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Using Butanol Fermentation Wastewater for Biobutanol Production after Removal of Inhibitory Compounds by Micro/Mesoporous Hyper-Cross-Linked Polymeric Adsorbent

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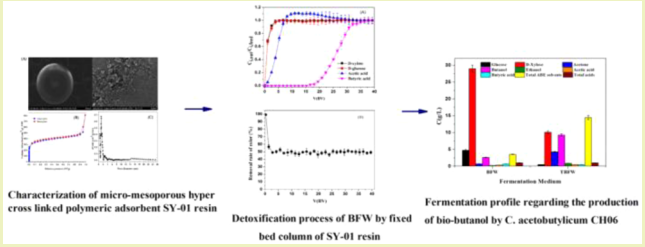
Supporting Information

ABSTRACT: In the present study, a novel micro/mesoporous hyper-cross-linked polymeric adsorbent, SY-01, was tested to remove several inhibitory compounds from butanol fermentation wastewater (BFW) for biobutanol production for the first time. Characterization of the SY-01 resin was determined by scanning electron microscopy, nitrogen adsorption−desorption isotherms, Fourier transform infrared spectroscopy and elemental analysis. The results showed that the SY-01 resin possessed a high Brunauer−Emmett−Teller surface area (1334 m^2/g) with large micropores and mesopores volumes (0.42 and 0.69 mL/g, respectively). After fixed-bed column adsorption, more than 96.0% of D-xylose and 95.0% of D-glucose remained in the treated butanol fermentation wastewater (TBFW). Acetic acid removal varied from 5.1% to 18.7%, butyric acid removal varied from 64.9% to 100% and color removal was effective between 52.9% and 99.2%. In the column desorption process, 99.4% of acetic acid and 99.1% of butyric acid were recovered by an acetone solution. Furthermore, the TBFW was used as substrate for biobutanol production by *Clostridium acetobutylicum* CH06. The detoxification by the SY-01 resin column increased the maximum acetone−butanol−ethanol concentration by 4.08 times and enhanced the total sugar utilization by 1.95 times. In conclusion, our results suggest a new approach for treating the butanol fermentation wastewater.



KEYWORDS: *Adsorption, butanol fermentation wastewater, detoxification, resin adsorbent, inhibitory compounds*

INTRODUCTION

Butanol is an important platform of C4 compounds and has recently received considerable attention due to its favorable fuel properties as well as diminishing oil reserves and an increase of green house gases in the atmosphere.[1,2] As a potential fuel and/or gasoline substitute, butanol has superior properties compared to ethanol, including a higher energy density, lower volatility and hygroscopicity, less flammability and corrosiveness, as well as the ability to be mixed with gasoline and diesel oil in high proportions.[3,4] However, high butanol-induced toxicity to microorganisms limits its yield in traditional ABE fermentation broth, resulting in low butanol titer (~13 g/L), high cost for butanol recovery from the product stream and large quantities of wastewater for disposal.[5] As a result, downstream product recovery and butanol fermentation wastewater (BFW) treatment are major economic drawbacks in industrial biobutanol production processes.[6] Different from other wastewaters, BFW contains various organic acids (mainly acetic and butyric acids) that are toxic to fermentation microorganisms and cause severe environmental pollution.[7] The inhibition of weak acids on microorganisms' growth has been proposed to be due to the inflow of undissociated acid from the extracellular environment into cytosol, leading to dissociation of weak acid in the neutral intracellular pH and therefore a decrease of cytosolic pH, which has a negative effect on cell proliferation and viability as well as pH-dependent fermentation processes.[8] Consequently, the efficient removal of inhibitory substances and recovery of residual sugars from BFW have increasingly drawn significant environmental concerns of researchers worldwide and serve as an attractive case study.

To date, there have been a limited number of studies focused on treatment of BFW to the best knowledge of the authors.[9−11] Chen et al.[10] and Peng et al.[11] used the BFW without any pretreatment and adding nutrients as substrate for lipid

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production by oleaginous yeast *Trichosporon coremiiforme* and *Trichosporon dermatis*, respectively. Although the treatment of BFW by oleaginous yeast can decrease the chemical oxygen demand (COD) in wastewater and obtain the microbial oil with economic value, the lipid fermentation cycle is long (5 days). Zhang et al. used an anaerobic baffled reactor with four compartments to treat BFW and produce methane.[9] However, the major problem in practical application of anaerobic fermentation is acidification phenomena in the reactor, possibly because biobutanol production is a biphasic fermentation process where acetic and butyric acids are formed and the final pH value of biobutanol fermentation broth is less than 5.0.[12] The acid fermentation might exceed the methane fermentation under such acidic conditions, which led to reducing the methanation rate and limiting the application of conventional biological treatment methods such as activated sludge and anaerobic fermentation. Herein, it is wise to employ a potential process technology for removal of inhibitory compounds from BFW and reutilization of treated butanol fermentation wastewater (TBFW) for biobutanol production.

