

Adsorptive separation and recovery of biobutanol from ABE model solutions

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Abstract Adsorption is one of the most energy efficient techniques for butanol separation from dilute fermentation broths. To develop an efficient butanol adsorption process, adsorption and desorption are equally important since it is paramount to be able to desorb the adsorbed butanol to produce a high concentration butanol product. Although there are a good number of investigations done to find suitable adsorbents for this process, only few studies considered the desorption process. In this study, activated carbon F-400 was used as the butanol adsorbent since it has a high adsorption rate and capacity and is selective to butanol in the presence of other fermentation broth components. The thermal desorption process was performed in adsorption–desorption cycles both for butanol–water and acetone–butanol–ethanol (ABE) model solutions. The results for 1.5 wt% feed butanol–water binary solutions showed that the butanol adsorption capacity and the recovery of butanol were fairly constant (around 302 mg/g and 84 %, respectively) in subsequent adsorption–desorption cycles confirming that all the amount of adsorbed butanol is desorbed and the adsorption column could preserve its initial adsorption capacity in different cycles. Similar performance was obtained for butanol separation from the ABE model solution containing 1.2, 0.5, 0.2, 0.5, 0.5, 0.4 and 0.4 wt% butanol, acetone, ethanol, butyric acid, acetic acid, glucose and xylose, respectively. The adsorption capacity and recovery for butanol were 170 mg/g and 80 %, respectively.

Keywords Bio-butanol · ABE model solution · ABE fermentation · Adsorption · Desorption · Activated carbon · Biofuels

1 Introduction

Biofuels have attracted a lot of attention in recent decades as suitable alternatives for fossil fuels. Although fossil fuels are still the most common fuels being used, there are major concerns about replacing them with eco-friendly fuels produced from sustainable resources (Abdehagh et al. 2013, 2014; Thompson et al. 2011, 2014; Harvey and Meylemans 2011). Amongst the biofuels being studied, biobutanol is considered as one of the most promising since its characteristics are very similar to those of gasoline. Butanol's net heat of combustion (NHOC) of 29.2 MJ/L is close to the NHOC value of 32.5 MJ/L for gasoline (Abdehagh et al. 2013, 2014). In addition, butanol is less volatile, less flammable, less corrosive and thus safer to work with, in comparison to other biofuels. The other main benefit of butanol is its capability to be blended into gasoline in any proportion and can be used as a fuel in existing car engines without requiring modifications (Thompson et al. 2011, 2014; Harvey and Meylemans 2011; Shapovalov and Ashkinazi 2008; Fouad and Feng 2008; Dürre 2007; Qureshi et al. 2005; Qureshi and Blaschek 1999). Also, it can be transferred using existing pipelines and equipment that, as a result, reduces the investment and operating costs for biobutanol production processes significantly (Dellomonaco et al. 2010; Antoni et al. 2007; Ezeji et al. 2003, 2004, 2007). All these reasons have triggered the interest of industrialists and scientists to biobutanol as one of the best alternatives to gasoline.

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However, there are some issues in biobutanol production processes. The first issue is related to the butanol fermentation process, called acetone–butanol–ethanol (ABE) fermentation, in which butanol, as the main product of fermentation, is toxic to the microorganism. Approximately 10 g/L (1 wt%) butanol or total ABE concentration of 20 g/L (20 wt%), the inhibition starts due to the presence of butanol and the fermentation process stops (Thirnal and Dahman 2012; Harvey and Meylemans 2011; Oudshoorn et al. 2009; Zheng et al. 2009; García et al. 2009; Meagher et al. 1998). To partly alleviate this problem, there are a number of investigations being done to (1) genetically modify butanol-producing microorganisms to render them more tolerant to higher concentrations of butanol, and (2) to develop efficient *in situ* or *ex situ* separation methods to tackle the low butanol concentration in ABE fermentation broths (Faisal et al. 2014; Ying et al. 2013; Xue et al. 2012, 2013; Lu et al. 2012; Garcia-Chavez et al. 2012; Dhamole et al. 2012; Li et al. 2010; Ha et al. 2010). The present study focuses on the separation of butanol. Distillation, which is the traditional technique used to separate butanol from dilute ABE fermentation broths, is very energy-intensive and not economically viable. Liquid–liquid extraction, gas stripping, pervaporation and adsorption are other techniques that were proposed for the *in situ* or *ex situ* separation of biobutanol (Hecke et al. 2012, 2013; Lin et al. 2012, 2013; Yen et al. 2012; Wei et al. 2012; Li et al. 2011).

