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Butanol production in acetone-butanol-ethanol fermentation with *in situ* product recovery by adsorption

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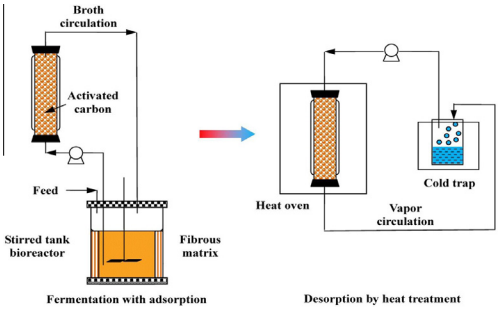
HIGHLIGHTS

- Activated carbon (AC) with a high capacity was selected for *n*-butanol adsorption.
- Fed-batch fermentation with AC adsorption produced ~230% more or ~54.6 g/L butanol.
- Productivity increased 32% to ~0.45 g/L·h, with a butanol yield of ~0.22 g/g.
- Thermal desorption was energy-efficient, producing a solution of 167 g/L butanol.
- Fermentation with AC adsorption offers an efficient process for butanol production.

GRAPHICAL ABSTRACT

An energy efficient process was developed for butanol production in acetone-butanol-ethanol fermentation with cells immobilized in a fibrous matrix attached to the inside wall of the stirred-tank bioreactor and butanol adsorption with activated carbon to alleviate butanol toxicity.



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ABSTRACT

Activated carbon Norit ROW 0.8, zeolite CBV901, and polymeric resins Dowex Optipore L-493 and SD-2 with high specific loadings and partition coefficients were studied for *n*-butanol adsorption. Adsorption isotherms were found to follow Langmuir model, which can be used to estimate the amount of butanol adsorbed in acetone-butanol-ethanol (ABE) fermentation. In serum-bottle fermentation with *in situ* adsorption, activated carbon showed the best performance with 21.9 g/L of butanol production. When operated in a fermentor, free- and immobilized-cell fermentations with adsorption produced 31.6 g/L and 54.6 g/L butanol with productivities of 0.30 g/L·h and 0.45 g/L·h, respectively. Thermal desorption produced a condensate containing ~167 g/L butanol, which resulted in a highly concentrated butanol solution of ~640 g/L after spontaneous phase separation. This *in situ* product recovery process with activated carbon is energy efficient and can be easily integrated with ABE fermentation for *n*-butanol production.

1. Introduction

Due to concerns about depletion of crude oils and escalating prices of petroleum-derived products, biobutanol has attracted

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attention as a liquid transportation fuel (Dürre, 1998; Wang et al., 2014; Xue et al., 2013a). However, due to severe product inhibition caused by butanol, conventional acetone-butanol-ethanol (ABE) fermentation is limited by low product titer, yield, and productivity (Kumar and Gayen, 2011), resulting in intensive energy consumption for product recovery by distillation (Abdehagh et al., 2014; Vane, 2008; Xue et al., 2014a). Although intensive efforts have been made on improving butanol tolerance and production by solventogenic clostridia through adaptation, mutagenesis and metabolic engineering (Lee et al., 2008; Xu et al., 2015; Yang and Zhao, 2013), 2% (w/v) of butanol production is still a bottleneck in the development of ABE fermentation (Zhao et al., 2013). Fermentation with *in situ* product recovery (ISPR) can alleviate product inhibition and thus improve conversion and productivity (Staggs and Nielsen, 2015; Xue et al., 2014a; Yang and Lu, 2013). Several online integrated butanol recovery methods, including adsorption (Nielsen and Prather, 2009; Qureshi et al., 2005; Wiehn et al., 2014; Yang et al., 1994), liquid-liquid extraction (Roffler et al., 1987), pervaporation (Matsumura et al., 1988; Xue et al., 2014b) and gas stripping (Lu et al., 2013; Xue et al., 2012, 2013b, 2014c) have been investigated. Among them, adsorption requires less energy, is easier to operate (Agueda et al., 2013; Oudshoorn et al., 2009b), and has been demonstrated as an effective process for separating butanol and reducing its inhibition in ABE fermentation (Liu et al., 2014; Yang and Tsao, 1995).