Recently, several technologies are available to remove hydrophilic organic carboxylic acid from the fermentation broths including crystallization,[13] liquid−liquid extraction,[14] distillation,[15] reverse osmosis,[16] pertraction,[17] pervaporation,[18] electrodialysis,[19] ion-exchange resin adsorption[20,21] and adsorption.[20,22] These processes each have respective advantages and disadvantages in terms of industrial scale, removal efficiency, capacity, selectivity, fouling, clogging, operational simplicity, energy requirement or generation of secondary pollutants. Technologies in terms of distillation and solvent extraction are high energy extensive process. As the distribution coefficient and solubility of carboxylic acid between the organic and aqueous system are low, the amount of solvent required for extraction is very high and economically ineffective.[23] Application of membrane technology in terms of reverse osmosis, pertraction and pervaporation for removal and recovery of carboxylic acid is an efficient process, but it is still in its infancy. The cost of building an electrodialysis unit for large scale operation is not economically feasible.[24] Compared with other techniques, only chromatographic separation technology has been shown to be an efficient and effective method for removing inhibitory compounds from butanol fermentation wastewater in industrial application.[20] Adsorption by activated carbon is generally used to remove organic contaminants from water and wastewater in industrial scale application due to its large specific surface area and a predominant proportion of micropores.[25] Nevertheless, wastewater treatment by activated carbon for large scale application is limited owing to its low selectivity and difficult regeneration and reuse.[26] In contrast, synthetic polymeric adsorbents are becoming the alternatives because of their favorable physicochemical stability, structural diversity and feasible regeneration. Ion-exchange adsorption is considered to be an effective method for carboxylic acids removal. The major drawback of the ion-exchange adsorption method is that the fermentation broth contains other anions, which compete with the acidic sites on the ion-exchange materials. Furthermore, the ion-exchange method also requires the use of additional chemicals (salt solutions) to recover the acid from the resin. The regeneration process of ion-exchange resin requires acid and alkali, which produces large amounts of acid and alkali wastewaters. Until present time, no published work has specifically focused on inhibitory compounds removal and recovery from BFW using adsorption resin. This is due to the lack of suitable polymer resin adsorbent that would remove inhibitor compounds from BFW while retaining fermentable sugars (D-xylose and D-glucose) in the raffinate solution. There are also no reports on the evaluation of micro/mesoporous hyper-cross-linked polymeric adsorbent for removal of inhibitory compounds from butanol fermentation wastewater for biobutanol production.

In the present study, a micro/mesoporous hyper-cross-linked resin adsorbent, SY-01, was tested to remove two inhibitory compounds, namely, acetic and butyric acids from BFW to eliminate the effect of those inhibitory compounds and reach a safe detoxification state of the effluent before recycling. Characterization studies of the SY-01 resin have been done using scanning electon microscopy (SEM), nitrogen adsorption−desorption isotherms, Fourier transform infrared spectroscopy (FTIR) and elemental analysis. Moreover, D-xylose and D-glucose recovered from BFW can be utilized for further fermentation tests. Fermentation of TBFW was conducted to evaluate the effects of removing inhibitors by chromatographic adsorption. Recycling the BFW into the fermentation phase would enable both water consumption and wastewaters discharge to be reduced.

MATERIALS AND METHODS

Material. The chemicals and media components used in this study were purchased from Sinopharm Chemical Reagent and were of analytical grade. The BFW was kindly provided by Laboratory of Energy and Chemical Engineering, Guangzhou Institute of Energy Conversion, Chinese Academy of Science. The hyper-cross-linked resin adsorbent SY-01 was kindly supplied by Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences (Guangzhou, China). Prior to packing the columns, the SY-01 resin was pretreated with 70% ethanol for 2 h and was repetitively decanted to neutral pH with deionized water.

