Adsorption (2013) 19:1263–1272
DOI 10.1007/s10450-013-9566-8

Adsorbent screening for biobutanol separation by adsorption: kinetics, isotherms and competitive effect of other compounds

N. Abdehagh · F. H. Tezel · J. Thibault

Received: 15 April 2013 / Accepted: 6 August 2013 / Published online: 18 August 2013
© Springer Science+Business Media New York 2013

Abstract Butanol, considered as one of the best renewable alternatives for gasoline, has attracted significant attention in recent years. However, biobutanol production via fermentation is plagued by the low final product concentration due to product inhibition. It is possible to enhance productivity by selectively removing biobutanol from the fermentation broth. Adsorption is one of the most promising and energy-efficient techniques for butanol separation and recovery. In the present study, different adsorbents were tested by performing kinetic and equilibrium experiments to find the best adsorbent for butanol separation. Activated carbon (AC) F-400 showed the fastest adsorption rate and the highest adsorption capacity amongst ACs and zeolites tested. AC F-400 also showed the highest affinity toward butanol and to a lesser extent for butyric acid whereas its adsorption capacity for the other main components present in acetone–butanol–ethanol fermentation broths was very low. In addition, the butanol adsorption capacity was not affected by the presence of ethanol, glucose and xylose while the presence of acetone led to a slight decrease in adsorption capacity at low butanol concentrations. On the other hand, the presence of acids (acetic acid and butyric acid) showed a significant effect on the butanol adsorption capacity over a wide range of butanol concentration and this effect was more pronounced for butyric acid.

Keywords Butanol adsorption · Adsorbent screening · Activated carbon · Zeolites · Kinetic and equilibrium experiments

N. Abdehagh · F. H. Tezel · J. Thibault (✉)
Chemical and Biological Engineering Department, University of Ottawa, 161 Louis Paster St., Ottawa, ON K1N 6N5, Canada
e-mail: Jules.Thibault@uottawa.ca

List of symbols

a	Equation constant (Eq. 2)
b	Langmuir constant, L/g
C	Butanol concentration at time t, g/L
C_0	Initial butanol concentration, g/L
C_e	Equilibrium butanol concentration in solution, g/L
k	Pseudo-second order Lagergren's rate constant, g/g min
M_{ads}	The amount of adsorbent used, g
n	Freundlich constant, (dimensionless)
q	Butanol adsorption capacity at time t, g/g
q_e	Butanol adsorption capacity at equilibrium state, g/g
q_s	Maximum butanol adsorption capacity, g/g
t	Time, min

Abbreviations

ABE	Acetone–butanol–ethanol
AC	Activated carbon
NHOC	Net heat of combustion
MWCNT	Multi-walled carbon nano tube

1 Introduction

Depletion of oil resources combined with the continuous rising of oil prices, political instability in oil-producing countries and environmental challenges are some of the reasons that have motivated significant interest for producing alternative biofuels from renewable and sustainable resources. Amongst these fermentation-derived fuels, butanol bioproduction is currently attracting attention given the advantages biobutanol has over other biofuels (Ezeji et al. 2004; Antoni et al. 2007; Dellomonaco et al. 2010). Butanol (C_4H_9OH) is a colorless liquid with a very low solubility in water and organic solvents (Thirmal et al. 2012). In recent decades, biobutanol has been considered as one of the most promising biofuels since it has enviable properties in comparison to other biofuels such as bioethanol. Higher energy density, better solubility in existing hydrocarbon fuels, net heat of combustion (NHOC) close to the one for gasoline, low vapor pressure and low corrosiveness are some of the advantages which make butanol easier to handle, transfer and work with (Ezeji et al. 2003; Dürre 2007; Fouad et al. 2008; Qureshi et al. 2005; Shapovalov et al. 2008; Harvey et al. 2011; Thompson et al. 2011). Acetone–butanol–ethanol (ABE) fermentation is the fermentative method used to produce butanol. The microorganisms used in this bioprocess are mostly anaerobic solventogenic clostridia including *Clostridium acetobutylicum* and *C. beijerinkii*. The feedstock used in ABE fermentation could be the low cost substrates such as algal biomass, soy molasses, wheat straw, corn stover, switchgrass and other agricultural wastes. Using these sources as feedstock will reduce the waste build-up that has been one of the serious concerns in recent decades (Ezeji et al. 2004; Zheng et al. 2009; Thirmal et al. 2012). The product of ABE fermentation is typically a mixture of acetone, butanol and ethanol with the ratio of 3:6:1 (by weight) and the butanol concentration in the broth is less than 2 wt% and usually in the order of 1 wt% (Meagher et al. 1998; Qureshi et al. 1999, 2005; Dürre 2007; Ezeji et al. 2007; García et al. 2009; Li and Parnas 2010; Harvey et al. 2011). Given the very low concentration of butanol and also the presence of other components in the fermentation broth, even at very low concentrations, the major challenge remains to develop a cost-effective technique to separate and recover butanol as the final product. Distillation is the traditional recovery technique used for butanol separation and it is still the technique that is widely used for this purpose. The energy requirement for butanol separation by steam stripping distillation (24.2 MJ/kg) is comparable to the butanol NHOC (36 MJ/kg) (Qureshi et al. 2005; Shapovalov et al. 2008; Harvey et al. 2011; Oudshoorn et al. 2009a). Thus, finding another technique with lower energy demand is very important to make the biobutanol production process economically viable. Other techniques used for butanol separation from fermentation broths include liquid–liquid extraction, gas stripping, perstraction, pervaporation and adsorption. According to different investigations, the energy requirement for adsorption is the lowest compared to other techniques, as shown in Fig. 1 (Qureshi et al. 1999, 2005; El-Zanati et al. 2006; Oudshoorn et al. 2009a; Tong et al. 2010).