Butanol recovery from dilute solution by adsorption is usually carried out in two steps: adsorption followed by desorption to obtain a concentrated butanol solution with adsorbent regeneration (Agueda et al., 2013; Vane, 2008). Three types of adsorbents have been widely studied for butanol adsorption: activated carbon (AC), zeolite (SiO_2/Al_2O_3), and polymeric (typically ion-exchange) resins (Abdehagh et al., 2015; Liu et al., 2014; Nielsen and Prather, 2009; Oudshoorn et al., 2009a; Qureshi et al., 2005). In general, adsorbents should have a high butanol adsorption capacity, affinity, and selectivity, and be inexpensive and easy to be regenerated for reuse. Although some zeolites and silicalite could adsorb almost all butanol from a dilute solution of less than 10 g/L and be thermally regenerated to produce a butanol solution of >80% (w/v) (Milestone and Bibby, 1981; Saravanan et al., 2010), their biocompatibility for *in situ* butanol recovery during fermentation has not been studied. Meanwhile, a recent study showed that activated carbon F-400 was the best butanol adsorbent with the highest adsorption capacity and fastest adsorption rate among ACs and zeolites tested (Abdehagh et al., 2013). However, its application in ISPR for butanol production has not been demonstrated. To date, most of prior studies of ISPR by adsorption focused on polymeric resins, which are relatively expensive and have only moderate butanol adsorption capacity and selectivity (Liu et al., 2014; Nielsen and Prather, 2009; Nielsen et al., 2010; Wiehn et al., 2014; Yang et al., 1994), which have limited their commercial applications.

The goal of this study was to investigate and demonstrate the feasibility of *in situ* adsorption for high-titer butanol production in fed-batch fermentation with *Clostridium acetobutylicum* JB200 (Yang and Zhao, 2013). We first screened a variety of commercial adsorbents, including AC, ion exchange resins and zeolites, for their ability to adsorb n-butanol from model solutions. Promising adsorbents were then evaluated for their adsorption isotherms and uses in ISPR for butanol production in ABE fermentation with cells immobilized in a fibrous bed bioreactor (Du et al., 2015). For the first time, our results demonstrate that activated carbon Norit ROW 0.8, a relatively inexpensive adsorbent, is biocompatible and effective for *in situ* butanol recovery for high-titer butanol production in ABE fermentation.

2. Materials and methods

2.1. Screening adsorbents for butanol adsorption

Nine different adsorbents (activated carbon Norit ROW 0.8, ion exchange resins Amberlite IRA-900, Amberlite XAD-4, Diaion HP-2MG, Diaion HP-20, Dowex Optipore L-493, Dowex Optipore SD-2, and zeolites CBV901 and CBV28014) representing different types were selected based on literature data (Abdehagh et al., 2013; Nielsen and Prather, 2009; Nielsen et al., 2010; Oudshoorn et al., 2009a; Qureshi et al., 2005; Saravanan et al., 2010). The zeolites were obtained from Zeolyst International (Conshohocken, PA) while all other adsorbents were purchased from Sigma-Aldrich (St. Louis, MO). They were tested for their ability to adsorb *n*-butanol in capped tubes, each containing 25 mL of the model solution (~10 g/L butanol) and 1 g of a tested adsorbent, at 37 °C. The amount of butanol adsorbed per unit weight of the adsorbent or specific loading (q) was determined from the difference between the initial and final (equilibrium) butanol concentrations, as follows:

$$q = (C_{eq} - C_o)V/W \quad (1)$$

where V is the solution volume, W is the mass of adsorbent, and C_o and C_{eq} are the butanol concentrations in the solution at initial and equilibrium, respectively. The partition coefficient (K_r), which indicates the affinity or potential of an adsorbent to take up butanol from the aqueous solution, can be determined from the following equation:

$$K_r = q/C_{eq} \quad (2)$$

2.2. Adsorption isotherm

Norit ROW 0.8, Dowex Optipore L-493 and SD-2, and CBV901 with high butanol adsorption capacity found in the screening tests were further studied for their adsorption isotherms at 37 °C and 60 °C. Various amounts of adsorbents, ranging from 0.25 g to 6 g, were added to 15 mL of the model solution (butanol concentration: 39.6 ± 1.8 g/L) and allowed to equilibrate for 24 h with agitation at 150 rpm. The adsorption isotherm for activated carbon, which was the best among the four adsorbents studied, was further studied with a model solution containing ~20 g/L glucose, ~20 g/L acetone, ~40 g/L butanol, ~4 g/L ethanol, ~10 g/L acetic acid, and ~4 g/L butyric acid to evaluate butanol and acetone adsorption in the presence of glucose and acids.

2.3. Adsorption dynamics in a packed column of activated carbon

Continuous adsorption with 25 g Norit ROW 0.8 packed in a glass column (15 cm in length; 2.1 cm in inner diameter) by feeding 10 g/L butanol solution at 20 ml/min was studied for ~90 min. Samples from the effluent were collected periodically to monitor butanol concentration until complete breakthrough was confirmed. The fully loaded activated carbon was regenerated by heating at 200 °C overnight, and then washed with three volumes of distill water and reused for the next cycle of adsorption run. Continuous adsorption with a model solution containing 10 g/L butanol, 5 g/L acetone, 2 g/L ethanol, 4 g/L acetic acid and 2 g/L butyric acid was also studied.

2.4. Desorption dynamics

Desorption of butanol, water and ABE mixture from activated carbon was first studied by thermogravimetry. Briefly, butanol, water and ABE mixture with a ratio of 6:3:1 were first adsorbed