Characterization of the Resin Adsorbent. The topology of the SY-01 resin surface was observed by a Hitachi S-4800 scanning electron microscope (Hitachi, Japan) operated at 1.0 kV and 10 μA. The specific surface area, pore volume and pore diameter distribution of the SY-01 resin were measured via the nitrogen adsorption−desorption isotherms at liquid nitrogen temperature using an ASIQMO002-2 analyzer (Quantachrome, USA). Prior to the measurement, the sample (~60 mg) was outgassed at 90 °C for 16 h to remove the adsorbed gases and other impurities. Surface functional groups existed on the resin were identified by FTIR spectroscopy. The elemental analysis of the SY-01 resin including the carbon, hydrogen, nitrogen and sulfur (CHNS) was analyzed using VarioEL cube (Elementar, Germany). The detail pretreatment and analysis processes are given in the Supporting Information.

Separation of BFW Inhibitors Using the SY-01 Resin Column. The dynamic adsorption, desorption, regeneration and readsorption experiments were performed using fixed-bed column techniques.[3,27,28] The detail processes of batch dynamic adsorption, desorption and regeneration experiments were described in the Supporting Information. The desorbed and regenerated fixed-bed column was reused in the next cycle. In this study, the above adsorption−desorption−regeneration−readsorption cycle was repeated seven times.

Microorganism and Inoculum Preparation. *Clostridium acetobutylicum* CH06 (stored by Laboratory of Energy and Chemical Engineering, Guangzhou Institute of Energy Conversion, Chinese Academy of Science) was used in all of the fermentation experiments. Details about inoculum preparation are provided in the Supporting Information.

Biobutanol Fermentation Studies. Batch fermentations were carried out in φ15 × 150 mm test tubes containing 10 mL of medium (BFW and TBFW) with 8% inoculum of the secondary seed culture.

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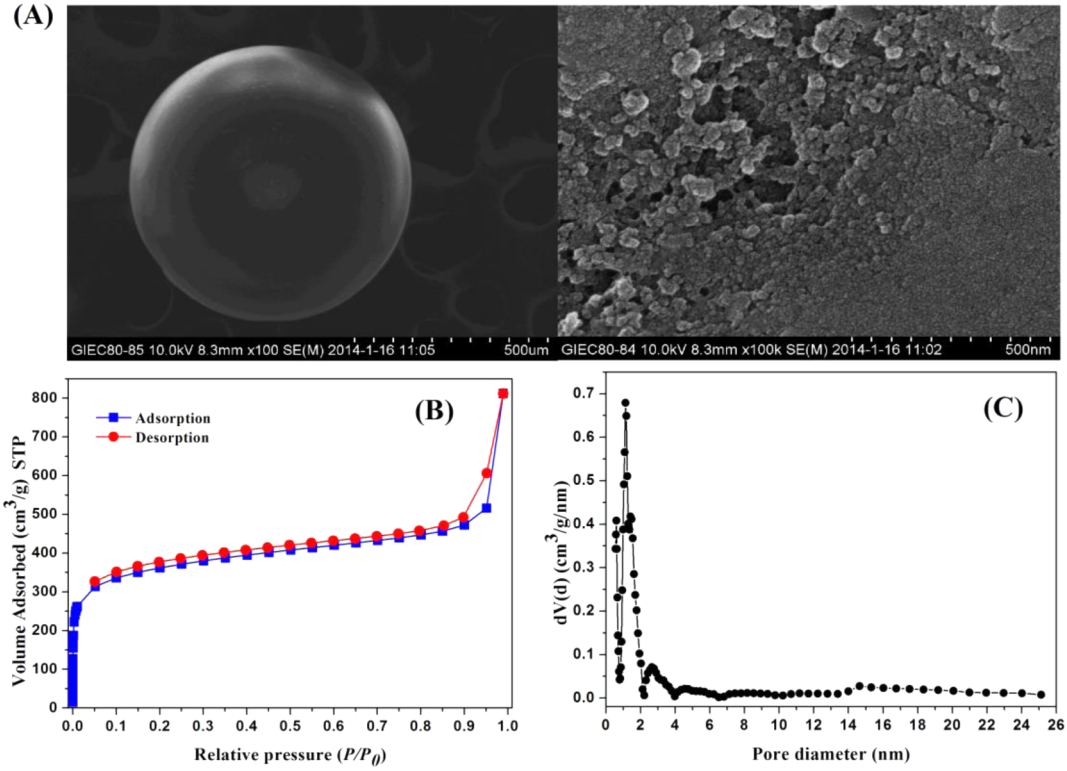

Figure 1. Typical scanning electron micrograph image (A), nitrogen adsorption−desorption isotherms at 77 K (B) and pore size distribution (C) of the SY-01 resin by applying the density functional theory (DFT).