Adsorption is one of the most energy-efficient techniques to remove butanol from dilute solutions. To develop an efficient integrated adsorption process, it is necessary to use a suitable adsorbent for the specific application. There are some factors that should be considered in adsorbent screening: adsorption capacity, adsorption rate, selectivity for the desired component and ease of desorption. There are numerous studies in the literature about developing an efficient adsorption process for butanol separation using various adsorbents such as Ionic liquids (Rabari and Banerjee 2014), polyvinylpyridine (Yang et al. 1994), polymeric resins (Liu et al. 2014; Nielsen and Prather 2009; Nielsen et al. 1988; Groot and Luyben 1986; Maddox 1982), activated carbon (AC) and zeolites (Thompson et al. 2011; Sharma and Chung 2011; Saravanan et al. 2010; Holtzapple and Brown 1995; Sowerby and Crittenden 1988; Groot and Luyben 1986; Maddox 1982).

According to the results of these studies, zeolites and ACs have the highest adsorption capacity for butanol separation from dilute solutions (Abdehagh et al. 2013, 2014; Oudshoorn et al. 2012; Remi et al. 2011, 2012; Zheng et al. 2009; Takeuchi et al. 1995; Regdon et al. 1994a, 1994b). However, there are only few studies that have considered the effect of the presence of other components on butanol adsorption as well as the desorption process for the adsorbed butanol. In our previous study, the effect of the presence of

other compounds in ABE broths was investigated using AC F-400 since this adsorbent showed very high maximum adsorption capacity (around 300 mg/g) and high adsorption rate for butanol adsorption (Abdehagh et al. 2013). Results showed that this adsorbent is more selective to butanol in comparison to other compounds present in the ABE broths. In the case of butanol recovery, adsorption and desorption are equally important to produce solutions with high concentrations of butanol as the product. In addition, the capability of reusing the adsorbent for numerous separation cycles is equally important. However, desorption methods are not as well considered in the literature as adsorption is (Abdehagh et al. 2014; Faisal et al. 2014; Rabari and Banerjee 2014; Sharma and Chung 2011; Remi et al. 2011; Groot and Luyben 1986). Saravanan et al. (2010) have reported a desorption recovery of 80 % with the hypothesis that the rest of the butanol was strongly adsorbed and could not be desorbed using argon as the purge gas at a temperature of 150 °C and at higher temperature (more than 250 °C), butanol was desorbed as butene. Remi et al. (2012) have reported that the effluent of the desorption column had a butanol concentration of 43.3 % when the column was saturated with ethanol and butanol. The latter result did not change when they increased the temperature from 90 to 150 °C. In the present study, the butanol desorption process from butanol–water and ABE model solutions was investigated for numerous adsorption–desorption cycles to assess the performance of the process in long-term applications.

2 Materials and methods

2.1 Materials

To prepare butanol–water and ABE model solutions, n-butanol (99 % pure, Acros), acetone (95 % pure, Acros), n-butyric acid (99 % pure, Acros) and 99 % pure ethanol, acetic acid, glucose and xylose (Fisher Scientific Co., Fair Lawn, NJ) were used. Deionized distilled water was used to prepare all model solutions. The adsorbent used for this study was F-400 activated carbon (AC F-400) purchased from Calgon Corporation, Mississauga, ON, Canada, which showed the

Table 1 Some of the properties of activated carbon F-400 used as the butanol adsorbent in this study

Activated carbon F-400	
Shape	Granule
Surface area	1090 (m ² /g)
Mean particle diameter	0.55–0.75 (mm)
Mesh size	12 × 40
Micropore volume	0.43 (cm ³ /g)

best potential, among tested adsorbents, for butanol adsorption in our previous studies (Abdehagh et al. 2013). Table 1 shows some of the properties of this adsorbent.

2.2 Methods

2.2.1 Adsorption breakthrough experiments

Adsorption experiments were performed in a packed bed having an inner diameter of 0.02 m and a length of 0.195 m. For breakthrough experiments, the feed solution was pumped to the column using a peristaltic pump and samples of the effluent were taken at specific time intervals until the adsorbent bed reached complete saturation. The concentrations of butanol, ethanol, acetone, acetic acid, butyric acid and sugars in the solutions and samples were determined by high performance liquid chromatography (HPLC) (Waters, Canada). Figure 1a shows the schematic diagram of the experimental system used in this investigation for breakthrough adsorption experiments.

2.2.2 Thermal desorption experiments

When an adsorption experiment was complete and the column reached complete saturation, the column was carefully drained to remove the liquid present in the column. It was then placed in the desorption setup (Fig. 1b) within an oven, where a purge stripping gas (CO_2) was circulated through the column until the adsorbed

components were completely desorbed and the adsorbent was regenerated. The gas stream exiting the column during desorption was passed through a cold trap to condense the majority of the desorbed products.