An important number of studies have been carried out to separate and recover butanol from model solutions and aqueous mixtures. A wide range of materials such as activated carbon (AC), polymeric resins, polyvinylpyridine, zeolites are commonly used as butanol adsorbents from model solutions and fermentation broths (Maddox 1982; Groot et al. 1986; Nielsen et al. 1988; Sowerby et al. 1988; Yang et al. 1994; Holtzapple and Brown 1995; Nielsen 2009; Oudshoorn et al. 2009b, 2012; Saravanan et al. 2010; Sharma et al. 2011; Thompson et al. 2011; Remi et al. 2011, 2012). According to the results of these studies, zeolites and ACs have the highest adsorption capacity for butanol separation from dilute solutions (Regdon and Dekany 1994; Takeuchi et al. 1995; Regdon and Dekany 1994; Oudshoorn et al. 2009b; Zheng et al. 2009; Saravanan et al. 2010; Sharma et al. 2011). However, only a few studies were performed using different adsorbents to investigate the adsorption rate and the effect of other components present in fermentation broths (Nielsen et al. 1988). The studies carried out in the literature for different adsorbents tested for butanol separation using model solutions were mainly concerned with their adsorption capacity and less attention was devoted to other significant factors influencing the adsorbent selection. In the present study, different types of zeolites and ACs were tested in adsorbent screening experiments to investigate their performance as butanol adsorbents. The adsorption capacity and the rate of adsorption were measured for different adsorbents. In addition, the effect of the presence of other ABE broth components on butanol adsorption was also investigated.

2 Materials and methods

2.1 Materials

To test the adsorbents, a series of model solutions were prepared to simulate representative concentrations of the main chemicals present in a typical fermentation broth during the production of butanol. *n*-Butanol (99 % pure, Acros), acetone (95 % pure, Acros), *n*-butyric acid (99 % pure, Acros) and 99 % pure ethanol and acetic acid were obtained from Fisher Scientific (Fisher Scientific Co., Fair Lawn, NJ). Deionized distilled water was used to prepare all model solutions. The adsorbents tested in this study were ACs F-400 and F-600 (Calgon, Mississauga, ON, CA), zeolites NaY, ZSM-5 (CBV8014) and silicalite (Hisiv3000) (UOP, Des Plaines, IL, USA) and Multi-walled carbon nano tubes (MWCNT), 95+ % pure (MK Impex-Cor. Mississauga, ON, CA). Table 1 provides the list of adsorbents used in this study and some of their properties. The adsorbent properties were obtained from information provided by the companies or publications (Feirey et al. 2006; Harlick et al. 2004).

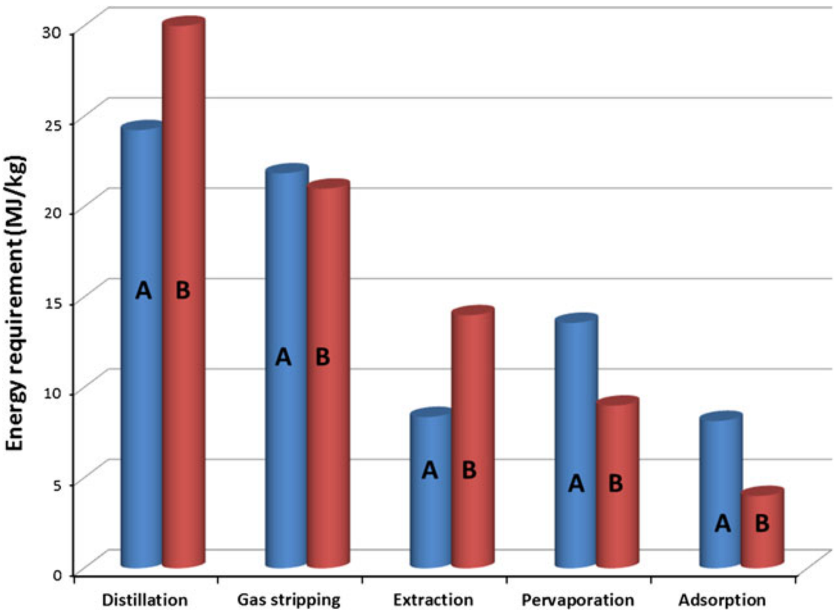

Fig. 1 Energy requirements for butanol separation from ABE broth. *A* for distillation, gas stripping, extraction, and pervaporation are reported in (Qureshi et al. 1999) but the details of the process are not reported. *B* for distillation: to increase butanol concentration from 1 to 99.99 wt% in the solution; *B* for gas stripping: to increase the butanol concentration to 50 wt%; *B* for extraction: to remove 75 % of butanol from the solution using oleyl alcohol as the extractant. *B* for pervaporation: to remove 25 % of butanol from the solution using silicone rubber as the membrane (Groot et al. 1992); *A* for adsorption: to remove butanol using silicalite as the adsorbent (Qureshi et al. 1999), and *B* for adsorption: the estimated energy required for butanol adsorption by Oudshoorn et al. 2009a)

Table 1 Different adsorbents tested in this study for butanol adsorption and some of their properties

Adsorbent	Shape	Surface area (m^2/g)	Mean particle diameter (mm)	Mean particle length (mm)	SiO_2/Al_2O_3	Mesh size	Mean pore diameter (nm)	Micropore volume (cm^3/g)
F-400	Granule	1,090	0.55–0.75	–	–	12 × 40	–	0.43
F-600	Granule	710	1	–	–	12 × 40	–	0.29
NaY	Rod	–	1.588	2.659	1.8	–	0.8	–
ZSM	Rod	425	1.6	12.11	80	–	0.6	–
Silicalite	Rod	400	1.6	2.86	>1,000	–	0.6	0.146
MWCNT	40–50	$>5 \times 10^{-5}$	$10–30 \times 10^{-3}$	–	–	–	–	–