Unless otherwise stated, D-xylose and D-glucose were added in order to reach a final concentration of 27.5 and 27.5 g/L, respectively. Details about the preparation of cultivation medium are given in the Supporting Information. The fermentation was incubated at a constant temperature of 30 °C for 72 h without agitation and samples (1 mL) were taken out from all cultures and were centrifuged using a microcentrifuge at 12000*g* at room temperature for 5 min to remove the cell mass. The cell-free supernatants were used for the determination of ABE and sugars concentrations. Batch fermentations were performed in triplicate and all results presented correspond to the average of the measurements.

Analytical Methods. The sugar concentrations (D-xylose and D-glucose) in the wastewater or fermentation broth were analyzed by high performance liquid chromatography (HPLC) (Waters 2685 systems, Waters Corp., USA) equipped with a refractive index detector (Waters 2414) and on an Aminex HPX-87H anion-exchange column (300 × 7.8 mm, Bio-Rad Corp., USA) using 5 mM sulfuric acid as mobile phase at a flow rate of 0.5 mL min^{-1} and the column temperature was maintained at 55 °C. The concentrations of acetone, ethanol, butanol, acetic acid and butyric acid in wastewater or fermentation broth were determined by gas chromatography (GC) according to our previous study.[29]

RESULTS AND DISCUSSION

Characterization of the Resin Adsorbent. The morphology and surface texture of the SY-01 resin observed by SEM is presented in Figure 1A. As it depicted, the SY-01 resin had a spherical form and rough internal surface. In addition, it is clearly observed from Figure 1A that a large number of micropores and mesopores existed on the surface of the SY-01 resin. The textural parameters of the SY-01 resin were obtained by nitrogen adsorption−desorption isotherms at 77 K, which is demonstrated in Figure 1B (high-resolution images, see Figure S1 of the Supporting Information). According to IUPAC recommendation, the shape of the nitrogen adsorption−desorption isotherms of the SY-01 resin seems close to type I. Notably, N_2 uptake increased sharply with the increment of relative pressure (P/P_0) below 0.05, reflecting the domination of micropores in the pore structure. A visible hysteresis loop between the adsorption and desorption curve at a medium relative pressure ($0.05< P/P_0 <0.95$) suggested that mesopores played a predominant role in the pore diameter distribution of the SY-01 resin. Moreover, an accelerated of the nitrogen uptake at a relatively higher pressure ($P/P_0 > 0.95$) demonstrated that the SY-01 resin contained the larger-sized mesopores or macropores.[30] All of the above analyses were accordant with pore size distribution of the SY-01 resin in Figure 1C (high-resolution images, see Figure S2 of the Supporting Information). As illustrated in Figure 1C, a peak in the micropore region was obviously observed in the pore size distribution curves of the SY-01 resin (at about 1.126 nm), which suggested that the micropores were dominant for the SY-01 resin.

Table 1 summarizes the quantitative results of the nitrogen adsorption−desorption isotherm analysis, i.e., the BET specific surface area, the total pore volume calculated from the adsorbed volume at saturation, the micropores volume calculated by the *t*-plot method, the mesopores volume calculated by the Barrett−Joyner−Halenda (BJH) equation, the macropores volume calculated by difference of pore volume[31] and the average pore diameter of the SY-01 resin. According to the IUPAC classification of pore dimensions, pores are classified as micropores ($d \leq 2$ nm), mesopores (2 nm < d <50 nm) and macropores ($d \geq 50$ nm). Based on Table 1, it can be concluded that the SY-01 resin contained a well-developed pore structure in both the region of micropores and mesopores. The majority of micro/mesopores volume was

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Table 1. Characteristics Properties of SY-01 Resin

resin	SY-01
grain shape	spherical beads
appearance	brown
structure	polystyrene divinylbenzene
polarity	moderate polar
particle size (mm)	0.80
average pore diameter (nm)	1.13[a]
BET surface area (m^2/g)	1334.29
micropore area, S_{micro} (m^2/g)	995.11
mesopore area, S_{meso} (m^2/g)	126.55
macropore area, S_{macro} (m^2/g)	212.63
total Pore volume[b] (cm^3/g)	1.26
micropore volume (cm^3/g)	0.42
mesopore volume (cm^3/g)	0.69
macropore volume (cm^3/g)	0.15
skeletal density (g/mL)	0.65−0.75
wet density (g/mL)	1.02−1.08

[a]At P/P_0 = 0.99. [b]Calculated by DFT.

about 88.10% of the total pore volume, and the micropore area contributed 74.60% to the total surface area.

