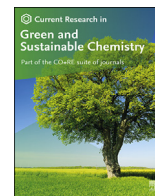


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Recovery of biobased 2,3-butanediol from fermentation broths by liquid-phase adsorption onto phenylboronate polymers

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ABSTRACT

In recent years, 2,3-butanediol (BDO) has been recognized as a valuable platform molecule suitable for production of bulk and fine chemicals. BDO can be efficiently produced biotechnologically in high titer. Recovery of high-boiling and highly polar BDO from the fermentation broths presents the major challenge. In this study, we propose adsorption of BDO onto polymers bearing phenylboronate groups as a method for selective and efficient recovery. We optimized the adsorption parameters, such as NaOH concentration and the dilution factor, using solutions of commercially available BDO. Under the optimized conditions, nearly quantitative complexation of phenylboronates occurs, which corresponds to a loading of $250 \text{ mg}_{\text{BDO}} \text{ g}_{\text{polymer}}^{-1}$. Desorption of BDO into acidic and neutral solutions was efficient. Most importantly, an 80%EtOH/20%H₂O mixture can be used to recover BDO with up to 93% desorption efficiency. Two fermentation broths obtained with *Bacillus licheniformis* DSM 8785 were applied for adsorption studies. The material capacities upon adsorption from the fermentation broths were as high as from the model solutions. BDO uptake from the fermentation broth was very selective, with only negligible co-adsorption of other components, such as acetoin, lactate or succinate. Utilization of the polymer in three adsorption and two desorption cycles proved recyclability of the material. ¹H, ¹¹B, and ¹³C MAS NMR were used to monitor the adsorption and desorption processes. This work shows a high potential of the polymers bearing phenylboronate functionalities for adsorptive recovery of BDO from fermentation broths.

1. Introduction

Industrial interest to biobased 2,3-butanediol (BDO) goes back to the beginning of the last century. Bio-BDO can be obtained with high titers up to 150 g L^{-1} [1,2] and can be used as a substrate for fine and bulk chemicals, shown in Fig. S1 in the electronic supplementary information (ESI) [3,4]. Dehydration of BDO gives rise to 1,3-butadiene [3] – an intermediate for synthetic rubber – or other olefins [5]. Alternatively, methylethylketone, a widely used solvent and a potential fuel blend [6–9], can be obtained. Dehydrogenation of BDO yields the fine chemicals acetoin and diacetyl (butane-2,3-dione) [10], whereas BDO ketalization results in dioxolans, which can be used as gasoline blending components or industrial solvents [11].

A large number of recent publications have reported on the biotechnological production of BDO, highlighting a renewed interest in this

platform chemical [12–19]. An efficient recovery of BDO from fermentation broths presents a bottleneck for large scale production [20–22]. This challenge is well known for bioprocesses, for which the downstream costs account for a large fraction of 20–50% of the total capital and operating costs of biorefineries [23]. A fermentation broth of BDO presents an aqueous solution containing organic substances and inorganic salts. The high boiling point of BDO of about 180 °C hampers its distillation. Distillative separation would first require evaporation of water, a solvent with a high heat of vaporization, and all other components with lower boiling points. Alternatively, organic acids and inorganic salts can be removed by precipitation upon treatment with light alcohols prior to recovery of BDO by vacuum distillation [24].

Recently proposed methods for BDO recovery, such as distillation [25,26], extraction followed by distillation [27–31], pervaporation [32], steam stripping [7], or reverse osmosis [22], appeared to be energy

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intensive. Interestingly, vacuum membrane distillation was proposed to enrich the BDO fermentation broths upon vaporization of water [32]. Owing to the high polarity of BDO, it exhibits low partition coefficients of *ca.* 1 or lower into the organic phase upon liquid-liquid extraction [33–35]. Somewhat better partitioning of BDO into oleyl alcohol compared to other conventional solvents was reported [29]. The partition coefficients into organic solvents can be improved to *ca.* 5–6 upon salt addition to an aqueous phase due to the salting out effect [36,37]. The salting-out effect for BDO extraction into ionic liquids enabled partition coefficients as high as 26 [38]. A combination of liquid-liquid extraction with pervaporation has also been reported [39,40]. Aqueous two-phase extraction (ATPE) appeared to be more efficient compared to conventional liquid-liquid extraction [41–45]. Utilization of concentrated solutions of salts has found only limited industrial application so far, though separation of ammonium sulfate using methanol as anti-solvent has been described [45,46].

