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Recovery of 1-butanol from aqueous solutions using zeolite ZSM-5 with a high Si/Al ratio; suitability of a column process for industrial applications

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ABSTRACT

Commercially available zeolites (CBV28014, CBV901) with a high Si/Al ratio were tested as adsorbents to recover 1-butanol from aqueous solutions such as acetone–butanol–ethanol (ABE) fermentation broth. It was found that these zeolites can quickly and almost completely adsorb 1-butanol from aqueous solutions containing ~1 wt% of 1-butanol. The binding capacity of the zeolites appeared to be around 0.12 g 1-butanol/g zeolite, and remained constant till equilibrium concentration as low as 0.04 wt% 1-butanol in water. Extrudates were prepared and tested in a column set-up to get an impression of the suitability of these zeolites for industrial applications. Extrudates of 80% zeolite and 20% alumina binder with 16–24 mesh (0.7–1.0 mm) size showed the best adsorption results in a packed bed column with up-flow of ABE broth. The adsorbent loading at 10% breakthrough was calculated to be 0.085 g 1-butanol/g zeolite (9.3 min residence time). A subsequent temperature swing leads to desorption. By choosing the temperature program carefully, it was possible to separate the water/ethanol/acetone and 1-butanol fractions. The resulting 1-butanol concentration in the 1-butanol fraction was 84.3 wt% and thus a concentration factor of 65 was achieved in one step, which is a higher value compared to other isolation techniques. Only 80% of adsorbed 1-butanol could be recovered, the remainder could only be desorbed at higher temperatures as butene. However, this should not be a problem in an industrial process as all stronger binding, catalytic sites will be blocked after the first adsorption/desorption round. A mathematical model was developed to simulate the breakthrough data and a mass transfer coefficient ($k_p a$) of 0.052 min^{-1} was obtained. Comparison of simulated $k_p a$ for different sizes of extrudates clearly indicated that the adsorption rate is determined by solid phase diffusion.

1. Introduction

The 1-butanol can be produced from both C_5- and C_6-sugars by fermentation using Clostridia bacteria (e.g. *C. acetobutylicum* or *C. beijerinckii*). This acetone–1-butanol–ethanol (ABE) fermentation process used to be the main process for industrial production of acetone and 1-butanol until mid 20th century. However, the low 1-butanol tolerance of Clostridia bacteria leads to very dilute aqueous solutions (1–2 wt% 1-butanol) and thus high-energy consumption during the product recovery. Due to the high process and feedstock costs, the traditional ABE fermentation process could not compete with the petrochemical processes for the production of these solvents.

Increased yield and productivity combined with a more energy efficient product recovery technique will improve the economics of this fermentation process and may turn it into an interesting future option for the biofuel production [1]. In order to remove the 1-butanol during fermentation, a number of in situ product isolation techniques such as adsorption, pervaporation, extraction, gas stripping and ionic liquids have been investigated [2–8]. Oudshoorn et al. [9] reported that adsorption and pervaporation based techniques are energy efficient recovery methods. They predicted the 1-butanol recovery energy requirement to be <4 MJ/kg 1-butanol by the adsorption and pervaporation methods. There are number of studies conducted based on the adsorption technique to recover 1-butanol from the fermentation broth. Nielsen and Prather [10] studied a number of polymeric resins for in situ 1-butanol recovery from fermentation broth. They reported that the poly(styrene-co-divinyl-benzene) resin to have a very high 1-butanol adsorption potential. Qureshi et al. [11] also reported a comparative study on the 1-butanol recovery from fermentation broth based on energy requirement. They concluded that adsorption using silicalite (a lab-made Al-free zeolite analogue) is the most energy efficient method (1948 kcal/kg of 1-butanol), compared to gas stripping, pervaporation and liquid–liquid extraction. Besides a high adsorption capacity and 1-butanol selectivity, silicalite has small pores preventing adsorption of more complex molecules such as sugars, medium components and bacterial cells, which make them

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very suitable for in situ product removal. Furthermore, zeolites are known to be robust and insensitive to repeated heating and cooling.

Milestone and Bibby [12] described the recovery of 1-butanol from model solutions (1-butanol or ABE in water) by adsorption to silicalite. Water and 1-butanol could be separated by thermal desorption in two steps: water being removed at 40 °C, and 1-butanol by further heating to about 150 °C. Mass balances were not determined in that study and the final 1-butanol concentration was erroneous (98% (w/v), whereas the 1-butanol density is 0.81 g/cm^3). The use of silicalite filled membranes to adsorb 1-butanol from ABE fermentation broth has also been described [13]. Shao and Kumar used a ZSM-5 zeolite-filled polydimethylsiloxane membrane to separate 1-butanol from 1-butanol/2,3-butandiol mixture [14].

Milestone and Bibby also studied adsorption of alcohols to different forms of self-prepared ZSM-5 zeolites [15]. They found that the amount of alcohol adsorbed decreased as the ionic size of the cation increased (H, Na, K, Cs). Furthermore, increasing percentages of Al_2O_3 (1%, 2%, and 4%) lead to lower adsorption capacities for 1-butanol and higher ones for ethanol. The presence of Al_2O_3 also catalyzed the dehydration of 1-butanol during desorption at higher temperatures from ZSM-5 containing 4% Al_2O_3. The (relative) amount of degraded ethanol and 1-butanol was not determined. Catalytic activity was not observed in Na-ZSM-5 zeolites prepared by Falamaki et al. [16], which was ascribed to the different synthesis routes followed. A conceptual design for a 1-butanol adsorption/desorption process has been described by Holtzapple and Brown [17].