The FTIR spectrum of the SY-01 resin is displayed in Figure 2. As shown in Figure 2, the −OH stretching vibration appears

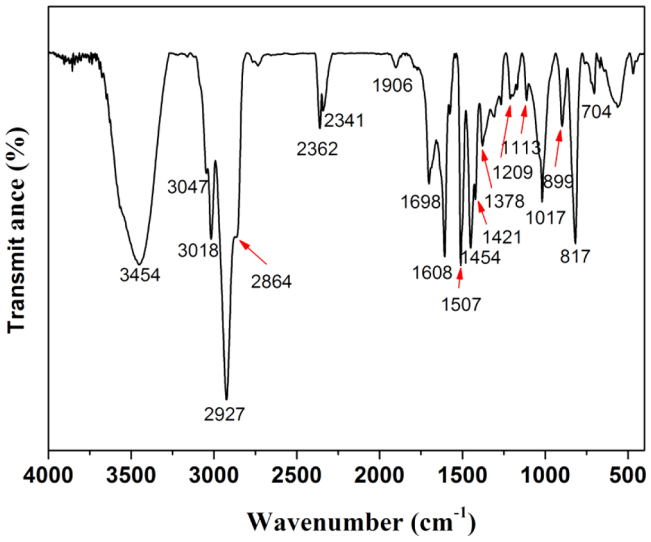

Figure 2. FTIR spectrum of the micro/mesoporous hyper-cross-linked polymeric resin adsorbent SY-01.

around 3454 cm^{-1}; the vibrational peak at 2926 cm^{-1} is due to the stretching bands of the C—H groups, the vibrational peak at 1698 cm^{-1} reveals imine C═N and amide C═O stretching vibrations; the vibrational peak at 1017 cm^{-1} is attributed to the C—O—C group. In addition, the presence of the C═C group is confirmed by the presence of peaks at 1608, 1507 and 1454 cm^{-1}. The presence of benzene rings peaks around 1576 and 1608 cm^{-1} can be identified. This result is the same with the elementary analysis (Table 2). Elemental analysis showed the composition of the SY-01 resin as C, 85.30%; N, 0.02%; H, 6.89%; O, 7.79%.

Separation of BFW Inhibitors Using the SY-01 Resin Column. The breakthrough curve of the SY-01 resin packed column was measured using the BFW, which contained 10.04 g/L of D-xylose, 1.04 g/L of D-glucose, 2.01 g/L of acetic acid

Table 2. Elementary Analysis of SY-01 Resin

element	content (wt %)
carbon	85.30
hydrogen	6.89
nitrogen	0.02
sulfur	ND[a]
oxygen content[b]	7.79

[a]ND: not determined. [b]By difference.

and 1.97 g/L of butyric acid. The pH of the BFW was adjusted to 3.0 by 4 M HCl solution to convert all organic acids to the undissociated form before pumping it through the packed column. It is observed from the preliminary adsorption experiment that the undissociated acetic and butyric acids were much more easily adsorbed onto the SY-01 resin compared to the dissociated one. A typical example of the adsorption breakthrough profiles for the dynamic adsorption of BFW on the SY-01 resin column obtained at a volumetric flow rate of 3.0 mL/min is shown in Figure 3A. Apparently, D-xylose

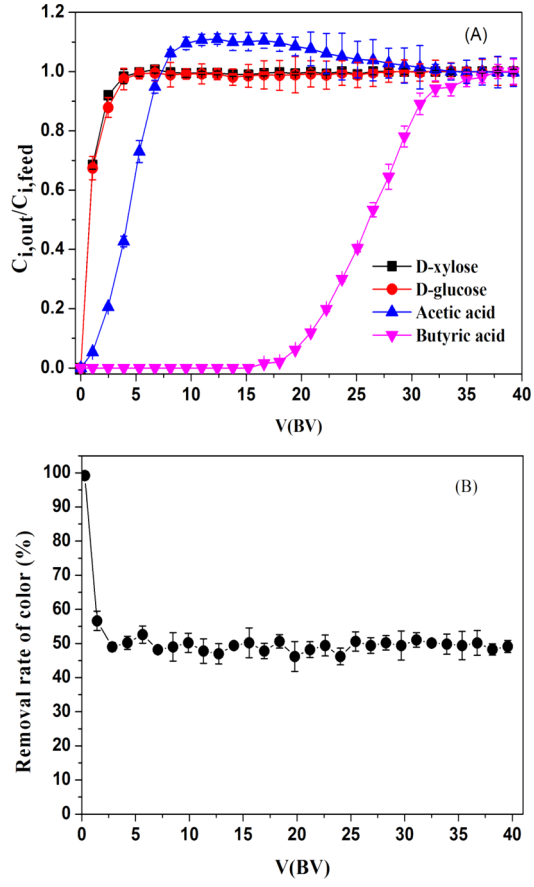

Figure 3. Breakthrough curve of SY-01 resin packed column using actual biobutanol fermentation wastewater (A), and time course of color removal rate (B).