Extractive methods for separation of BDO using *in situ* derivatization have been reported. For example, reactive extraction of BDO in forms of acetals using butyraldehyde [47,48] or formaldehyde [49] can be used. However, the BDO recovery requires rather harsh conditions, namely distillation with 0.5 HCl or 0.5 M H₂SO₄. Reactive esterification of BDO with formic or acetic acid and H₂SO₄ as a catalyst followed by pyrolysis of the esters gave rise to 1,3-butadiene [50].

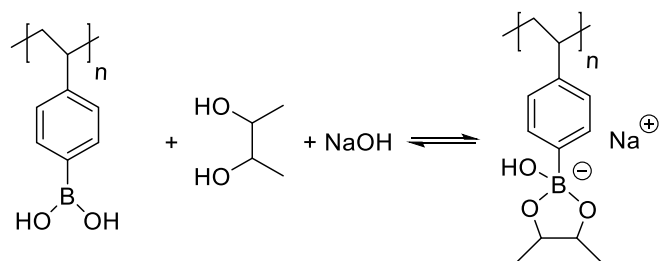
We have recently reported recovery of BDO *via* complexation with phenylboronates. The complexation takes place in alkaline medium *via* contact with an organic phase containing phenylboronic acid, Aliquat® 336, and 1-octanol as diluent. BDO can be back-extracted upon acidification to neutral conditions [51]. This method has been used for separation of 1,2-propanediol [52], 1,2,4-butanetriol [53], and saccharides [54–61]. A high selectivity for recovery of molecules bearing a 1,2-*vic* diol structural motif presents an advantage of this method. Nevertheless, the need to apply a hazardous organic diluent and amines as well as partial carry-over of phenylboronic acid into the aqueous phase stimulates search for alternative methods.

Adsorption of molecules with a 1,2-*vic* diol fragment onto materials bearing phenylboronate groups according to Scheme 1 presents a potentially more environmentally benign alternative compared to extraction. In the last 20 years, this method has attracted particular attention for separation, due to the rapid development of x-omics, such as proteomics, metabolomics, and glycomics [62]. The adsorption remains much less explored for separation in bio-refining, although the polymers can be exploited to recover a number of diols, saccharides, and sugar alcohols [63]. The adsorption can be used for separation of D-fructose from D-glucose [64,65] or lactulose from lactose [66]. In this work, we explore a possibility to isolate BDO from fermentation broths *via* adsorption onto polymers functionalized with phenylboronate groups.

2. Experimental section

2.1. Chemicals

p-vinylphenylboronic acid (*p*-VPBA, 97%) was provided by ChemPUR. BDO (98%) and sodium acetate (≥99%) were supplied by Sigma Aldrich. Acetonitrile (99.9%), anhydrous benzyl alcohol (>99.8%), ethanol (99.9%), sodium hydroxide microgranulate (≥98.8%), and sulfuric acid (98%) were supplied by GeyerChemSolute. Diethanolamine (DEA, 99%) and divinylbenzene (DVB, 80% divinylbenzene: 20% ethylbenzene mixture, 99%) were purchased from Alfa Aesar. Ethylene glycol dimethacrylate (EDMA, 98%) stabilized with 100 ppm methoxyphenols (mehq) was obtained from Th. Geyer. Sodium dihydrogen phosphate was purchased from Merck. Sodium hydrogen carbonate (>99%) and chloroform (>99%) from Roth, and conc. hydrochloric acid (37 wt%) from Honeywell were used. All chemicals were used without further purification and all solutions were prepared in distilled water.



Scheme 1. Complexation of phenylboronate moieties with BDO and NaOH taking place via adsorption (forward reaction) and desorption (backward reaction).

2.2. Production of BDO fermentation broth

Microbial production of BDO was performed with *Bacillus licheniformis* DSM 8785. A detailed description of the initial cultivation medium and the cultivation procedure can be found in a previous work [67]. Briefly, the cultivation was performed in 250 mL shake flasks starting from a medium containing 180 g L⁻¹ glucose. An orbital Climo shaker ISF1-X from (Adolf Kühner AG, Birsfelden, Switzerland) with a shaking diameter of 50 mm and a shaking frequency of 100 rpm and a temperature of 37 °C was used. A pH above 5.5 during fermentation was maintained by supplementing the medium with 100 mM MES buffer. The microbial reaction was monitored with a modified Respiration Activity Monitoring System (RAMOS) [68]. By variation of the filling volumes and harvesting time of the cultivation, two BDO fermentation broth solutions of different composition, FB1 (15 mL filling volume) and FB2 (20 mL filling volume), were obtained. The concentrations were measured by HPLC. The *meso*-to-*rac* ratios of the fermentation broth solutions FB1 and FB2 are 1.8 and 0.8, respectively.