The adsorption capacities were determined using the breakthrough curves by integrating the area above the breakthrough curve which is proportional to the total amount adsorbed in the column as expressed by Eq. 1.

$$q_i = \frac{t_i \times m_{\text{flow},i}}{m_{\text{adsorbent}}}, \quad (1)$$

where q_i , $m_{\text{flow},i}$ and $m_{\text{adsorbent}}$ represent the adsorption capacity for component i (g/g adsorbent), the mass flow rate for component i (g/s), and the mass of adsorbent (g) in the column, respectively.

The term t_i corresponds to the integration of the area above the normalized breakthrough curve (Eq. 2).

$$t_i = \int_0^\infty \left(1 - \frac{c_i}{c_{i0}}\right) dt, \quad (2)$$

where c_i and c_{i0} represent the outlet and inlet concentrations for component i (g/L), respectively.

2.2.3 Analytical method

The concentrations of butanol, ethanol, acetone, acetic acid, butyric acid, glucose and xylose were determined using HPLC. The HPLC used in this study was purchased from Waters, Canada. The detector, pump and auto-sampler were

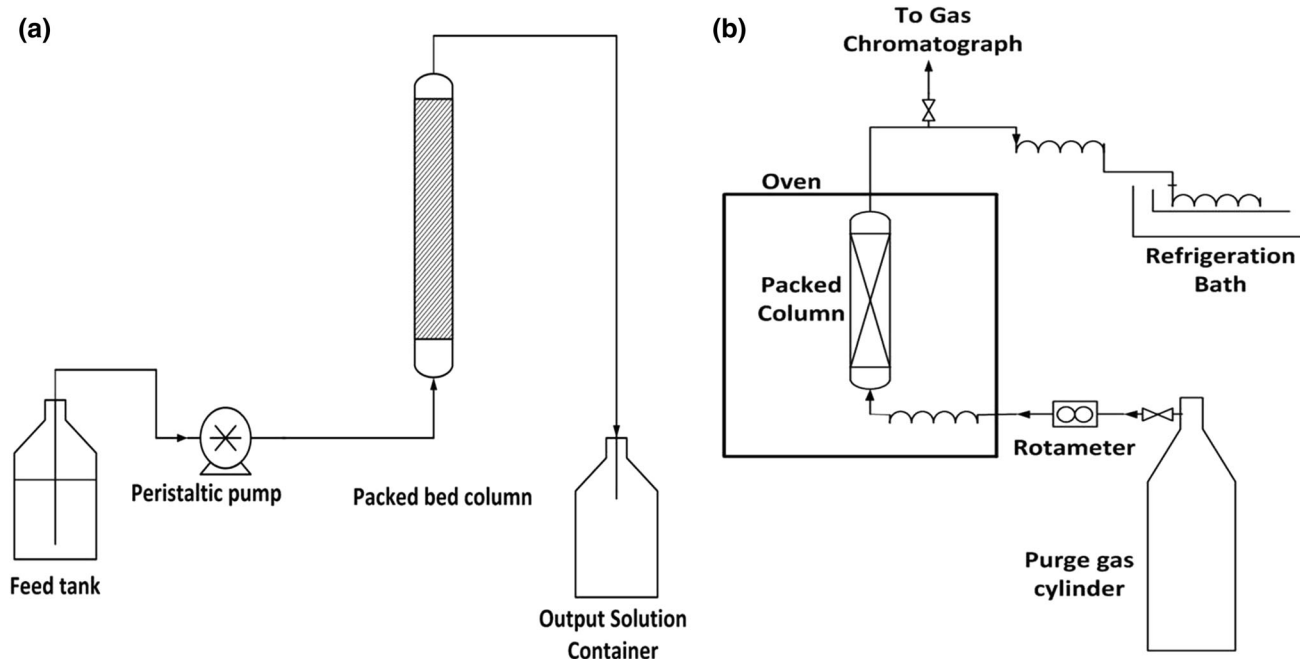


Fig. 1 **a** Schematic diagram of the adsorption experimental setup used for breakthrough adsorption experiments. **b** Schematic diagram of the desorption experimental setup used in this study

Refractive Index Detector (Waters 2414), Isocratic HPLC pump (Waters 1515) and Autosampler (Waters 717 plus), respectively. To heat the column to the desired temperature, an external column heater was used. The column used to detect the ABE solutions in this study was the Vertex column (300×8 mm, KNAUER, Germany) packed with Eurokat H, 10 μ m. The software used to operate the HPLC was Breeze purchased from Waters, Canada. The mobile phase used in HPLC analysis was 0.01 N sulfuric acid with a flow rate of 0.8 mL/min and the temperature of the column was kept at 85 °C. The experiments in this study were repeated once. More repetitions were considered in some minor experiments based on the results.

