the definitely higher affinity to the adsorbents than the nutrients and unknown compounds in broth due to the hydrophobicity of 1-butanol, so the adsorption of the 1-butanol is not disturbed by those compounds. Thus, the kinetic model developed from the model broth experiments is considered to be suitable for predicting the adsorption phenomena in the real fermentation broth.

![Butanol Adsorption Isotherm](image1)

![Acetone Adsorption Isotherm](image2)

![Ethanol Adsorption Isotherm](image3)

![Butyric Acid Adsorption Isotherm](image4)

![Acetic acid Adsorption Isotherm](image5)

Fig. 2. Experimental and best-fit Langmuir isotherm of 1-butanol, ethanol, acetone, butyric acid, and acetic acid with Dowex Optipore L-493 resin.
Fig. 3. Experimental and prediction data of competitive adsorption with multi-component mixture

Fig. 4. Experimental and fit data of multi-components adsorption kinetics of model broth

Fig. 5. Experimental and Prediction data of multi-components adsorption kinetics of real fermentation broth
6. CONCLUSIONS

Dowex Optipore L-493, poly (styrene-co-divinylbenzene) resin was evaluated to be a good candidate adsorbent for the recovery of 1-butanol from ABE fermentation broth due to its high capacity and selectivity for 1-butanol. Its hydrophobic property caused the increment of selective adsorption of 1-butanol.

The parameters of the Langmuir isotherm model and the kinetic adsorption model were estimated with the data from the single and multi-components experiments. These models were extended to predict the competitive adsorption of aqueous mixture of 1-butanol, acetone, ethanol, acetic acid, and butyric acid. The predicted values were well matched with the experimental data of real fermentation broth without any modification. Thus, we may conclude that the developed adsorption models are sufficiently accurate to predict the adsorption phenomena of the components in the ABE fermentation broth. The developed kinetic models are expected to contribute significantly to designing a large-scale adsorption process for recovery of biobutanol.

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REFERENCES


