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Adsorptive separations for the recovery and purification of biobutanol

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Abstract A conceptual adsorption process for the recovery and purification of biobutanol is proposed. Different porous materials are tested on their ability to perform the adsorptive separations relevant to the process. The metal-organic framework ZIF-8, silicalite zeolite and active carbon were compared with respect to their adsorption capacity of 1-butanol dissolved in water, as obtained in static and dynamic conditions by respectively batch and breakthrough measurements at room temperature. Batch experimentation showed that other compounds present in a real ABE fermentation have no significant effect on the adsorption of 1-butanol on ZIF-8. The breakthrough separation of 1-butanol from an aqueous ABE mixture was performed with a ZIF-8 packed column. The desorption of 1-butanol from a saturated ZIF-8 packed column by a stepwise increase of the temperature to 423 K in combination with a purge of a nitrogen gas (60 ml/min) shows that 1-butanol desorbs at low temperature from ZIF-8. Adsorption isotherms of ethanol, 1-butanol and water in liquid phase on the zeolite SAPO-34 were determined by batch adsorption at 298 K. Also the separation of an ethanol/1-butanol mixture and the removal of ethanol from 1-butanol could be achieved with a SAPO-34 packed column. From this experimental work, two materials—ZIF-8 and SAPO-34—thus emerged as suitable adsorbents for the recovery and purification of biobutanol by adsorption.

Keywords Adsorption · Alcohols · Recovery · ABE · Purification

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Nomenclature

$C_{0,i}$	initial concentration of component i (wt%)
$C_{eq,i}$	equilibrium concentration of component i (wt%)
$C_{in,i}$	concentration of component i at the inlet (g/ml)
L	length of column (cm)
m_{ads}	adsorbent mass after activation (g)
$m_{vl,o}$	total mass of external liquid phase before adsorption (g)
q_i	amount adsorbed of component i by the adsorbent column (g/g)
$x_{i,0}$	fraction of component i at time 0
$x_{i,t}$	fraction of component i at time t
v	interstitial velocity (cm/s)
ε	bed porosity
ϑ	micropore volume (ml/g)
ρ_i	density of component i (g/ml)
ρ_p	adsorbent particle density (g/ml)
τ_i	average breakthrough time of component i (s)

1 Introduction

The depletion of the oil reserves and the growing world population push the chemical sector continuously to develop alternative and sustainable processes that require less energy, that use another feedstock than petroleum, that have a low environmental impact and that exhibit a higher global efficiency. Alternative sources of chemicals like alcohols are gaining more and more interest as potential substitutes for fossil sources because they can be produced by the fermentation of renewable feedstock's (Antoni et al. 2007). The properties of 1-butanol—high energy density, viscosity, no corrosive and low volatility—make it a promising molecule. The fermentative production of butanol, called

Table 1 Adsorbent properties

Adsorbent	Supplier	Commercial name	Type	Class	T_{reg} (K)	Pore volume (ml/g)
ZIF-8	Sigma-Aldrich	Basolite^{TM} Z1200	MOF	SOD	403	0.60
Silicalite	Alsi-Penta	Silikalit	Zeolite	MFI	523	0.21
Active carbon	Chemivron	AP3-60	Coal	/	523	0.36
SAPO-34	Tiajin Chem. Sci.	SAPO-34/CTF-03	Zeolite	CHA	723	0.30