and D-glucose were not adsorbed onto the SY-01 resin and leaked out directly after starting the dynamic separation experiment and quickly saturated the column. Then, acetic acid and butyric acid were eluted from the column in that order. Interestingly, the concentration of acetic acid after its breakthrough points rose above its inlet concentration (overshooting). The reason for this phenomenon might be

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ascribed to the replacement adsorption among acetic acid (weakly adsorbed species) and butyric acid (strongly adsorbed species), which is a typical characteristic of the competitive adsorption.[3,32]

For a fixed-bed column operation, breakthrough volume and dynamic capacity are more significant for judging whether the adsorbents can be applied in real field application or not than the saturated volume and dynamic capacity. As shown in Table 3, the breakthrough volume of acetic acid from BFW was determined to be 1.06 BV, and butyric acid did not leak out until 19.44 bed volume (BV). It is observed from Figure 3A shows that acetic acid removal varied from 5.1% to 18.7%, and butyric acid removal was effective between 64.9% and 100%. Meanwhile, more than 96.0% of D-xylose and 95.0% of D-glucose remained in the raffinate solution after fixed-bed column adsorption. In addition, it is observed from Figure 3B that 52.9% color removal by the SY-01 resin matched with the highest values of butyric acid removal (V = 19.44 BV). Comparison of various adsorbents for color and acid removal as well as sugars loss is provided in Table 4. Although the ion-exchange resin (AG 1-X-8 and A 103 S) and activated carbon possessed a high removal rate of carboxylic acid, the losses of fermentable sugar were relatively high.[33,34] It should be noted that acetic acid is not removed by A860S, C155S, CS14GC and KA-I resin, which is mainly due to the effects of competitive adsorption of different species in mixed system.[3,33,34] Thus, considering that an ideal adsorbent would remove inhibitor compounds from BFW while retaining fermentable sugars (D-xylose and D-glucose) in the raffinate solution, the SY-01 resin tested in the present work was shown to be very effective for BFW treatment, which indicated the high removal efficiency of the inhibitory compounds and low loss of the sugar recovery in the detoxifying process.

Table 3. Breakthrough and Saturation Parameters of D-xylose, D-Glucose, Acetic Acid and Butyric Acid Adsorption by SY-01 Resin in Fixed-Bed Column

biobutanol fermentation wastewater	V_B[a] (BV)	V_T (BV)	q_B[b] (g/L)	q_T (g/L)
D-xylose	0.00	2.48	0.00	1.51
D-glucose	0.00	2.48	0.00	0.38
acetic acid	1.06	6.75	1.92	5.38
butyric acid	19.44	33.55	36.95	49.93

[a] V_B, breakthrough volume (BV); V_T, total saturation volume (BV). [b] q_B, breakthrough dynamic capacity (g/L); q_T, total saturation dynamic capacity (g/L).

Considering cost-effective application of an ideal adsorbent in the BFW treatment process, the possibility of its regeneration ability and reusability was further investigated. In the present study, after the dynamic adsorption breakthrough experiments, the exhausted SY-01 resin loaded with organic acids and color in the fixed-bed column was gently rinsed with 2.0 BV of deionized water for removing the D-xylose and D-glucose from the void of the resin column bed as well as the resin surface. Subsequently, the fixed-bed column was eluted with an acetone aqueous solution, which is a byproduct of the biobutanol fermentation process, at 0.5 BV/h at room temperature for removing the adsorbed organic acids. It is evident that acetic acid and butyric acid from the resin column can be easily desorbed using an acetone aqueous solution. The recovery efficiencies of acetic acid and butyric acid were achieved to 99.4% and 99.1% as the acetone aqueous solution was applied as the desorption solvent. After seven adsorption−desorption−regeneration−readsorption cycles (see Figure 4), the relative standard deviations of column q_B were below 5.0%, which indicated that the column had stable and better adsorption ability. Moreover, the capacity of the resin reached its original level again and kept basically constant in the