2.2 Methods

2.2.1 *Kinetic experiments*

In kinetic experiments, the butanol adsorption rate was determined at room temperature for each adsorbent by recording the concentration in the aqueous phase throughout the experiment until thermodynamic equilibrium was achieved. Figure 2 shows the schematic diagram of the experimental system used in this investigation for both kinetic and equilibrium experiments.Aqueous solutions were prepared by adding known amounts of butanol and water in the Erlenmeyer flasks to obtain butanol–water solutions with different initial concentrations. The column was packed with a specific adsorbent. It is important to note that all experiments were conducted in the same column with a specific volume of 30 cm^3. However, based on the differences in the shape and density of the different adsorbents, the amount of materials needed to pack the column was different. The amounts of each adsorbent are provided in the figure legends specifically for each experiment. The butanol solution was pumped through the packed column and recirculated to the feed tank at a high flow rate to ensure a low solution residence time throughout the column to minimize the transient effects of the adsorption column. The comparative determination of the adsorption kinetics was performed in a packed column instead of in a shake flask in order to maintain the physical integrity of the adsorbent particles and alleviate particle attrition. The length and diameter of the packed column were 17.5 and 1.5 cm, respectively. Small samples of approximately 1 mL were periodically removed from the

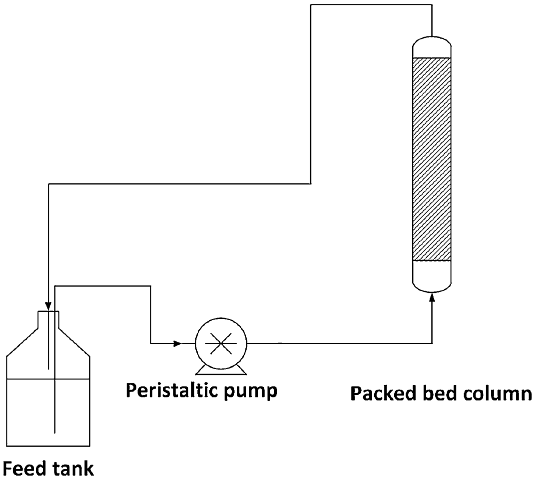

Fig. 2 Schematic diagram of the adsorption setup used for kinetic and equilibrium studies

Erlenmeyer flask and analyzed for butanol content. Using a simple mass balance, it was possible to estimate the amount of butanol adsorbed. The rate of change of butanol concentration in the flask was quantified. This allowed the estimation of the rate of adsorption.

2.2.2 *Equilibrium experiments*

For equilibrium experiments, adsorption runs were carried out with different initial butanol concentrations in model solutions. An aqueous solution containing known amounts of test chemicals was continuously re-circulated through the column until equilibrium was reached. After reaching equilibrium for different initial concentrations and determining isotherms of each adsorbent, the performance of all adsorbents in terms of adsorption capacities was compared. To perform butanol adsorption experiments with MWCNT as the adsorbent, batch experiments were used. 250 mL Erlenmeyer was loaded with specific volumes of butanol–water solution with known concentration. A certain amount of adsorbent was added to the flask. The flask was then placed in a shaker at room temperature to ensure mixing was adequate. The samples were filtered using a 0.45 μm filter before measuring the butanol concentrations. For the experiments of binary and ternary solution adsorption isotherms using AC F-400, the amount of adsorbent used varied between 13.5 and 13.8 g.

2.2.3 *Kinetic modeling*

A first-order kinetic equation (Eq. 1) and a pseudo-second order equation (Eq. 2) adapted from the Lagergren's pseudo-second order kinetic equation, were used to fit the experimental butanol concentration profile in the aqueous solution as a function of time. The time constant for each adsorbent was calculated according to these two kinetic models.

$$C = C_e + (C_0 - C_e)e^{-t/\tau} \qquad (1)$$

$$C = C_0 - \frac{a(C_0 - C_e)^2 t}{1 + a(C_0 - C_e)t} \qquad (2)$$

The time constant in both equations represents the time in which the butanol concentration in the aqueous solution decreased by 63.2 % of its total change ($C_0 - C_e$). For the calculation of the time constant, C_e was calculated from the curve fits of these two models to the experimental data. These experiments, done for different adsorbents, allowed comparison of the rate of butanol adsorption and determining the adsorbent with the fastest adsorption kinetics for butanol. The concentration of organic compounds in the solution was determined by high performance liquid chromatography (Waters, CA) using the ICPack column (Waters, Toronto, Canada).

Equations 1 and 2 modeled the variation of the butanol concentration in solution as a function of time. By a simple mass balance and knowing the amount of solids in the adsorption column, it is also possible to calculate the average amount of butanol adsorbed as a function of time. To model the kinetics of adsorption for each adsorbent, Eqs. 3 and 4 were used which are adapted from Eqs. 1 and 2, respectively. Equation 4 is the Lagergren's pseudo-second order equation which highlights the amount of adsorbate adsorbed in the solid, rather than the concentration change in the liquid phase and is usually used for modelling liquid adsorption from aqueous phase.

$$q = q_e(1 - e^{\frac{t}{\tau}}) \qquad (3)$$

$$\frac{t}{q} = \frac{1}{k{q_e}^2} + \frac{t}{q_e} \qquad (4)$$

2.2.4 *Equilibrium modeling*

An equilibrium isotherm equation was used to characterize the adsorption capacity of a specific adsorbent as a function of equilibrium concentration of the adsorbate in solution at a constant temperature. The isotherm model used in this study to fit the experimental data is the three-parameter Langmuir–Freundlich (Sips) model, given by Eq. 5. This isotherm model was selected since it showed better fits to experimental data compared to Freundlich and Langmuir isotherm models.