3 Results and discussion

3.1 Desorption process operating conditions

To select the operating conditions for the butanol desorption process, butanol–water model solutions with 1.5 wt% of butanol were used as the feed for the adsorption runs. After the column reached complete saturation, desorption runs were performed under different conditions. To find the optimum operating conditions for desorption experiments, different purge gas temperatures and flow rates were tested to achieve the highest butanol recovery. For an accurate operating condition optimization, it is desired to minimize the time of desorption, maximize butanol recovery, minimize the stripping gas temperature, minimize the amount of CO₂ used and to maximize the cold trap temperature. Obviously, for this multicriteria optimal problem it is not possible to find a unique solution to satisfy all these objectives simultaneously and a judicious compromise must be struck between all these objectives. However, it would be sufficient for our study to reach the highest butanol recovery. To find the best operating conditions based on the butanol recovery, a set of experiments was tested at different purge gas flow rates and temperatures to measure their impact on the achieved butanol recovery. The selected condenser temperature was determined by performing steady-state UniSim simulations to find the temperature at which most butanol would condense while trying to have the highest possible temperature.

The temperature of the purge gas was the first parameter to be tested, since it determines the most appropriate compromise between a high temperature for faster desorption and a low temperature for minimum heating requirements for the purge gas. The purge gas flow rate and the cold trap temperature were other parameters that were tested for the butanol desorption process. To find the suitable values of parameters, a series of experiments were performed and the results were compared. Five different

oven temperatures were tested: 100, 125, 150, 175 and 200 °C. It was found that at temperatures higher than 175 °C the recovery was constant at its maximum value (Fig. 2a). Different purge gas flow rates (20, 40, 60, 80, 100 mL/min) were also tested and it was observed that the highest recovery was obtained at a flow rate of 40 mL/min as shown in Fig. 2b. The corresponding purge gas superficial velocities were 0.001, 0.002, 0.003, 0.004 and 0.0053 m/s for the column size that was used.

To find the cold trap temperature, a simple simulation was performed using Honeywell UNISIM. The cold trap temperature was varied in the range from –40 to 20 °C to investigate its impact on the butanol recovery for an effluent purge gas stream containing a butanol:water mass ratio of 0.25:1 at atmospheric pressure. The fluid package used for this model was non-random two liquid model (NRTL) and was validated using vapour–liquid equilibrium data for butanol–water binary system (Khouri 2005). Figure 3 shows the predicted butanol recovery and mass fraction at different cold trap temperatures. It can be observed that the difference between the percentage recovery obtained at –40 and 2 °C is not significant with values of 100 and 98 %, respectively. It was also observed that the butanol mass fraction in the condensed phase obtained at –40, 2 and 20 °C were 0.25, 0.248 and 0.242, respectively. Even though there were some assumptions considered in Honeywell UNISIM simulations such as equilibrium conditions between the flowing gas phase and the condensed phase, 2 °C was selected as the experimental cold trap temperature since the difference between the recoveries at –40 and 2 °C was negligible (Rohani et al. 2014). This is justified considering the high energy requirement for low cold trap temperatures. Assuming thermodynamic equilibrium conditions implies that the rate of mass transfer from the flowing desorption gas and the cold trap walls is very high.

To find the optimum operating conditions for butanol desorption from ABE model solutions the same conditions (purge CO₂ gas flow rate of 40 mL/min (0.002 m/s) at 175 °C) were used for 6 h since based on the previous results, the desorption is almost complete within a few hours. For the purge gas temperature and flow rate in the next step of desorption, flow rates of 40, 60 and 80 mL/min at 185 and 200 °C were tested and it was observed that the highest butanol recovery was achieved at 60 mL/min (0.003 m/s) at 185 °C. The results showed that using these conditions would lead to a complete desorption of all components and the adsorption capacity of the adsorbent particles would be the same as its initial capacity afterwards.

3.2 Adsorption–desorption for butanol–water solutions

The desorption process were then used to perform a series of adsorption–desorption experiments using butanol–water