ABE (aceton-butanol-ethanol) fermentation, generates typically a mixture of acetone, 1-butanol and ethanol for only 2 wt% diluted in water (Liu et al. 2010). Preceding their utilization the different constituents must be separated. The development of cost-effective separation techniques is part of the major challenges in the production of alternative sources of chemicals and fuels to become economically viable (Garcia et al. 2011). Qureshi et al. (2005) and more recently Oudshoorn et al. (2009a, 2009b) compared different process designs, based on distillation, liquid-liquid demixing, freeze crystallization, pervaporation, reverse-osmosis, gas-stripping, extraction, perstraction or adsorption, to recover bio-butanol from the ABE fermentation broth. According to these assessments the adsorption based recovery was identified as the most energy efficient technique. Most of the studies have focused on the adsorption of 1-butanol from aqueous mixtures. A lot of different zeolites, polymeric resins and coals were tested to that purpose (Milestone and Bibby 1981; Maddox 1982; Groot and Luyben 1986; Nielsen et al. 1988; Regdon et al. 1994; Qureshi et al. 2005; Nielsen and Prather 2008; Oudshoorn et al. 2009a, 2009b; Saravanan et al. 2010). Few researchers also investigated the competitive adsorption of other compounds present in the fermentation. Bowen and Vane (2006) showed that acetic acid could reduce adsorption of ethanol on high silica zeolites. By increasing the pH the adsorption of reaction intermediaries, like butyric acid, could be prevented (Nielsen et al. 1988).

Thus a wide range of materials has already been tested for the adsorption of 1-butanol from aqueous mixtures. Less attention has been given to the removal of water and side-products from 1-butanol. Also a clear lack occurs in data from experiments in dynamic conditions and regarding desorption of 1-butanol from the adsorbents. Complete process designs for the separation of biobutanol are also scarce. Because of the potential of adsorption to perform highly selective and energy efficient separations, a conceptual process consisting of several adsorptive separations relevant to the recovery and purification of biobutanol is proposed in this paper. Different porous materials are studied for their ability to conduct these separations.

2 Material and methods

2.1 Materials

ZIF-8, silicalite and active carbon were compared in the separation of 1-butanol from aqueous mixtures. SAPO-34 was studied in the adsorption and separation of water and ethanol from 1-butanol. All these materials are commercially available and some of their properties are listed in Table 1.

The chemicals used in this study were all bought from Sigma Aldrich and all had a purity exceeding 99.7 %. Pure water was produced in the lab by a device that combines ion exchange, active carbon and filtration (SIMPAKOD2, Millipore).

2.2 Methods

2.2.1 Liquid phase batch adsorption

The batch adsorption technique was used to determine the adsorption capacities and adsorption isotherms in liquid phase (Denayer et al. 2003; Daems et al. 2005). Adsorbent samples (200 mg) were put in 10 ml glass vials and then heated at 1 K/min in a ventilated oven to a maximal temperature (see Table 1: T_{reg}). The samples were kept at their respective maximal temperature during 20 h. After cooling the adsorbent samples in a glove box under dry nitrogen atmosphere, liquid mixtures were added to the vials and well stirred. Liquid samples were taken after 16 hours and analysed by a gas chromatograph (GC) with a flame ionisation detector. The water concentration was determined by Karl Fisher (KF) titration (V30, Mettler-Toledo). The KF-liquids used were Solvent 5E Hydranal (Sigma Aldrich, Belgium). The adsorbed amount of adsorbate was calculated using the formula:

$$q_i = \frac{C_{0,i}.m_{vl,o} - C_{eq,i}(m_{vl,o} - \rho_i.\vartheta.m_{ads})}{m_{ads}}$$

2.2.2 Liquid phase breakthrough and desorption experiments

Liquid phase breakthrough experiments were performed with a high-throughput setup from ILS GmbH (Germany,

Berlin), described in detail by Duerinck et al. (2011). Pellets of 500–630 µm were packed into stainless steel columns of following dimensions: length: 14.8 cm, and internal diameter: 1.02 cm. The pellets were made by pressing preactivated adsorbent powder (see batch adsorption) with a hydraulic French press at 65 MPa into a cake. A mortar and a sieve were used to break the pellet cake into the desired pellet size fractions. The activation of the pellets was done under nitrogen flow (30 ml/min) by heating to 423 K at a rate of K/min, and maintaining this final temperature for 20 h. Afterwards the mixtures were pumped through the adsorbent columns at 303 K with a flow rate varying between 0.2 and 0.5 ml/min. Samples were collected at the column outlet and analysed by gas chromatography (Ultra-Fast Module GC Interscience, TCD detector, SGE SolGelWax capillary forte column). The adsorbed amount was calculated based on the material mass balance by using the following equation (Malek and Farooq 1997):

$$q_i = \left(\frac{v\tau_i}{L} - 1\right)\frac{\varepsilon}{1-\varepsilon}\frac{C_{in,i}}{\rho_p}$$