$$q_e = q_s \frac{b{C_e}^{1/n}}{1 + (bC_e)^{1/n}} \qquad (5)$$

3 Results and discussion

3.1 Kinetic results

Kinetic experiments were performed at room temperature with different adsorbents using water–butanol binary solutions with different initial concentrations to determine the dynamics of adsorption for each adsorbent. Determination of the time required to reach equilibrium and the initial uptake rate were the main objectives of this set of experiments. Figure 3 shows the results of the kinetic experiments for all adsorbents studied. Results revealed that for an aqueous solution with an initial butanol concentration of approximately 10 g/L, ACs F-400 and F-600 had much faster adsorption rates than the other adsorbents. By fitting the pseudo-second order equation (Eq. 2) to the experimental data and determining the time constant for all adsorbents, it was found that AC F-400 and F-600 had the lowest time constants (7.9 and 10.5 min, respectively), whereas this constant was much higher for other adsorbents specially for NaY which was 109.3 min. A first-order kinetic equation (Eq. 1) was also fitted to experimental data and it was found that the fits for both models were very good. Time constants given by these two equations are fairly similar for AC F-400, F-600 and silicalite. On the other hand, for ZSM-5 and NaY, the difference between calculated time constants for these two different models is significant (see Table 2) and this is due to the difference in the model structure and the number of parameters present in these models. The coefficient of determination (R^2), calculated for both Lagergren's pseudo-second order and the first-order kinetic equations, revealed that both of these equations can be used with confidence to model the kinetic behavior of the butanol adsorption system using all of the tested adsorbents (Table 2), with first-order kinetics having slightly lower (R^2) values. Figure 3 shows the results of the Lagergren's pseudo-second order equation fits to the experimental data for 10 g/L initial butanol concentration. Similar experiments were performed for other initial concentrations and all results showed the same trend.

The kinetic data for each adsorbent were fitted with Eq. 3 and Lagergren's pseudo second order model (Eq. 4) and Fig. 4 shows the results for the Lagergren's model since it had a slightly better fit. As clearly shown in Fig. 4, the model is a very good fit for the experimental data. Regardless of the amount of butanol adsorbed, the initial uptake rate and the time required to reach equilibrium is fairly similar for the ACs AC F-400 and F-600. In both experiments, the equilibrium state is reached in more or less 150 min whereas the initial uptake rate for NaY and ZSM-5 is significantly slower. For silicalite, the initial uptake rate was higher than the other two zeolites but slower than the ACs uptake rate. Table 3 shows the kinetic parameters obtained by fitting Lagergren's pseudo second order model to the experimental data for each of the adsorbents studied.

3.2 Adsorption equilibrium isotherms for water–butanol binary solutions

Adsorption equilibrium isotherms were used to compare the capacity of different adsorbents for butanol adsorption. As it was observed in kinetic experiments, equilibrium was reached in less than 2.5 h for ACs F-400 and F-600. To err on the safe side, 4-h runs were conducted for the determination of equilibrium data points for these two adsorbents. For the other adsorbents, 7-h experiments were carried out to reach the equilibrium state. Figure 5 shows the adsorption isotherms at room temperature for each of the adsorbents studied. This figure clearly shows that AC F-400 has the highest butanol adsorption capacity in comparison to other adsorbents. For example, at a 10 g/L butanol

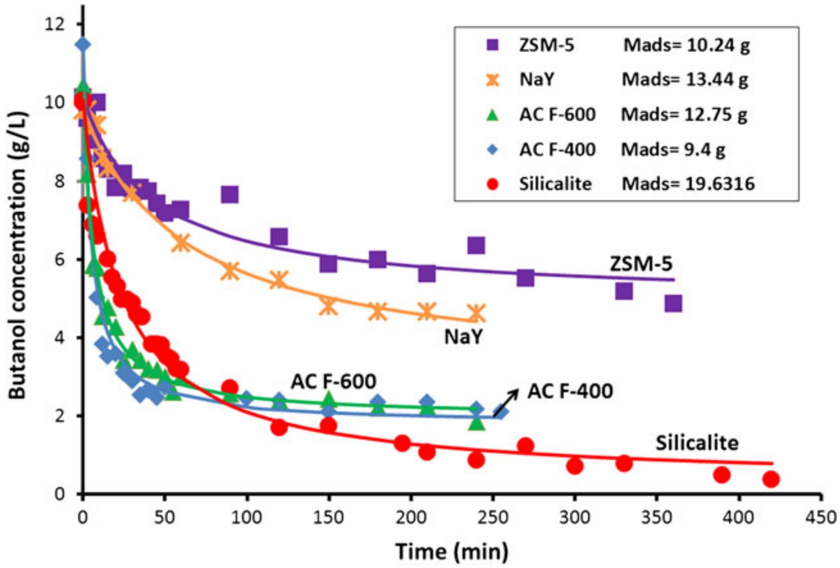

Fig. 3 Butanol–water adsorption kinetics at room temperature for 10 g/L initial butanol concentration; *Symbols* represent experimental data and the *lines* are predictions using the Lagergren's pseudo-second order equation (Eq. 2) (The solution volume was 0.2 L for all experiments)

Table 2 Time constants and coefficients of determination using the first-order and pseudo second order kinetic equations for each adsorbent

Adsorbent	Time constant first-order equation[a], Eq. 1 (min)	R^2	Time constant pseudo-second order equation, Eq. 2 (min)	(R^2)
AC F-400	7.6	0.989	8.2	0.973
AC F-600	9.6	0.952	11.3	0.986
Silicalite	32.5	0.927	39.2	0.970
ZSM-5	47.5	0.884	71.5	0.920
NaY	59	0.992	109.3	0.990

[a] The time represents the time required to achieve a butanol concentration corresponding to 63.2 % of its total change ($C_o - C_e$)