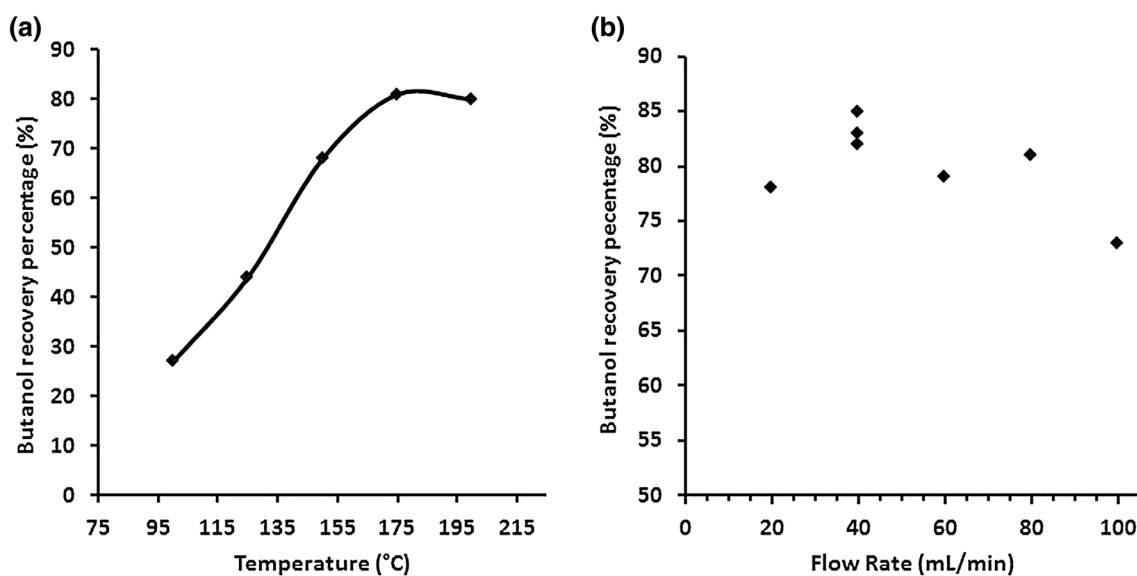


Fig. 2 Butanol desorption recovery results from butanol–water solutions for cold trap temperature of 2 °C for: **a** different purge gas temperatures at purge gas flow rate of 40 mL/min and **b** different purge gas flow rates at purge gas temperature of 175 °C

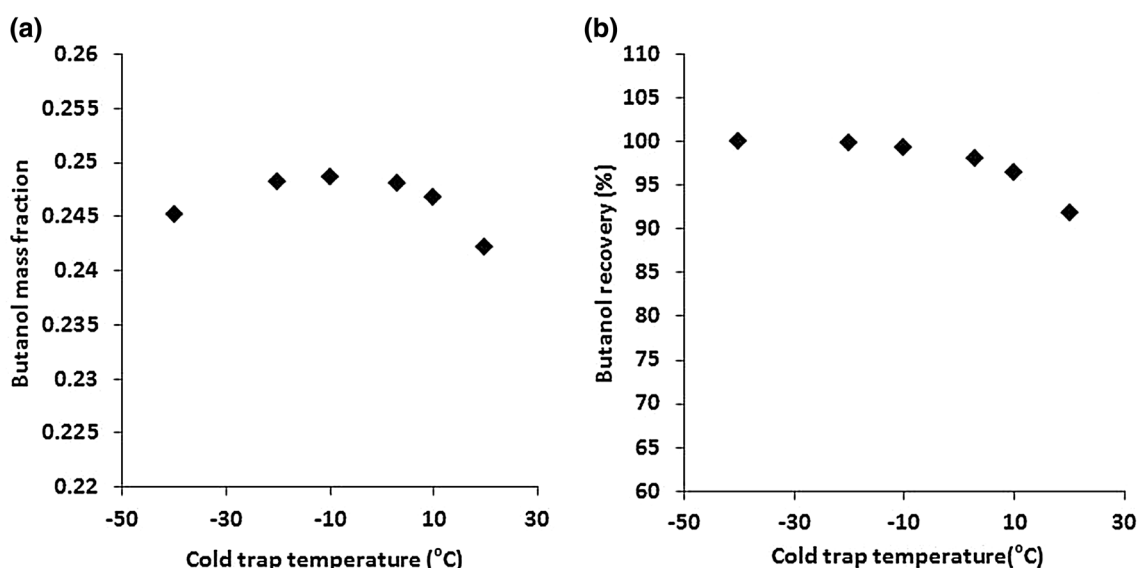
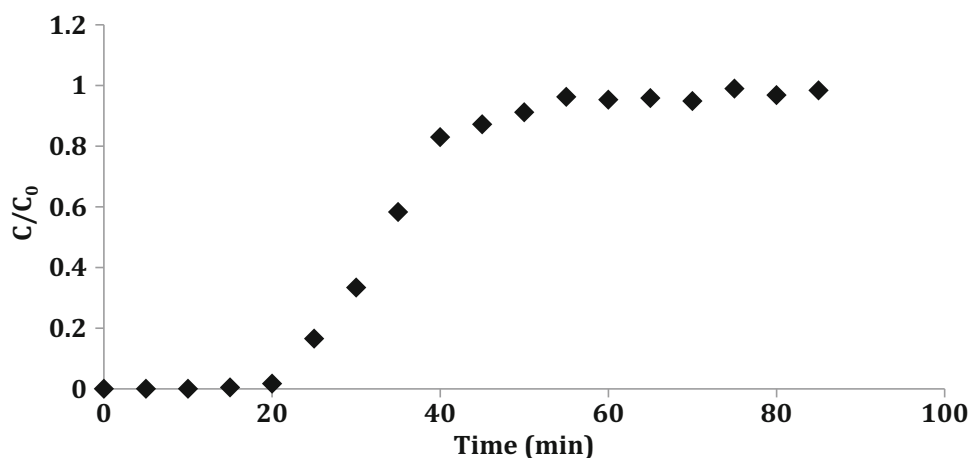