2.3. Synthesis of phenylboronate polymers

Cross-linked phenylboronate polymers were synthesized according to a previously optimized procedure [64], consisting of three main steps: (i) protection of *p*-VPBA monomer by esterification with DEA, (ii) radical polymerization of a cross-linker and *p*-VPBA with AIBN in benzyl alcohol at 70 °C under Ar atmosphere overnight, and (iii) workup, deprotection, and activation of the cross-linked *p*-VPBA polymer by grinding in a mortar and successive washing and drying with chloroform, aqueous 1 M HCl and 0.5 M NaH₂PO₄ buffer solution (pH adjusted to 7.5 with 4 M NaOH). Polymers were obtained as white powders.

2.4. Adsorption of BDO

The solutions for adsorption were prepared by a mixture of a corresponding amount of commercial BDO solution with water followed by addition of necessary volumes of 4 M or 10 M NaOH. Alternatively, the 4 M or 10 M NaOH solutions were added to fermentation broths. Adsorption experiments were performed in 5 mL vessels, where 100 or 200 mg of the polymer were placed together with 2.63 mL of the BDO solution. The adsorption was conducted for 3 h at RT at a stirring speed of 500 rpm. After adsorption, samples were taken, filtered through polyamide syringe filters (Chromafil PA 20/25), diluted, and analyzed by HPLC.

2.5. Desorption and recycling

Prior to desorption experiments, adsorption was performed using 13.1 mL of a 0.140 mol L⁻¹ BDO model solution and 500 mg of polymer. The polymer was filtered over a glass frit after adsorption and dried under high vacuum. Different acids, buffer solutions, organic solvents, and binary solvents were tested for desorption. The respective desorption

solution (2.63 mL) was added to 0.100 g loaded polymer and the solution was stirred for 4 h at 500 rpm at RT. The experiments with CO₂ were performed in 20 mL finger autoclaves with 5 mL glass inlets. The autoclaves were pressurized with 30 bar CO₂, and the desorption experiments were performed for 4 h at 50 °C. The solutions were analyzed by HPLC after filtration. For recycling experiments, polymers were filtered, dried as described above, and used in a subsequent cycle.

2.6. Characterization of the materials

Elemental analysis was performed using an ICP-OES Spectroblue Instrument from Spectro Analytical Instruments. 20–30 mg sample, 1 g KOH, and 0.12 g KNO₃ were fused in a china jar. The melt cake was added to 50 mL aqueous 10 wt% hydrochloric acid solution and analyzed.

Nitrogen adsorption/desorption isotherms were recorded on a Quadrasorb SI instrument from Quantachrome/3P Instruments. Prior to the measurement, the sample was degassed at 60 °C for 16 h.

Scanning electronic microscopy (SEM) images were acquired using a JEOL JSM7000F microscope with accelerating energy of 10 kV. The samples were coated with carbon prior to SEM investigation.

Solid-state NMR experiments were performed on a Bruker Avance III NMR Spectrometer at 14.1 T with 20 kHz MAS. A 3.2 mm HX probe was used. In all cases, the ¹H 90° pulse duration was 2.5 μs, the magic angle was calibrated with KBr and the chemical shifts were referenced using adamantane. ¹¹B NMR spectra were acquired using the Hahn-echo sequence. Spectral processing was done using the Bruker TopSpin 3.5 software and FIDs in ¹¹B Hahn-echo experiments were left-shifted to the echo maxima. ¹H-¹³C cross-polarization (CP) MAS NMR experiments were recorded with a ramp on the ¹H channel and SPINAL64 heteronuclear decoupling. All experiments were nominally performed at RT. However, frictional heating due to MAS results in a higher actual sample temperature.

2.7. HPLC analysis

The concentrations of *meso*- and *rac*-BDO were determined by HPLC on a Shimadzu Prominence LC-20 system equipped with a refractive index (RI) detector. Two organic acid columns (CS-Chromatography, 100 mm × 8.0 mm and 300 mm × 8.0 mm) were used for the separation. The measurements were performed at 40 °C in trifluoroacetic acid eluent (CF₃COOH (154 μl) in water (1L)) with a flow rate of 1 mL min⁻¹. The retention times for *meso*- and *rac*-BDO were, 15.78 min and 16.55 min, respectively.