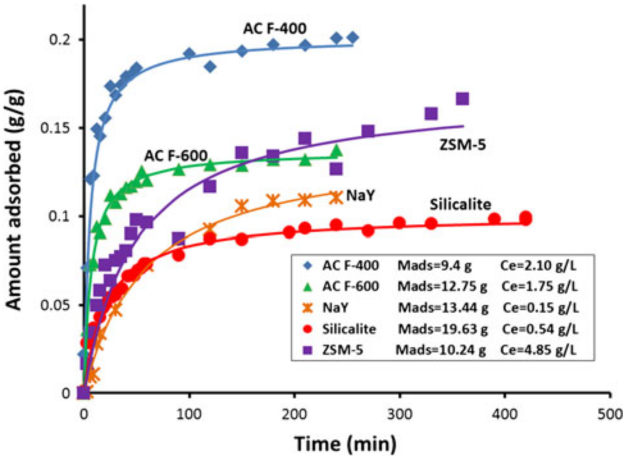

Fig. 4 Butanol–Water adsorption kinetics at room temperature with different adsorbents. *Symbols* represent experimental data and the *lines* are fitted kinetic model for Lagergren's pseudo-second order equation

concentration at equilibrium, the butanol adsorption capacity for AC F-400 is 258 mg/g, while it is 149, 139, 107 and 103 mg/g for AC F-600, ZSM-5, NaY, and silicalite, respectively. Interestingly, the adsorption capacities of AC F-400 and AC F-600 are quite different. This difference in adsorption capacities would be due to different raw materials or methods used in preparation processes for these two ACs. MWCNT was also used as butanol adsorbent for a 30 g/L butanol–water solution in a batch experiment and, as shown in Fig. 5, the butanol adsorption capacity obtained was very low (24 mg/g). It should be noted that to reach the equilibrium state, the experiment was run for 96 h and the equilibrium concentration was obtained at 24 h and did not change for the subsequent 3 days. For the three different types of zeolites tested in adsorbent screening experiments, it was observed that ZSM-5 had higher adsorption capacity for butanol in comparison to NaY. This higher adsorption capacity would be due to its higher SiO_2/Al_2O_3 ratio and/or due to different structures of these two zeolites. Increasing SiO_2/Al_2O_3 ratio increases the hydrophobicity of zeolites and since zeolitic hydrophobic adsorbents have higher selectivity for organic compounds over water, it is desired to use a zeolite with higher silica to alumina ratio for butanol adsorption. These hydrophobic zeolites have also some favourable characteristics such as homogeneity, low heat capacity and stability (Oudshoorn et al. 2009b). Accordingly, the experimental results showed that ZSM-5 with the SiO_2/Al_2O_3 ratio of 80 had higher butanol adsorption capacity in comparison to NaY with the SiO_2/Al_2O_3 ratio of 1.8 over the whole range of butanol concentration. Silicalite which has the same structure as zeolite ZSM-5 with a SiO_2/Al_2O_3 ratio of more than 1,000 was another adsorbent tested in this study. Interestingly, it was observed that although at low butanol concentrations the adsorption capacity of silicalite was higher than that for ZSM-5, at higher butanol concentrations, ZSM-5 showed higher capacity to adsorb butanol (Fig. 5).

In Fig. 5, the representation of the isotherms using the Sips adsorption model (Eq. 4) is also plotted. The Sips model was the one that represented the experimental isotherms the best.

It is clear from the adsorbent screening results (kinetics and equilibrium experiments) that AC F-400 is the best adsorbent amongst the different adsorbents tested in this study. This adsorbent showed the highest butanol adsorption capacity and also had the fastest adsorption kinetics.

3.3 Isotherms of binary solutions of water and other ABE fermentation components

To investigate the adsorbent selectivity toward butanol compared to other components present in the ABE broths, the isotherm experiments with binary solutions of water and each of the components (acetone, ethanol, glucose, xylose, acetic acid and butyric acid) were performed with AC F-400 and the results are presented in Fig. 6. Results clearly show that AC F-400 had a much higher selectivity toward butanol compared to other components. For example, at a concentration of 10 g/L of each component in the aqueous solutions at equilibrium, the adsorption capacities for butanol, butyric acid, acetone, acetic acid, glucose, xylose and ethanol were 294, 256, 115, 100, 96, 88 and 55 mg/g, respectively. Although the amount of

Table 3 Kinetic parameters for Lagergren's pseudo second-order model for 10 g/L initial butanol concentration

Adsorbent	k [(g ads) (g BuOH^{-1})(day^{-1})]	q_e (g BuOH/g Adsorbent)	R^2
Activated carbon F-400	1,206	0.206	0.97
Activated carbon F-600	1,536	0.137	0.99
ZSM-5	173	0.171	0.95
NaY	177	0.140	0.99
Silicalite	686	0.1	0.99

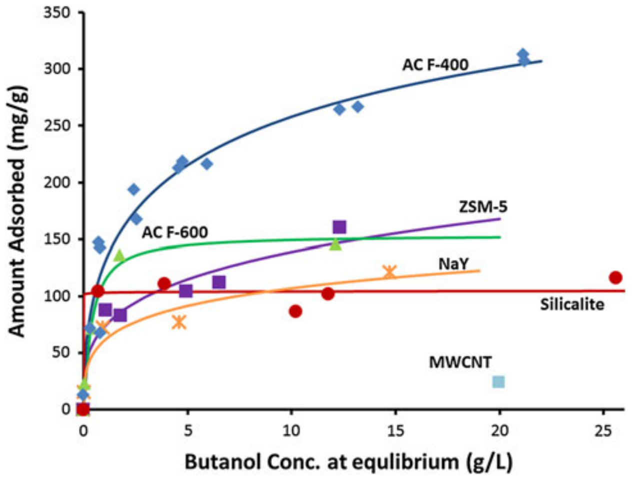

Fig. 5 Adsorption isotherms for different adsorbents at room temperature. *Symbols* represent experimental data and the *lines* are fitted Sips adsorption isotherm model