Fig. 3 Butanol mass fraction (**a**) and recovery (**b**) in the butanol desorption process from an effluent purge gas stream containing a butanol:water mass ratio of 0.25:1, using Honeywell UNISIM simulation

binary solutions. The concentration of butanol in the solution for the adsorption experiments was 15 g/L (1.5 wt%) which is typically the maximum butanol concentration that could be encountered in the ABE fermentation broths. After completion of the breakthrough experiment, the free liquid was allowed to drip off the column and then the saturated packed column was placed in the desorption setup and desorption was carried out for 24 h with a CO₂ purge gas passing through the column placed in an oven maintained at 175 °C. During the desorption experiments, samples of the condensed liquid phase

were taken at different time intervals and analyzed by HPLC. It was observed that after 15 h, desorption appears to be complete as no more condensate was collected in the cold trap. However, the purge gas continued circulating within the column to ensure that there is no more adsorbed component in the packed column. Using the breakthrough curve, the adsorption capacity was calculated using Eqs. 1 and 2 and the amount of butanol adsorbed was determined. For the adsorption breakthrough curve shown in Fig. 4, the estimated butanol amount adsorbed was 12.24 g and the adsorption capacity was 312 mg/g.

Fig. 4 Adsorption breakthrough curve for butanol–water solution at a flow rate of 24.4 mL/min at room temperature for activated carbon F-400



Following the completion of the adsorption breakthrough curve, desorption experiment was carried out at 175 °C with the purge gas flow rate of 40 mL/min (0.002 m/s) for 24 h. Results showed that 10.05 g of butanol was recovered. For this experiment, the ratio of the amount of recovered butanol to adsorbed butanol was 0.82 (g/g). Since the time given to one desorption experiment was definitely enough to displace all the compounds adsorbed onto the adsorbent particles, it was assumed that the unrecovered fraction of butanol is due to the cold trap conditions. The purge gas at the outlet of the column contains butanol and water in vapor phase which upon contact with the cold trap, the majority of butanol and water should ideally condense. However, this assumes that equilibrium between the purge gas stream and the walls of the cold trap prevails. The butanol recovery of 82 % is undoubtedly due to the loss of butanol and water being carried by the purge gas exiting the cold trap after the condensation. Ágüeda et al. (2013) used a cold trap temperature of −10 °C, 12 °C lower than that in this investigation, for desorption of butanol–water binary solution from silicalite pellets, for a butanol recovery of 95 %. Thus, although it is believed that the whole amount of adsorbed butanol in the column is desorbed, the condensed amount of butanol in the cold trap is less than the amount initially adsorbed onto the adsorbent surface in the column during adsorption. To investigate this phenomenon, subsequent cycles of adsorption–desorption experiments were performed.

Results obtained for the second adsorption–desorption cycle showed that the adsorption capacity was 294 mg/g and the recovery of butanol was 85.6 %. Since a slight decrease was observed in the adsorption capacity for the second cycle, a third cycle was carried out. The resulting adsorption capacity and the butanol recovery were 308 mg/g and 89.1 %, respectively. These results confirmed that the total amount of butanol adsorbed in each

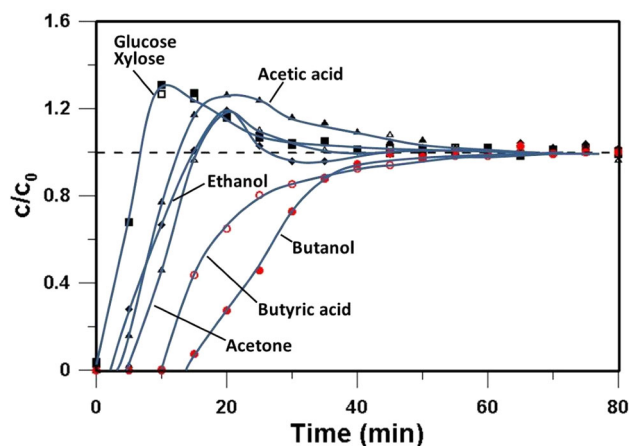
adsorption experiment was desorbed during the subsequent desorption cycle and the percentage recovery is relatively constant from cycle to cycle and the adsorption capacity is identical to the original adsorbent. Thus, these results reaffirm that the loss of butanol (between 10 and 18 wt%) is due to the incomplete condensation during the desorption process. In addition, the packed adsorption column preserved its initial adsorption capacity for several adsorption–desorption cycles.