By assuming constant flow rate and pressure, the average breakthrough time is conventionally given by:

$$\tau_i = \int_0^\infty \left(1 - \frac{x_{i,t}}{x_{i,0}}\right) dt$$

Desorption of ethanol and 1-butanol was conducted in the same setup as used for the breakthrough experiments. Firstly a ZIF-8 packed column was saturated by pumping (0.5 ml/min) a mixture of ethanol (4 wt%), butanol (4 wt%) and water (92 wt%) through the column. Desorption of ethanol and 1-butanol from ZIF-8 was obtained by a stepwise increase of temperature in combination with a nitrogen flow (60 ml/min).

A series of breakthrough experiments was performed using a so called "ABE mixture". This mixture contains acetone, butanol and ethanol in water, as is obtained in a typical butanol fermentation process.

3 Results and discussion

3.1 A conceptual adsorption process

The aim of this research is to develop a highly selective and energy efficient process for the recovery and purification of biobutanol by several adsorption steps. The concept consists of three adsorptive separations (Fig. 1). In the first step the adsorption of 1-butanol from an ABE mixture on adsorbent 1 takes place. Subsequently, 1-butanol is desorbed from adsorbent 1 and collected to obtain a concentrated product wherein phase separation will occur. This two-phase system contains an upper phase of 80 wt% of 1-butanol and side-products and 20 wt% of water; the lower phase consists of

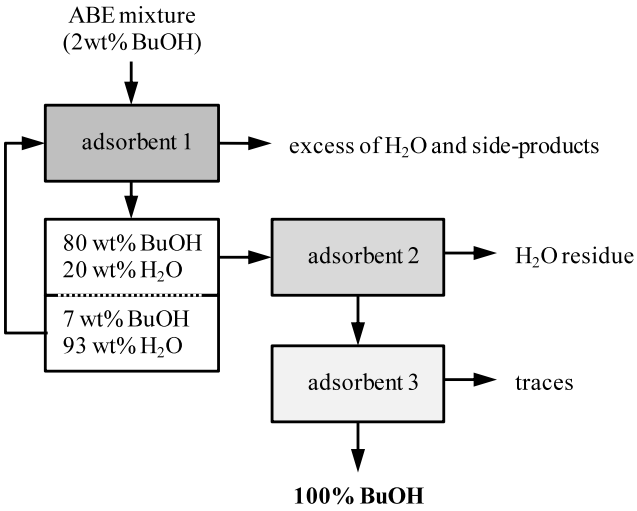

Fig. 1 A schematic diagram of the separation and purification of 1-butanol from an ABE mixture using several adsorbents

a mixture of products in water at a ratio of 7/93. The upper phase is pumped to adsorbent 2, while the lower is recycled through the first column. Adsorbent 2 will be used to adsorb the residue of water to produce a highly concentrated 1-butanol stream. In a final step, side-products and water traces still present are removed by adsorbent 3 to obtain pure 1-butanol at the outlet of the process. In this paper different adsorbent materials are tested for the separation and desorption in the first column (adsorbent 1) and for the purification of 1-butanol in the third column (adsorbent 3). Future work will be devoted to the separation of water from a concentrated biobutanol stream (adsorbent 2).