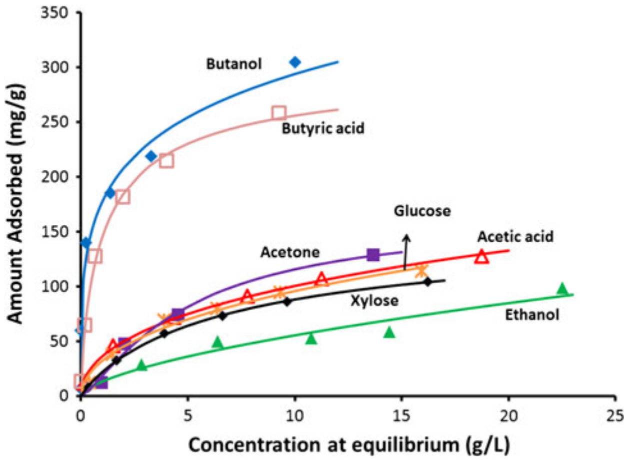

Fig. 6 Adsorption isotherms for different components using AC F-400 at room temperature. *Symbols* represent experimental data and the *lines* are fitted Sips adsorption isotherm model

butyric acid adsorbed is much higher than acetone, ethanol, acetic acid and the sugars amounts, it was still less than the amount of butanol that was adsorbed by the AC F-400. Overall, the results of this set of experiments showed that AC F-400 is more selective toward butanol and has a higher affinity for this component over the other compounds in ABE broths. From the results obtained in all adsorbent screening experiments, it can be concluded that it is possible to achieve high performance adsorption of butanol using AC F-400. The results showed that using AC F-400, it is possible to achieve a higher capacity of adsorption in a shorter time in comparison to other adsorbents tested. Thus, AC F-400 was selected in this investigation to be studied further.

3.4 Isotherms of ternary solutions of water, butanol and other components of ABE broths

To investigate the effect of the presence of other ABE fermentation broth components on butanol adsorption, experiments were performed to study the effect of each component separately with AC F-400 as the adsorbent. Thus, ternary mixtures were prepared, starting with acetone being the next most abundant product in ABE fermentation broths as well as ethanol, glucose, xylose, butyric acid and acetic acid. Equilibrium adsorption experiments were performed with various concentrations of these various ternary solutions. Figure 7a shows butanol isotherms obtained for butanol–water binary solutions, ternary solutions of butanol–water with 5 g/L initial concentration of acetone, and acetone–water binary solutions. Results showed that the presence of acetone does not affect butanol adsorption significantly. As the figure shows, there is a slight decrease of adsorption capacity at low equilibrium concentrations of butanol. This small decrease in adsorption capacity could be due to competitive adsorption of acetone at lower butanol concentration. Figure 7b shows that the presence of ethanol does not affect butanol adsorption over the whole range of butanol equilibrium concentration. As ethanol adsorption isotherm revealed, the adsorbent affinity for ethanol is very low and the probability of competitive effect of ethanol on butanol adsorption is low. The same effects were observed in the presence of glucose and xylose in Fig. 7c, d. The results showed that even 10 g/L initial concentration of glucose and xylose did not affect the amount of butanol adsorbed for all butanol concentrations. However, the presence of acids (acetic acid and butyric acid) led to a decrease in butanol adsorption capacity and

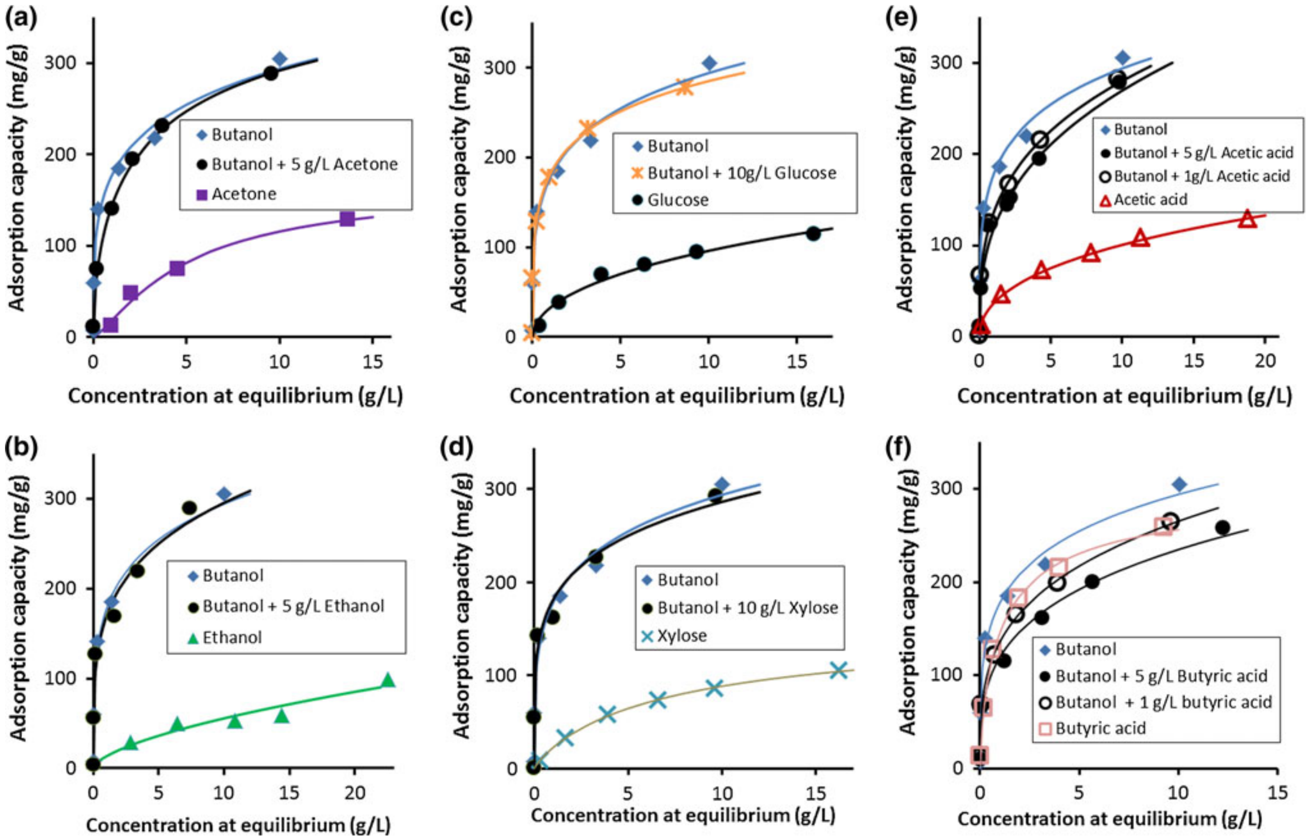

Fig. 7 The effect of the presence of other components on butanol adsorption using activated carbon F-400: **a** acetone; **b** ethanol; **c** glucose; **d** xylose; **e** acetic acid; **f** butyric acid. *Symbols* represent experimental data and the *lines* are fitted Sips isotherm model