To test the adsorbent lifetime and its capability to be used for numerous adsorption–desorption cycles, further adsorption–desorption cycles were carried out. A total of six adsorption–desorption experiments were carried out using the same adsorbent particles in the column. Table 2 presents the results of the six adsorption–desorption experiments. It can be observed that the adsorption capacity and percentage recovery are roughly identical for all cycles confirming that the AC F-400 is an excellent adsorbent for butanol separation since it has all the desired characteristics of a suitable adsorbent. AC F-400 has a very high adsorption capacity (293–312 mg/g) and adsorption rate. In addition, it is selective to butanol in the presence of other components (Abdehagh et al. 2013) and the desorption process can be completed using a thermal desorption method.

To improve the desorption process in increasing the recovery of the butanol, it would be possible to set a lower cold trap temperature as used by Ágüeda et al. (2013) but at the expense of higher cooling cost. It is believed that a better solution would be to re-heat and recirculate the purge gas stream exiting the cold trap to the packed column such that the amount of butanol, which did not condense in the cold trap, would not be discarded and the majority of the butanol would eventually condense in the cold trap. This would significantly increase the total percentage recovery. The current desorption system did not allow to recycle the exiting CO₂ stream.

Table 2 Results of the six adsorption–desorption cycles for butanol separation from butanol–water binary solutions using adsorption

Cycle	Initial butanol conc. (g/L)	Adsorption capacity (mg/g)	Butanol adsorbed (g)	Butanol desorbed (g)	Butanol conc. in desorbed phase (g/L)	Recovery (%)
1	15.1	312	12.2	10	302.2	82.1
2	15.4	294	11.6	9.9	279.2	85.6
3	15.1	308	12.1	10.8	293.4	89.1
4	15.2	303	11.9	9.8	272.9	82.3
5	14.9	293	11.5	9.4	259.3	82.0
6	15	306	12.0	9.7	260.6	81.0

**Fig. 5** Adsorption breakthrough curve for the ABE model solution at a flow rate of 24.4 mL/min at room temperature for activated carbon F-400

3.3 Adsorption–desorption for ABE model solutions

After testing numerous adsorption–desorption cycles for butanol–water binary solutions, the next step was to perform the adsorption–desorption processes for the ABE model solutions containing all of the main chemical components present in an actual ABE fermentation broth. The ABE model solutions contained butanol, acetone, ethanol, acetic acid, butyric acid, glucose and xylose at concentrations of 1.2, 0.6, 0.2, 0.5, 0.5, 0.4 and 0.4 wt%, respectively, as the feed into the column to carry out the adsorption runs.

Figure 5 shows the adsorption breakthrough curve obtained for the ABE model solution experiment performed with AC F-400. This figure shows that glucose and xylose breakthrough curves are nearly identical. Sugars, acetic acid, ethanol and acetone were adsorbed initially in the column and were later desorbed and displaced by butyric acid and butanol. This is the reason for the column exit concentrations of sugars, acetic acid, ethanol and acetone to exceed their concentrations in the feed upon desorption. For the AC F-400, butanol and butyric acid are preferentially adsorbed such that they will be adsorbed in the unsaturated part of the column and decrease to very low

concentrations outside of the butanol/butyric acid adsorption zone in the column and, of course, at the exit of the column. Because their concentrations are very low toward the exit in the column in fluid phase, the adsorption sites there can be occupied by the other chemical species until the adsorption zone of butyric acid and butanol reaches these adsorption sites and the other less selective molecules are displaced from the adsorbed phase.

For the breakthrough curves of Fig. 5, the final adsorption capacity for butanol, acetone, ethanol, acetic acid, butyric acid, glucose and xylose upon saturation of the column were 193.3, 25, 7, 4.5, 64.5, 0 and 0 mg/g, respectively. It was observed that in the presence of other compounds, the adsorption capacity of butanol decreased from around 300–170 mg/g and this decrease is mainly due to the presence of butyric and acetic acid according to our previous published results (Abdehagh et al. 2013). Based on the effluent concentration profiles of Fig. 5, it appears that glucose and xylose are first excluded from the adsorption sites by the other species that have greater adsorptive affinity. It seems that other components such as acetone, ethanol and acetic acid have displaced the sugars and, in turn, these components were excluded from the adsorption sites by the stronger affinity of butyric acid and butanol. These results will be confirmed by modelling of the breakthrough experiments, which is currently being conducted. After the completion of the adsorption of all the components in the fluid phase (i.e. after the complete saturation of the column), all the column outlet compositions return to the feed compositions for all the components in the system.

It is important to note that the final amount of sugar being adsorbed is estimated to be zero. This observation is important because if sugars were to occupy adsorption sites, they would not be desorbed with the hot purge gas and would accumulate in the column. The fact that the adsorption capacity is not altered from cycle to cycle confirms these results.