3. Results and discussion

3.1. Adsorption of BDO from model solutions

The polymers were synthesized according to the previously reported procedure [63–65]. *p*-vinylphenylboronic acid was protected with diethanolamine. Free radical polymerization of the obtained ester with divinylbenzene (DVB) or ethylene glycol dimethacrylate (EDMA) as cross-linkers in ratio of 80-to-20 mol-to-mol gave rise to the sorption material. The schemes of the synthesis are provided in Figs. S3–S4. These materials proved to show excellent adsorption capacity and high stability under the operational conditions in the previous studies [64]. The exact content of boron was determined after solubilization of the materials by ICP-OES. The experimentally determined boron content accounts for 0.260 and 0.366 mmol_B g_{Polymer}⁻¹ for the polymers cross-linked with DVB and EDMA, respectively. The polymer in dry form presented a non-porous material with specific surface area of ca. 1 m² g⁻¹, as determined by low-temperature N₂ physisorption. This result is in good agreement with previously reported data [63,64]. We characterized the

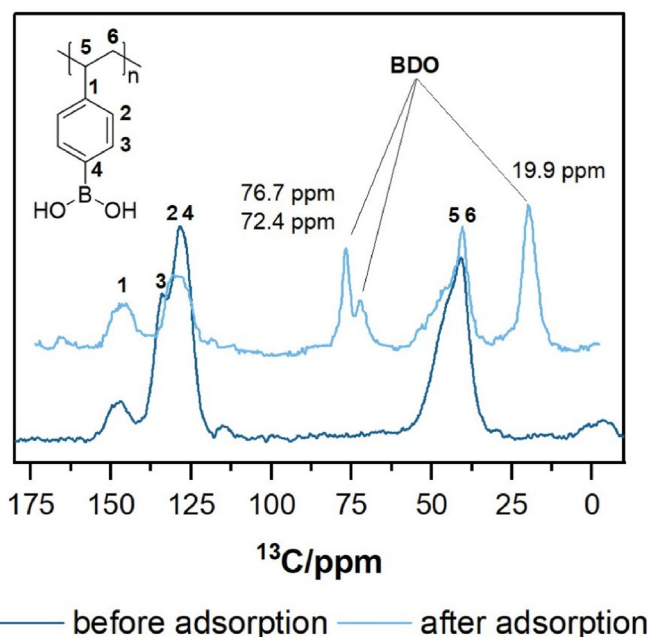


Fig. 1. ¹³C CP MAS NMR (20 kHz MAS, contact time 2.0 ms) of the phenylboronate-functionalized polymers before (1600 scans, 2.5 s interscan delay) and after adsorption (5000 scans, 4 s interscan delay). Adsorption was conducted by stirring the polymer in the solution of 70 mg g⁻¹ BDO and 2 equivalents NaOH for 4 h at RT. The recovered polymer was filtered and dried under high vacuum prior to NMR measurements.

polymer using scanning electron microscopy (SEM) and observed particles of irregular shape, with a size ranging from 100 to 300 μm and possessing a rough surface. In agreement with the N₂ physisorption data, no pores can be found on the surface of the polymers (the SEM images can be found in ESI, Fig. S5). The polymers were examined using ¹H, ¹¹B, and ¹³C MAS NMR. The characteristic resonances corresponding to aromatic atoms in the range of 120–150 ppm and backbone atoms corresponding to the aliphatic chemical shifts of 30–55 ppm were present in the ¹³C MAS NMR spectrum, as Fig. 1 shows. The spectra were free from any signals other than the polymer resonances, which points to a high purity of the obtained polymers.

In a previous study, we explored adsorption of various saccharides, sugar alcohols, and diols onto the polymers functionalized with phenylboronate. The adsorption capacities correlated rather well with the molecular complexation constants of the substrates K^{B-S} [63]. Since BDO exhibits a moderate complexation constant ($K^{B-S} = 0.54$) [69], moderate loading could be expected. In the first screening, adsorption of BDO in carbonate buffer at pH 10 was tested, and indeed only 160 mg_{BDO} g_{Polymer}⁻¹ loading of BDO could be obtained, which corresponds to ca. 0.64 mol_{BDO} mol_B⁻¹ of available phenylboronate moieties of the polymer.