this effect was more significant for the presence of butyric acid as shown in Fig. 7e, f. Figure 7e shows that the presence of 1 g/L initial acetic acid decreased the butanol adsorption capacity by 19 % and this effect became more significant when 5 g/L of acid was added to butanol–water solutions (26.5 % decrease). The effect of the presence of butyric acid was even more pronounced than the effect of acetic acid. As Fig. 7f shows, butanol adsorption capacity decreased significantly in the presence of 1 and 5 g/L butyric acid. The adsorption capacity decreased by 19.5 and 28.8 % in the presence of 1 and 5 g/L butyric acid, respectively. These results nevertheless show that the competitive adsorption appears to favor butanol.To develop an integrated process for butanol adsorption, two strategies can be considered. The first one is the in situ product recovery in which butanol would be removed while the fermentation is in progress. In the second strategy product recovery would be implemented at the end of the fermentation. Favorable characteristics of AC F-400 such as high adsorption rate, capacity and affinity for biobutanol make this adsorbent one of the best candidates for butanol separation from ABE fermentation broths using both strategies.

4 Conclusions

Amongst different butanol separation techniques, adsorption can be considered as a promising and energy efficient technique. Adsorption performance mainly depends on the adsorbent used in the process, and adsorption rate and capacity are two important characteristics that should be taken into account in selecting a suitable adsorbent. In this study, by performing the adsorbent screening experiments, these two characteristics were investigated for different adsorbents. Results from the kinetic experiments indicated that ACs F-400 and F-600 had the fastest kinetics for butanol adsorption amongst the tested adsorbents. According to the equilibrium experimental results, AC F-400 had the highest adsorption capacity for butanol. Interestingly, there was a huge difference between AC F-400 adsorption capacity and all other adsorbents capacity for butanol adsorption. To ensure that AC F-400 is suitable for butanol adsorption, its selectivity toward the main components of ABE broths was investigated and it was confirmed that this adsorbent had the highest affinity for butanol adsorption and to a lesser extent for butyric acid whereas the adsorption capacity for other fermentation broth components was very low. The fast kinetics and the favorable adsorption model indicate the ability of this adsorbent to reach a high adsorption capacity even at low butanol concentrations. Thus, AC F-400 was selected as the adsorbent and further experiments were performed to investigate the effect of the presence of other components in ABE broths. The results showed that the presence of ethanol and sugars (glucose and xylose) did not have any effect on butanol adsorption and the presence of acetone slightly decreased the butanol adsorption capacity at low butanol concentrations. However, the presence of acids affected the adsorbent capacity significantly for butanol and this effect was more pronounced for the presence of butyric acid. These results show that acids compete with butanol to be adsorbed on the adsorbent surface. Future works are planned to couple ABE fermentation with an adsorption unit to selectively remove butanol during the course of fermentation to reduce product inhibition. Also, it is essential to investigate butanol desorption to ensure that butanol can be desorbed efficiently and economically. To gain a deeper understanding of the interactions between different species, breakthrough experiments will be performed in addition to desorption experiments in the future. The complete performance assessment of butanol adsorption using AC F-400 will allow us to design a high performance process to produce a high butanol concentration product from dilute ABE fermentation.

Acknowledgments The authors would like to thank University of Ottawa and Natural Sciences and Engineering Research Council of Canada (NSERC0 for their financial contributions for this study.

References

Antoni, D., Zverlov, V.V., Schwarz, W.H.: Biofuels from microbes (mini review). Appl. Microbiol. Biotechnol. **77**, 23–35 (2007)

Dellomonaco, C., Fava, F., Gonzalez, R.: The path to next generation biofuels: successes and challenges in the era of synthetic biology. Microb. Cell Fact. **9**, 3 (2010)

Dürre, P.: Biobutanol: An attractive biofuel. Biotechnol. J. **2**, 1525–1534 (2007)

El-Zanati, E., Abdel-Hakim, E., El-Ardi, O., Fahmy, M.: Modeling and simulation of butanol separation from aqueous solutions using pervaporation. J. Membr. Sci. **280**, 278–283 (2006)

Ezeji, T.C., Qureshi, N., Blaschek, H.P.: Production of acetone, butanol and ethanol by *Clostridium beijerinckii* BA101 and in situ recovery by gas stripping. World J. Microbiol. Biotechnol. **19**, 595–603 (2003)

Ezeji, T.C., Qureshi, N., Blaschek, H.P.: Butanol fermentation research: Upstream and downstream manipulations. Chem. Rec. **4**, 305–314 (2004)

Ezeji, T.C., Qureshi, N., Blaschek, H.P.: Bioproduction of butanol from biomass: from genes to Bioreactors. Curr. Opin. Biotechnol. **18**, 220–227 (2007)

Feirey, J.L., Speitel, G.E. Jr, katz, L.E.: Impact of natural organic matter on reduction by granular activated carbon: The role of porosity and electrostatic surface properties. Environ. Sci. Technol. **40**, 4268–4273 (2006)

Fouad, E.A., Feng, X.: Use of pervaporation to separate butanol from dilutes aqueous solutions: Effects of operating conditions and concentration polarization. J. Membr. Sci. **323**, 428–435 (2008)

García, V., Pongracz, E., Muurinen, E., Keiski, R.L.: Recovery of *n*-butanol from salt containing solutions by pervaporation. Desalination **241**, 201–211 (2009)

Groot, W.J., Luyben, K.Ch.A.M.: In situ product recovery by adsorption in the butanol/isopropanol batch fermentation. Appl. Microbiol. Biotechnol. **25**, 29–31 (1986)

Groot, W.J., Van der Lans, R.G.J.M., Luyben, K.Ch.A.M.: Technologies for butanol recovery integrated with fermentations. Process Biochem. **27**, 61–75 (1992)