To ensure that the adsorption system can preserve its performance in subsequent cycles, the adsorption–desorption experiments were also performed for a total of seven

Table 3 Results of butanol adsorptive separation from the ABE model solutions for the 7 adsorption–desorption cycles

Cycle	Initial butanol conc. (g/L)	Adsorption capacity (mg/g)	Amount adsorbed (g)	Amount desorbed (g)	Butanol conc. in desorbed phase (g/L)	Recovery (%)
1	12	193.3	7.5	5.4	153.8	72
2	12	167.3	6.5	5.2	142.9	80
3	11.9	165	6.4	5	143.1	78
4	11.9	145.4	5.6	4.6	128.8	81
5	11.9	169.2	6.6	5.7	165.5	86.5
6	12	172.6	6.7	5.2	146.6	78
7	12	162.9	6.3	5.2	140.9	82.5

Table 4 Adsorption–desorption results for acetone, ethanol, acetic acid, butyric acid and sugars in 7 adsorption–desorption cycles for adsorptive butanol separation from the ABE model solutions

Cycle	Initial conc. (g/L)	Adsorption capacity (mg/g)	Recovery (%)	Cycle	Initial conc. (g/L)	Adsorption capacity (mg/g)	Recovery (%)
Acetone				Ethanol			
1	5.2	25.0	62	1	2.8	7.0	20
2	5.3	11.7	100	2	2.7	9.6	100
3	5.2	24.3	15	3	2.9	13.7	20
4	5.5	18.6	42	4	2.8	9.0	85
5	5.8	27.8	44	5	2.9	14.5	100
6	5.5	24.5	40	6	2.9	14.3	80
7	5.6	0.4	100	7	3.1	7.2	95
Acetic acid				Butyric acid			
1	4.9	4.5	100	1	5.1	64.5	74
2	4.9	9.7	80	2	5.2	49.5	96
3	5.0	7.2	75	3	5.2	49.4	96
4	5.1	3.9	100	4	5.4	44.7	100
5	5.2	5.1	100	5	5.1	57.8	67
6	5.0	8.9	66	6	5.1	51.7	90
7	5.1	8.7	100	7	5.2	58.9	100

cycles using the same adsorbent particles for the ABE model solution. Table 3 shows the results for butanol desorption from the ABE model solutions for these seven cycles. These results showed that although the butanol adsorption capacity slightly decreased in the second cycle, it was fairly constant for the next six cycles and the recovery obtained varied between 72 and 86.5 % in all seven adsorption–desorption experiments that were performed. For acetone, ethanol, acetic acid and butyric acid, the adsorption capacity and recovery were also constant in all seven adsorption–desorption cycles (Table 4). Traces of sugars were observed in the desorbed phase, which might be due to the liquid retained in the column after draining.

Table 3 shows that the adsorption process for butanol separation from a dilute ABE model solution was able to increase the concentration of butanol from 1.2 wt% (12 g/L) to approximately 15 wt% (150 g/L).

To improve the recovery of butanol, the same method applied for desorption of butanol–water binary solution could be implemented for the ABE model solution. Re-circulation of the purge gas from the cold trap to the packed bed column would prevent the loss of butanol as well as other solvents in the gas phase. However, it was concluded that during the desorption process, all of the adsorbed components were desorbed completely and the adsorbent particles preserved their adsorbent characteristics during the entire adsorption process, that is for the seven adsorption–desorption cycle experiments.

4 Conclusions

Although biobutanol has attracted a lot of attention as a biofuel to replace fossil fuels, there are significant issues in

its bioproduction process such as the separation methods used to remove and recover butanol from dilute ABE fermentation broths. Adsorption is one of the most efficient methods to separate butanol from dilute solutions. There are numerous investigations done to find the best adsorbent for this application. However, only few studies have investigated the desorption and recovery of butanol following the adsorption process. AC F-400 is one of the best adsorbents for this application since it has high adsorption capacity and high adsorption rate as well as being selective to butanol in comparison to other components present in the ABE fermentation broths.

In this study, butanol adsorption and desorption from butanol–water and ABE model solutions were investigated and it was found that a thermal desorption method is an efficient technique for the butanol separation and recovery process. In different subsequent adsorption–desorption cycles, the adsorption capacity of AC F-400 for butanol was between 293 and 312 mg/g and the butanol recovery varied between 81 and 89.1 % for butanol separation from butanol–water binary solutions. For butanol separation from the ABE model solutions the average butanol adsorption capacity and recovery were 170 mg/g and 80 %, respectively. It was observed that the adsorption capacity and recovery were fairly constant both for the butanol–water and the ABE model solutions. Thus, it was concluded that the whole amount of adsorbed butanol and other compounds were desorbed completely in each desorption experiment. The results confirmed that AC F-400 is one of the best adsorbents for butanol separation processes since in addition to the high adsorption capacity and adsorption rate, adsorbed butanol could be desorbed and recovered as a high butanol concentration product, using a thermal desorption process.

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