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Modeling of breakthrough curves of single and quaternary mixtures of ethanol, glucose, glycerol and acetic acid adsorption onto a microporous hyper-cross-linked resin

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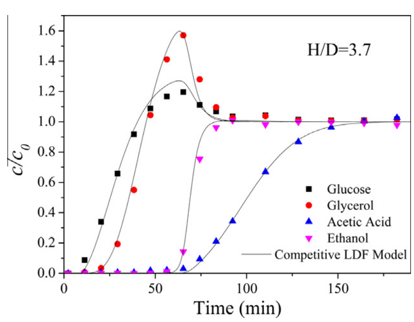
HIGHLIGHTS

- Adsorption of ethanol from actual fermentation broth in packed beds was conducted.
- HD-01 resin shows large adsorption capacity and high selectivity for ethanol.
- Effect of pH on the adsorption of quaternary mixtures was investigated in detail.
- Multicomponent mass transport model was proposed and validated by experiment data.
- Satisfactory fit of breakthrough curves in single/multi-component systems.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of quaternary mixtures of ethanol/glycerol/glucose/acetic acid onto a microporous hyper-cross-linked resin HD-01 was studied in fixed beds. A mass transport model based on film solid linear driving force and the competitive Langmuir isotherm equation for the equilibrium relationship was used to develop theoretical fixed bed breakthrough curves. It was observed that the outlet concentration of glucose and glycerol exceeded the inlet concentration ($c/c_0 > 1$), which is an evidence of competitive adsorption. This phenomenon can be explained by the displacement of glucose and glycerol by ethanol molecules, owing to more intensive interactions with the resin surface. The model proposed was validated using experimental data and can be capable of foresee reasonably the breakthrough curve of specific component under different operating conditions. The results show that HD-01 is a promising adsorbent for recovery of ethanol from the fermentation broth due to its large capacity, high selectivity, and rapid adsorption rate.

1. Introduction

Ethanol produced from lingo-cellulosic biomass has been recognized as one of the most important second-generation liquid biofuels (Nigam and Singh, 2011). However, ethanol fermentation is a product inhibition process, which leads to low concentrations

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of ethanol in the final fermentation broth. The effect of feedback inhibition can be circumvented through integrated bioreactor designs employing in situ product recovery (ISPR) methods, e.g., fermentation coupled with gas stripping (Hashi et al., 2010), adsorption (Jones et al., 2011) or pervaporation (Chen et al., 2012) and so on. Among proposed technologies, ethanol fermentation coupled with adsorption is one of the most promising methods (Vane, 2008). It was found that direct addition of hydrophobic adsorbents to the fermentation flask promoted the glucose consumption and ethanol production rates of strains (Einicke et al., 1991; Ikegamai et al., 2000; Jones et al., 2011). However, the spent sorbents in fermentation broth are difficult to recover. Moreover, the fermentation is hard to operate in the continuous mode. Accordingly, Yang and Tsao (1995) proposed a process to integrate the repeated fed-batch fermentation with continuous product removal by adsorption with two externally located adsorption columns. The separation process can be made cyclical by alternating between adsorption and desorption with the two columns.

Adsorption in a fixed bed is more preferable in industrial production because of its ability to process large quantities of feed in the continuous mode. To date, many studies have been conducted to concentrate ethanol from aqueous solution on a fixed bed (Delgado et al., 2013; Jones et al., 2010; Kawabata et al., 1988; Pitt et al., 1983). However, most of them used ethanol–water binary aqueous to simulate fermentation broth, while the effect of other main components co-existing in the fermentation broth are neglected. In addition to ethanol, by-products (e.g., glycerol, and organic acids) and substrate sugars co-exist in fermentation broth. These impurities may have negative effect on the adsorption of ethanol. Bui et al. (1985) found that glucose could compete with ethanol for the same adsorption sites on the surface of activated carbon thus reduce the ethanol adsorption capacity. Bowen and Vane (2006) observed that the presence of small amounts of acetic acid (<0.6 wt%) significantly reduced the ethanol adsorption on zeolite ZSM-5. These studies were conducted with the binary system (glucose/ethanol, acetic acid/ethanol) in a batch adsorber. Reports on the adsorption of ethanol from the quaternary systems (ethanol/glycerol/glucose/acetic acid) and actual fermentation broth in a packed bed are few and fragmentary.