Harlick, P.J.E., Tezel, F.H.: An experimental adsorbent screening study for CO_2 removal from N_2. Microporous Mesoporous Mater. **76**, 71–79 (2004)

Harvey, B.G., Meylemans, H.A.: The role of butanol in the development of sustainable fuel technologies. J. Chem. Technol. Biotechnol. **86**, 2–9 (2011)

Holtzapple, M.T., Brown, R.F.: Conceptual design for a process to recover volatile solutes from aqueous solutions using silicalite. Sep. Technol. **4**, 213–229 (1995)

Li S., Srivastava, R., Parnas, R.S.: Separation of 1-butanol by pervaporation using a novel tri-layer PDMS composite membrane. J. Membr. Sci. **363**, 287–294 (2010)

Maddox, I.S.: Use of silicalite for the adsorption of *n*-butanol from fermentation liquids. Biotechnol. Lett. **4**, 759–760 (1982)

Meagher, M.M., Qureshi, N., Hutkins, R.: Silicalite membrane and method for the selective recovery and concentration of acetone and butanol from model ABE solutions and fermentation broth. US patent 5755967, 1998

Nielsen L., Larsson M., Hoist O., Mattiasson B.: Adsorbents for extractive bioconversion applied to the acetone–butanol fermentation. Appl. Microbiol. Biotechnol. **28**, 335–339 (1988)

Nielsen D.R., Prather, K.J.: In situ product recovery of *n*-butanol using polymeric resins. Biotechnol. Bioeng. **102**, 811–821 (2009)

Oudshoorn, A., Van der Wielen, L.A.M., Straathof, A.J.J.: Assessment of options for selective 1-butanol recovery from aqueous solution. Ind. Eng. Chem. Res. **48**, 7325–7336 (2009a)

Oudshoorn, A., Van der Wielen, L.A.M., Straathof, A.J.J.: Adsorption equilibria of bio-based butanol solutions using zeolite. Biochem. Eng. J. **48**, 99–103 (2009b)

Oudshoorn, A., Van der Wielen, L.A.M., Straathof, A.J.J.: Desorption of butanol from zeolite material. Biochem. Eng. J. **67**, 167–172 (2012)

Qureshi, N., Blaschek, H.P.: Production of acetone butanol ethanol (ABE) by a hyper-producing mutant strain of *Clostridium beijerinckii* BA101 and recovery by pervaporation. Biotechnol. Prog. **15**, 594-602 (1999)

Qureshi N., Hughes S., Maddox I.S., Cotta M.A.: Energy-efficient recovery of butanol from model solutions and fermentation broth by adsorption. Bioprocess Biosyst. Eng. **27**, 215–222 (2005)

Qureshi N., Ezeji, T.C.: Butanol, 'superior biofuel' production from agricultural residues (renewable biomass): Recent progress in technology. Biofuels Bioprod. Bioref. **2**, 319–330 (2008)

Regdon I., Kiraly, Z., Dekany I., Lagaly G.: Adsorption of 1-butanol from water on modified silicate surfaces. Colloid Polym. Sci. **272**, 1129–1135 (1994)

Regdon I., Dekany I., Lagaly G.: A new way for calculating the adsorption capacity from surface excess isotherms. Colloid Polym. Sci. **276**, 511–517 (1994)

Remi, J.C.S., Rémy, T., Van Hunskerken, V., Van de Perre, S., Duerinck, T., Maes, M., De Vos, D., Gobechiya, E., Kirschock, C.E.A., Baron, G.V., Denayer, J.F.M.: Biobutanol separation with the metal-organic framework ZIF-8. ChemSusChem **4**, 1074–1077 (2011)

Remi, J.C.S., Baron, G.V., Denayer, J.F.M.: Adsorptive separation for the recovery and purification of biobutanol. Adsorption **18**, 367–373 (2012)

Saravanan, V., Waijers D.A., Ziari M., Noordermeer M.A.: 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. Biochem. Eng. J. **49**, 33–39 (2010)

Shapovalov, O.I., Ashkinazi, L.A.: Biobutanol: Biofuel of second generation. Russ. J. Appl. Chem. **81**(12), 2232–2236 (2008)

Sharma, P., Chung, W.J.: Synthesis of MEL type zeolite with different kinds of morphology for the recovery of 1-butanol from aqueous solution. Desalination **275**, 172–180 (2011)

Sowerby, B., Crittenden B.D.: Vapour phase separation of alcohol-water mixtures by adsorption onto silicalite. Gas Sep. Purif. **2**, 177–183 (1988)

Takeuchi, Y., Iwamotob, H., Miyata, M., Seiichi Asano, S., Haradac, M.: Adsorption of l-butanol and p-xylene vapour with high silica zeolites and their mixtures. Sep. Technol. **5**, 23–34 (1995)

Thirmal, C., Dahman, Y.: Comparison of existing pretreatment, saccharification, and fermentation processes for butanol production from agricultural residues. Can. J. Chem. Eng. **90**, 745–761 (2012)

Thompson, A.B., Cope, S.J., Swift, T.D., Notestein, J.M.: Adsorption of *n*-butanol from dilute aqueous solution with grafted calixarenes. Langmuir **27**, 11990–11998 (2011)

Tong C., Bai Y., Wu J., Zhang L., Yang L., Qian J.: Pervaporation recovery of acetone–butanol from aqueous solution and fermentation broth using HTPB-based polyurethaneurea membranes. Sep. Sci. Technol. **45**, 751–761 (2010)

Yang X., Tsai GJ., Tsao GT.: Enhancement of in situ adsorption on the acetone-butanol fermentation by *Clostridium acetobutylicum*. Sep. Technol. **4**, 81–92 (1994)

Zheng, Y.N., Li, L.Z., Xian, M., Ma, Y.J., Yang, J.M., Xu, X., He, D.Z.: Problems with the microbial production of butanol. J. Ind. Microbiol. Biotechnol. **36**, 1127–1138 (2009)