3.2 Adsorption of 1-butanol

3.2.1 Comparison of silicalite, active carbon and ZIF-8

The adsorption of 1-butanol from aqueous mixtures has been studied by batch and breakthrough experiments. The 1-butanol adsorption capacity obtained by both methods on silicalite, active coal and ZIF-8 are given in Fig. 2. Silicalite, being the reference in the literature for the uptake of 1-butanol from aqueous mixtures, clearly shows the lowest adsorption capacity of the three tested materials for 1-butanol in the static (batch) as well as in the dynamic (breakthrough) conditions. In static conditions active coal exhibits the same adsorption capacity for 1-butanol as ZIF-8, although it has a lower capacity than ZIF-8 in dynamic conditions. The differences in adsorption capacities between the batch and the breakthrough experiments are related to diffusion phenomena. The diffusion of 1-butanol in ZIF-8 seems fast enough to reach equilibrium under dynamic conditions. In the case of silicalite and active coal a slower diffusion results in a reduction in amount adsorbed 1-butanol in dynamic experiments, while the equilibrium capacity is reached in batch

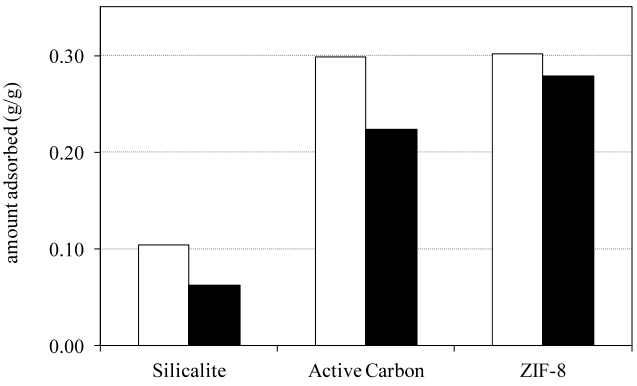

Fig. 2 Adsorption capacities of 1-butanol (4 wt%) dissolved in water on silicalite, active carbon and ZIF-8 at room temperature as determined from batch and breakthrough measurements (respectively *empty* and *filled bars*)

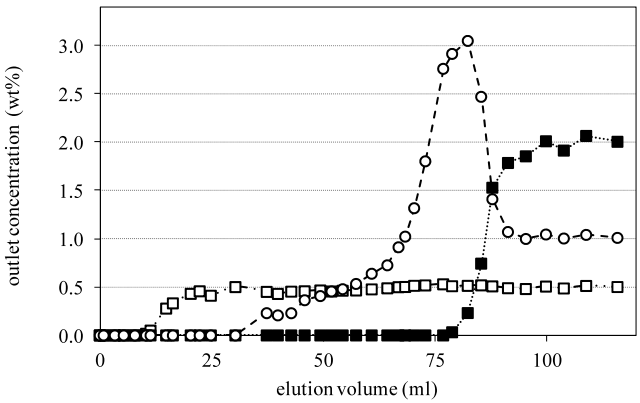

Fig. 3 Breakthrough profiles of (□) ethanol (0.5 wt%), (○) acetone (1 wt%) and (■) 1-butanol (2 wt%) diluted in water on a ZIF-8 packed column at 303 K and a flow rate of 0.5 ml/min

experiments as a consequence of the longer contact time. In this paper, we will further focus on the adsorption and desorption properties of the metal-organic framework ZIF-8.

3.2.2 Separation of 1-butanol from ABE mixture

The separation of 1-butanol from an ABE fermentation broth was assessed by pumping a model solution, consisting of acetone/1-butanol/ethanol with a total concentration of 3.5 wt% (ratio 3:6:1) diluted in water through a ZIF-8 packed column. The result of this breakthrough experiment is shown in Fig. 3. The three components are clearly separated from each other, with 1-butanol being preferentially adsorbed over ethanol and acetone. Apparently ZIF-8 can discriminate these three molecules based on their polarity, as ethanol is the most polar and 1-butanol the least polar molecule. Interestingly the breakthrough curve of acetone shows an overshoot indicating that acetone is adsorbing, but it is pushed out when 1-butanol enters the ZIF-8 pores, which results in a concentration of acetone at the outlet of the column. The amount adsorbed on ZIF-8 for ethanol, acetone and 1-butanol are respectively 0.006, 0.044 and 0.227 g/g. The total amount of product adsorbed corresponds closely to the adsorption capacities previously determined. The selectivities of 1-butanol over ethanol and acetone, being 10.2 and 2.6, shows that ZIF-8 is a promising adsorbent to separate the side-products from 1-butanol in aqueous environment.