Therefore, this work is focused on the adsorption of ethanol from quaternary systems in a fixed bed. In our previous study, a microporous hyper-cross-linked resin HD-01 with large adsorption capacity and rapid kinetics for ethanol from aqueous solution was screened. As a continuation of our previous works, the main aims of the present study are:

(1) Evaluate the adsorption selectivity for ethanol from actual fermentation broth on HD-01 resin.
(2) Establish a mass transport model to predict the competitive breakthrough curves of ethanol, glucose, glycerol and acetic acid in a HD-01 resin packed bed.
(3) Investigate the effects of operating conditions, including flow rate, bed length, initial concentration of the solutes and pH on the performance of HD-01 bed.

2. Methods

2.1. Materials

2.1.1. Chemicals

Ethanol, acetic acid, glucose and glycerol were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals used were analytical grade reagents, and distilled de-ionized water was used in the preparation of all solutions.

2.1.2. Resin

The microporous hyper-cross-linked polymeric resin HD-01 was kindly provided by the National Engineering Technique Research Center for Biotechnology (Nanjing, China). The main physico-chemical properties of HD-01 were listed in Table 1.

2.1.3. Fermentation broth preparation

The detailed ethanol fermentation process could be found in S1 (Supplementary materials). Prior to use, the fermentation broth was centrifuged at 8000 rpm and 15 min to remove the yeast cell. After about 40 h of culture, the fermentation broth contained 90.0 ± 5.0 g/L ethanol and 9.0 ± 2 g/L glucose. In addition, the fermentation broth contained 9.0 ± 1.0 g/L glycerol and 1.5 ± 0.5 g/L acetic acid as by-products.

2.2. Experimental methods

2.2.1. The static equilibrium adsorption experiments

Batch uptake experiments were performed to study the single/multi-component equilibrium adsorption isotherms of ethanol (or other solutes of interest) from single/multi-component systems onto resins at the temperature of 298 K. The mass ratios of ethanol:glycerol:glucose:acetic acid in quaternary mixture solution was equal to 100:10:10:5, which was close to the ratio of these components in actual final fermentation broth. The solution with different initial concentrations (50 mL) were added to erlenmeyer flasks (100 mL) containing 5 g wet resin. After that, the flasks were sealed and shaken at 200 rpm in a shaker for 8 h at 298 K to attain the equilibrium. Then a sample was withdrawn from the supernatant fluid with a syringe and the concentration of solute of interest was measured by HPLC.

The equilibrium adsorption capacity of the individual solute onto resin was determined by the following relationship:

$$q_{i,e} = \frac{(c_{i,0} - c_{i,e})V}{m} \tag{1}$$

where $c_{i,0}$ and $c_{i,e}$ represent the initial and equilibrium aqueous concentration of ethanol (or other solutes of interest) (mmol/L), respectively. V is the volume of the aqueous solution (L); m is the mass of the resin used (kg).

2.2.2. Dynamic column adsorption experiments

Dynamic adsorption experiments were carried out in a water jacketed glass column with a diameter of 2.05 cm and a length of 30 cm. The column was packed with wet resin of given mass (20, 30, or 40 g). The void faction of the bed (ε_b) was 0.27, which was calculated according to (Kleinübing et al., 2012). By doing this, a bed height around 7.6–15.2 cm was obtained. A peristaltic pump (BT300, longer pump, China) was used to pump the solution downwards through the column at a given flow rate (0.2–1.2 mL/min). By using an automatic fraction collector (BSZ-100, Qingpu, Shanghai), samples of approximately 5 mL were collected at different times. The concentration of ethanol (or other components of inter-

Table 1
Physicochemical properties of the microporous resin HD-01.

Property	
Matrix	Poly(styrene-co-divinylbenzene)
Appearance	Brown–red, translucent
Polarity	Weak polar
BET surface area (m^2/g)	1645.5
Particle size (mm)	0.42–0.56
Moisture capacity (%)	43.0
HK desorption average pore diameter (nm)	1.92
Total pore volume ($cm^3\ g^{-1}$)	0.732