This paper describes the adsorption and desorption characteristics of commercially available zeolites with a high Si/Al ratio (CBV28014, CBV901). Zeolites were used in the form of extrudates to be able to test them in a column set-up to get an indication of their suitability for industrial applications. Especially desorption was studied in more detail as quantitative information was lacking. A mathematical model has been developed to simulate the breakthrough data obtained from the experimental studies by iterating the solid phase mass transfer coefficient (k_pa).

2. Experimental

2.1. Materials

Two commercial zeolites (CBV28014 and CBV901) purchased from Zeolyst International were used. Their structural and physical properties are listed in Table 1. Both zeolites were in powder form. Before use, the zeolites were dried at 300 °C for at least 2 h in the nitrogen atmosphere. This converted the ammonium form of CBV28014 into hydrogen form. Thus CBV28014 in hydrogen form was used in all the experiments.

2.2. Methods

2.2.1. Extrudate preparation

Extrudates were made of 80% zeolite and 20% of alumina binder or 50% zeolite and 50% of silica binder. Zeolite powder, alumina/silica powder and proportionate water were mixed in a Z-blade kneader to form an extrudable paste. Acetic acid was used as a peptizing agent. Additives like Superfloc N100 and Methocel K15 were dosed to improve the extrusion behavior. Extrusion was carried out over a 1 in. Bonnot single screw extruder, using a 0.8 mm trilobe die-plate. The extrudates were dried in a stationary ventilated oven at 120 °C for 3 h, subsequently the temperature was raised to the calcination temperature of 550 °C and kept for 3 h. The calcinated extrudates were broken and sieved.

Table 1
Structural and physical properties of CBV28014 and CBV901.

Properties	CBV28014	CBV901
Zeolite type	ZSM-5 in ammonium form	Zeolite H-SDUSY form
SiO_2/Al_2O_3 mole ratio (SAR)	280	80
Surface area (m^2/g)	400	700
Na_2O weight %	0.05	0.03

2.2.2. Adsorption kinetics

The adsorption kinetics of powder and extrudates were determined by adding 64 g/l zeolite to a solution of 10 g/l (1 wt%) of 1-butanol in water. Closed reaction vessels were stirred on a roller bank at room temperature (20 °C). After different time intervals, one vessel was removed, zeolite particles were separated by microfiltration, and the liquid samples were analyzed by GC-FID (CP-wax column) with diethylene glycol dimethyl ether (diglyme) as an internal standard. Adsorption loading was calculated from the initial and final concentration of 1-butanol in the aqueous phase.

2.2.3. Equilibrium isotherms

Different ratios of ABE model solution having 1.28 wt% of 1-butanol and CBV28014 extrudates (16–24 mesh size) were incubated on a roller bank overnight to allow adsorption to complete. 1-Butanol concentrations were determined as described in Section 2.2.2.

2.2.4. Desorption characteristics determined by TGA-MS

After adsorption in an aqueous solution of 1 wt% 1-butanol, zeolite extrudates were removed from the liquid with a metal sieve and 0.2–0.4 g was transferred to a TGA-MS apparatus (thermo gravimetric analyzer with an online mass spectrometer) to follow the desorption. In the TGA, the zeolite samples were slowly heated up and the weight loss was continuously monitored. For optimal desorption, the temperature was first increased to 45 °C, kept at this level for 20 min, and then further increased to 118 °C. Released compounds were swept away with a small argon flow and analyzed by online mass spectrometry. To prevent condensation of the compounds on the walls of the TGA or in the connector to the MS, these needed to be heated as well.

2.2.5. Column experiments

2.2.5.1. Adsorption. A glass column with a diameter of 1.08 cm was filled with 5 g of zeolite extrudates. In the case of down-flow, the column was continuously fed from the top with cell free ABE broth (a kind gift of A. Lopez-Contreras, AFSG Wageningen) containing 1.28 wt% 1-butanol, 0.4 wt% acetone and 0.03 wt% ethanol or with a model ABE solution, containing acetone, 1-butanol and ethanol in water in the same concentrations as in ABE broth. In the case of up-flow, the column was fed from the bottom by an HPLC pump with a flow controller. Aliquots of 3 ml were collected and analyzed as described in Section 2.2.2. This study was conducted at room temperature (20 °C).

2.2.5.2. Desorption. The desorption study was conducted in a glass column placed in an electrically heated oven. The column was filled with 1-butanol-loaded extrudates. The column temperature could be programmed using a PID controller. Argon gas was continuously passed through the column at 50 ml/min and the effluent was analyzed by online mass spectrometry. The *m*/*e* signals of 18, 31 and 56 were used for the quantification of water, 1-butanol and 1-butene, respectively. Prior to the experiment, the mass spectrometer was calibrated using argon saturated with water, 1-butanol or butene. The calibration factors were used to convert the specific ion mass fraction into mole fraction of the corresponding component.