3.2.3 Effect of nutrients and reaction intermediates on butanol adsorption

Real ABE fermentation broths are composed of cells of micro-organism, nutrients, reaction intermediates and the fermentation products (acetone, ethanol and 1-butanol). The direct contacting of these mixtures with the adsorbents may foul the adsorbents severely (Groot and Luyben 1986). To overcome this problem different techniques are possible to remove the cells and agglomerates present in the fermentation broth. Nielsen et al. (1988) and Yang and Tsao (1995) proposed to use a centrifugation or a micro/ultrafiltration unit upstream of the adsorption process to maintain high recovery efficiency. These methods will not retain small molecules, like salts, sugars or reaction intermediates. Therefore the adsorption of 1-butanol from aqueous mixtures has been studied in the presence of different salts, glucose, acetic acid and butyric acid by batch experimentation. The mixtures used for this purpose are specified in Table 2.

Table 2 Mixtures of 1-butanol (2 wt%) in water in presence of other fermentation compounds

No.	Compound	Concentration (g/l)
1	Butyric acid	2.0
2	Acetic acid	2.0
3	NaCl	0.01
4	$MgSO_4$	0.2
5	$MnSO_4$	0.01
6	K_2HPO_4	0.3
7	Glucose	60.0
Blank	/	/

The results of these experiments, as shown in Fig. 4, indicate that the adsorption of 1-butanol is not disturbed by the presence of other compounds in the aqueous mixture with the adsorbent ZIF-8. The effect of the deposition of salts crystals on the surface of the adsorbents and the repeatedly contact of the acids on the life time of the materials has not yet been considered.

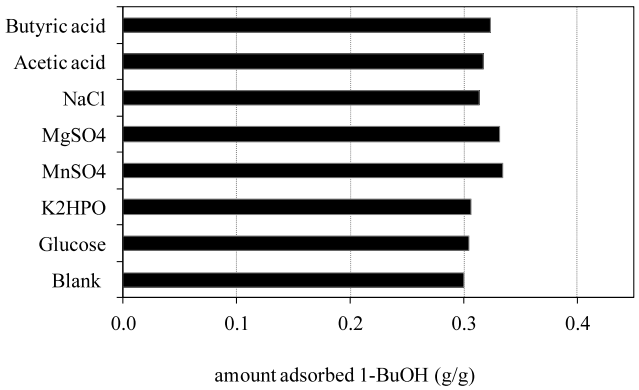

Fig. 4 Adsorption of 1-butanol from an aqueous mixture on ZIF-8 in the presence of different compounds typically present in the ABE fermentation broth

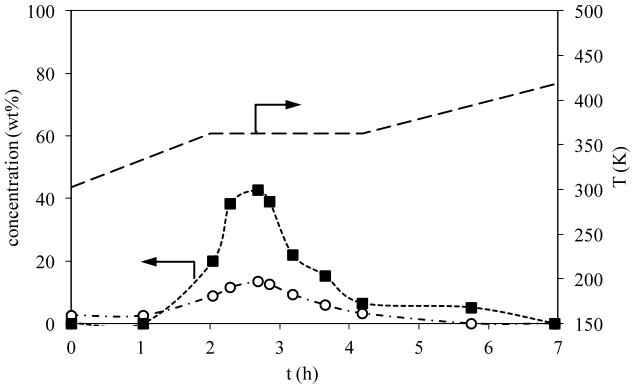

Fig. 5 Desorption profiles of (○) ethanol and (■) 1-butanol from column packed with ZIF-8 pellets obtained by a stepwise increase of temperature in combination with a nitrogen flow (60 ml/min). ZIF-8 was firstly saturated by pumping (0.5 ml/min) a mixture of ethanol (4 wt%), butanol (4 wt%) and water (92 wt%) through the column