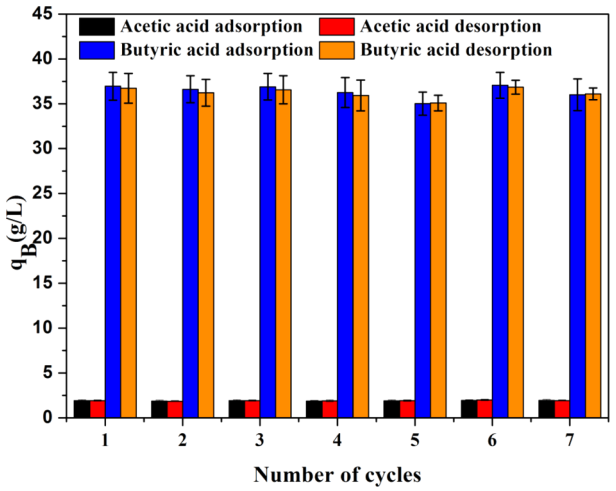

Figure 4. Effect of the recycle number on the equilibrium of acetic and butyric acids on SY-01 resin from biobutanol fermentation wastewater.

Table 4. Comparison of Color and Acid Removal as well as Sugars Loss by Various Adsorbents in Different Adsorption Systems

adsorbent	adsorbent system	pH	color removal (%)	acid removal (%)		sugars loss (%)		reference
				acetic acid	butyric acid	D-xylose	D-glucose	
AG 1-X-8	spruce hydrolyzate	10	ND[a]	96.0	ND	ND	26.0	34
		5.5	ND	89.0	ND	ND	8.0	
A 103 S	corn stover hydrolyzate	1.5	95.0	100.0	ND	6.0	ND	33
A 860 S			41.0	0.0	ND	3.0	ND	
C 155 S			83.0	0.0	ND	8.0	ND	
CS 14 GC			75.0	0.0	ND	0.0	ND	
activated carbon	woody hydrolyzate	3.4	ND	3.1−33.0	ND	2.3−35.1	4.2−38.0	35
KA-I	butanol fermentation broth	ND	ND	0.0	3.3−13.3	ND	0.0	3
SY-01	butanol fermentation wastewater	3.0	52.9−99.2	5.1−18.7	64.9−100.0	4.0	5.0	this work

[a] Not determined.

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ACS Sustainable Chem. Eng. 2015, 3, 702−709

following adsorption−desorption-regeneration-readsorption cycles. Hence, this encouraging result strongly suggests that the SY-01 resin is a promising replacement for many commercial adsorbents for removal and recovery of inhibitory compounds from BFW.

Butanol Production Using BFW and TBFW as Substrates. The recovered sugar samples (see Table 5) were tested for fermentability using a standard fermentation test procedure using *Clostridium acetobutylicum* CH06. For comparison, a standard mixture of pure sugars and the original BFW were fermented at the same time. Prior to fermentation, D-xylose and D-glucose (1:1, wt/wt) were added in the samples to reach a final concentration of 55.0 g/L, respectively. In addition, the initial pH of the samples was adjusted to 6.5 by aqueous ammonia. Table 6 shows the results of the fermentation with sugars from different sources.

Table 5. Concentrations of D-Xylose, D-Glucose, Acetic Acid and Butyric Acid in Raffinate Solution Collected at the Outlet of Fixed-Bed Column at Different Times

experiment	D-xylose (g/L)	D-glucose (g/L)	acetic acid (g/L)	butyric acid (g/L)
Run 1[a]	27.50	27.50	0.00	0.00
Run 2[b]	10.04	1.04	2.01	1.97
Run 3[c]	9.44	0.97	1.26	0.00
Run 4[d]	9.98	1.03	2.14	0.03
Run 5[e]	10.02	1.04	2.03	0.82
Run 6[f]	10.04	1.04	1.95	1.84

[a]Control. [b]Original BFW. [c]Raffinate solution collected from 0.00 to 9.54 BV. [d]Raffinate solution collected from 10.96 to 19.44 BV. [e]Raffinate solution collected from 20.85 to 29.33 BV. [f]Raffinate solution collected from 31.74 to 39.22 BV.