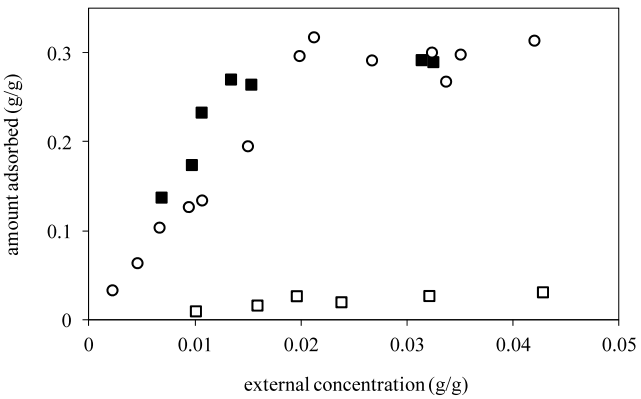

Fig. 6 Adsorption isotherms of (■) ethanol, (□) 1-butanol (diluted in iso-octane) and (○) water (diluted in acetonitrile) on SAPO-34 at 298 K

3.3 Butanol recovery by desorption

The desorption of the product from the adsorbent is often the most critical factor in the development of an adsorption process. Therefore an attempt was made to desorb 1-butanol from a ZIF-8 column by combining a stepwise increase of temperature with a nitrogen gas flow. Proceeding desorption, the ZIF-8 column was saturated with an ethanol/1-butanol aqueous mixture. Figure 5 shows the concentration profile at the outlet of the column. During the initial period only small amounts of ethanol and 1-butanol diluted in water are detected at the outlet of the column. After 1 hour, at 363 K, a concentrated mixture desorbed from the ZIF-8 column with maximal concentrations of 1-butanol and ethanol being 42.2 wt% and 13.5 wt%, resulting in a concentration factor of 10.6 and 3.4. Although the temperature was further increased to a maximum of 423 K no further products desorbed from the column in a significant amount. Undoubtedly, this desorption procedure could be improved by using other temperature profiles and desorbents (gases or liquids) or even by performing desorption at isothermal conditions. Nevertheless, this result indicates that the products can be efficiently desorbed and concentrated at low temperature from ZIF-8.

3.4 Purification of 1-butanol with SAPO-34 zeolite

3.4.1 Adsorption isotherms of ethanol, 1-butanol and water

Liquid phase isotherms of ethanol, 1-butanol (diluted in iso-octane) and water (diluted in acetonitrile) on SAPO-34 are given in Fig. 6. These three molecules exhibit a type I adsorption isotherm. The saturation adsorption capacities are 0.03 g/g for 1-butanol and 0.3 g/g for both ethanol and water. The isotherms point out that at low concentrations the pores of SAPO-34 are efficiently filled with the small molecules ethanol and water, while the larger molecule 1-butanol is almost fully excluded from the pores of SAPO-34 over the whole concentration range. This is in perfect agreement with the results obtained by Daems et al. (2007) and Remy et al. (2011) regarding the adsorption of 1-alcohols on chabazite type adsorbents. These studies highlighted the occurrence of a window effect resulting in a strong chain-length dependent adsorption and diffusion. The remarkable adsorption properties of SAPO-34 are of great interest for the purification of biobutanol, because ethanol and water traces must be removed to obtain pure butanol.