It is worth noting that the original BFW had the worst fermentability, whereas the sugars collected from the column packed with the SY-01 resin (0.00−9.54 BV) had the best fermentability. For *Clostridium acetobutylicum* CH06, the average ABE concentration in TBFW reached 14.46 g/L after 72 h, while the corresponding value in BFW was only 3.54 g/L. The residual sugars in the TBFW and BFW were 10.60 and 33.74g/L, respectively. In other words, the detoxification by the SY-01 resin column increased the maximum ABE yield by 4.08 times and enhanced the total sugar utilization by 1.95 times. These indicated that BFW contained more inhibitory compounds for the fermentation of *Clostridium acetobutylicum* CH06 than TBFW. The average final yield of biobutanol, 10.80 g/L, and total ABE solvents, 16.67 g/L, were obtained in the TBFW medium (0.00−19.44 BV). Interestingly, the total ABE concentration and sugar utilization were higher than those obtained in the pure sugar mixture (Table 6). Some reasons could explain this phenomenon: on the one hand, the detoxification before BFW recycling might be effective, and on the other hand, the environment of BFW was suitable for the biobutanol fermentation of *Clostridium acetobutylicum* CH06.

Furthermore, it can be observed from Tables 5 and 6 that the concentrations of butyric acid in the raffinate solution increased with the increase of effluent volume, resulting in the gradual decrease of total ABE concentration and sugar utilization. This observation suggested that butyric acid had strong toxic effect on the metabolism of *Clostridium acetobutylicum* CH06. The concentrations of D-xylose, D-glucose, acetic acid and butyric acid in raffinate solution collected from 31.74 to 39.22 BV were quite similar to the original BFW (see Table 5). However, the total ABE concentration and sugar utilization obtained in the TBFW medium (31.74−39.22 BV) were higher to those obtained in the original BFW (Table 6), indicating that color in the BFW at a certain level might influence the metabolism of *Clostridium acetobutylicum* CH06. Thus, the removal of color should be considered as an index of BFW detoxification. In the present work, the color removal index varied from 52.9% to 99.2%. In summary, all of these findings provide new insights and approaches for making large scale of biobutanol production from BFW economically feasible.

CONCLUSIONS

In the present work, the SY-01 column was tested to remove several inhibitory compounds from BFW for the first time with the purpose of reusing this wastewater as fermentation substrate. The results showed that the original BFW had the worst fermentability, whereas the sugars collected from the column packed with SY-01 resin had the best fermentability, which was higher than that of the pure sugar mixture. In summary, the SY-01 resin with proper microporosity and mesoporosity has a very promising future in removal and recovery of inhibitor compounds from BFW for its excellent adsorption and desorption performance.

ASSOCIATED CONTENT

Supporting Information

General details of characterization of the resin adsorbent, separation of BFW inhibitors using the SY-01 resin column, microorganism and inoculum preparation, biobutanol fermentation studies were provided in Supporting Information. Figures of nitrogen adsorption−desorption isotherms of the SY-01 resin at 77 K and pore size distribution of the SY-01 resin by applying the density functional theory. This material is available free of charge via the Internet at http://pubs.acs.org/.

Table 6. ABE Fermentation Products from Six Mediums

mediums	D-glucose (g/L)	D-xylose (g/L)	acetone (g/L)	butanol (g/L)	ethanol (g/L)	acetic acid (g/L)	butyric acid (g/L)	total ABE solvents (g/L)	total acids (g/L)
control (Run-1)	0.35	10.95	4.52	9.36	0.47	0.92	0.76	14.35	1.68
original BFW (Run-2)	4.74	29.00	0.73	2.61	0.20	0.35	0.68	3.54	1.03
TBFW (Run-3)	0.23	4.70	4.78	11.06	0.85	0.57	0.34	16.69	0.91
TBFW (Run-4)	0.36	9.57	4.98	10.53	1.13	0.50	0.18	16.64	0.68
TBFW (Run-5)	0.44	10.50	3.92	8.26	0.80	0.88	0.64	12.98	1.52
TBFW (Run-6)	0.96	15.64	3.54	7.21	0.76	0.12	0.75	11.51	0.87

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ACS Sustainable Chem. Eng. 2015, 3, 702−709

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Author Contributions

All authors have given approval to the final version of the paper.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

ABE, acetone−butanol−ethanol; BET, Brunauer−Emmett−Teller; BFW, butanol fermentation wastewater; BJH, Barrett−Joyner−Halenda; BV, bed volume; CHNS, carbon, hydrogen, nitrogen and sulfur; COD, chemical oxygen demand; FTIR, Fourier transform infrared spectroscopy; GC, gas chromatography; HPLC, high performance liquid chromatography; SEM, scanning electron microscopy; TBFW, treated butanol fermentation wastewater

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