3.4.2 Separation of 1-alcohols from 1-butanol

Two cases are studied in this section. Firstly the breakthrough of a mixture consisting of ethanol and 1-butanol diluted in iso-octane has been investigated. Secondly breakthrough experiments were performed with a 1-butanol feed containing a small amount of a shorter 1-alcohol (methanol, ethanol or 1-propanol). Figure 7 shows the breakthrough profiles of ethanol and 1-butanol (diluted in iso-octane) on

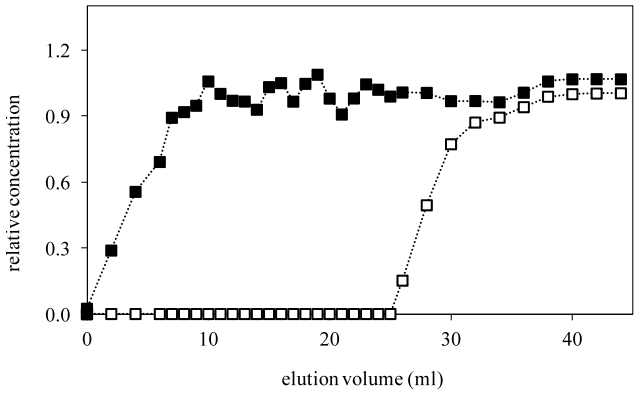

Fig. 7 Breakthrough profile of (□) ethanol (2 wt%) and (■) 1-butanol (2 wt%) diluted in iso-octane on column packed with pellets of SAPO-34 (500–630 μm) at 303 K (with feed flow rate of 0.2 ml/min)

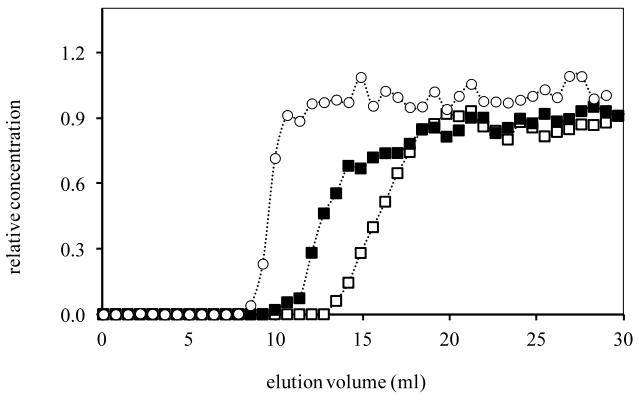

Fig. 8 Single compound breakthrough curves of (□) methanol, (■) ethanol and (○) 1-propanol at 10 wt% diluted in 1-butanol on column packed with SAPO-34 powder at 303 K with a feed flow rate of 0.5 ml/min

a column packed with SAPO-34 pellets. As expected from the adsorption isotherms and the results obtained by Remy et al. (2011), ethanol and 1-butanol are separated efficiently with a high selectivity towards ethanol. 1-butanol does not adsorb at all and leaves the column directly with the solvent, while ethanol adsorb in a significant amount (0.23 g/g), similar to that observed in the batch adsorption (0.27 g/g). More related to the proposed adsorption process is the removal of ethanol from a 1-butanol feed with a SAPO-34 column. This has been studied also by breakthrough experimentation. Single compound breakthrough measurements of small 1-alcohols diluted in 1-butanol are given in Fig. 8. The results indicate that smaller 1-alcohols can be removed efficiently from 1-butanol by adsorption on a SAPO-34 column. This observation shows that SAPO-34 has interesting sieving properties applicable in the purification of biobutanol.

4 Conclusions

From the experimental work two materials emerged—ZIF-8 and SAPO-34—to be suitable for the proposed adsorption process. ZIF-8 shows a high adsorption affinity and capacity for 1-butanol in an aqueous mixture, a high selectivity of 1-butanol over the side-products and easy desorption. The presence of other fermentation compounds in the aqueous mixture did not affect the adsorption of 1-butanol on ZIF-8. The second material, SAPO-34, adsorbs water and ethanol with high affinity, while 1-butanol is almost fully exclude from the pores. Accordingly a very selective separation of ethanol from 1-butanol with SAPO-34 was achieved. These results suggest that the combination of ZIF-8 and SAPO-34 is very attractive for the recovery and purification of biobutanol by adsorption.

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