In accordance with the reaction shown in Scheme 1, which takes place upon adsorption, an increase of the OH⁻ and BDO concentrations should result in an improved loading. We used different amounts of aqueous NaOH to dilute BDO solutions. Increasing volumes of NaOH resulted in an increase of OH⁻ equivalents and a simultaneous decrease of BDO concentration due to dilution. The cross-linked with DVB polymer was explored. Fig. 2 shows the results for various equivalents of NaOH and amounts of the polymer. Noteworthy, application of equimolar amounts of NaOH and BDO results in a nearly quantitative loading corresponding to ca. 0.93 mol_{BDO} mol_B⁻¹ complexation of phenylboronate groups. Increase of the OH⁻-to-BDO ratio to 2:1, 4:1, or 10:1 results in improvement of the loadings up to nearly 100%. This corresponds to a BDO loading of ca. 250 mg_{BDO} g_{Polymer}⁻¹. Interestingly, a further dilution

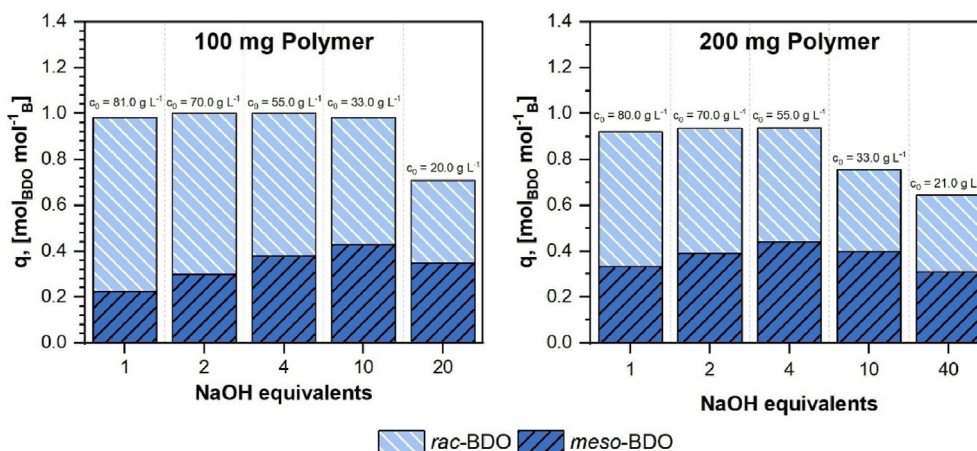


Fig. 2. Results of BDO adsorption on the polymer cross-linked with DVB; conditions: commercial BDO (75% *meso*-BDO, 25% *rac*-BDO) was used as a substrate, 2.63 mL model solution containing BDO in concentrations c_0 provided on the graphs, and NaOH (NaOH equivalents refer to the molar ratio of NaOH-to-BDO) were stirred with 100 mg polymer (left) or 200 mg polymer (right) for 3 h at RT.

with NaOH solution led to a decrease of the BDO loading. This can be explained by a significant dilution of the solution due to addition of NaOH solution, which results in an unfavorable shift of the equilibrium of Scheme 1 to the left. In accordance with Le Chatelier's principle, decrease of BDO concentration in the solution seems to be the major reason for low loading. In all the experiments, at least 1 equivalent of NaOH with respect to BDO was used. According to the ¹¹B MAS NMR, all the boron atoms were sp³ hybridized (tetragonal) under these conditions. For the optimized adsorption conditions, a compromise between significantly high NaOH concentration and minimizing BDO dilution is required.

Commercially available BDO was used to prepare the model solutions for the adsorption tests. This chemical is composed of a mixture of stereoisomers, namely 75% *meso*-BDO and 25% *rac*-BDO. Interestingly, the composition of the adsorbed species significantly varied from the composition of the BDO in the solution. For all the tested conditions, adsorption of *rac*-BDO dominated, yielding ca. 40% *meso*-BDO and 60% *rac*-BDO. This result reflects the thermodynamic stability of the complexes formed by the BDO diastereomers with the phenylboronate moieties: the complexes with the *cis*-diols are significantly more stable than with *trans*-diols.

We studied the stability of the polymer upon adsorption. The liquid phase was analyzed for boron leaching using ICP-OES. A minor boron leaching corresponding to ca. 7% boron loss was observed in this work. This differs from the previous studies with buffer solutions as adsorption medium [63,64], where no boron leaching was detected. A ¹³C CP MAS NMR spectrum of the polymer loaded with BDO is shown in Fig. 1. The characteristic resonances of the polymer backbone are still present in the spectrum, indicating robustness of the material under the applied adsorption conditions. In addition, new resonances appeared in the spectrum at 19.9 ppm being assigned to the methyl groups of BDO, as well as the signals at 72.4 and 76.7 ppm correspond to C-H fragments of BDO. In the ¹¹B Hahn-Echo MAS NMR spectrum, major signals at 6.4 and 9.3 ppm were attributed to the complexes of BDO with boronate. In addition, the ¹¹B MAS NMR spectrum exhibited a minor signal at 3.1 ppm corresponding to the R-B-(OH)₃ boronate groups. No resonances of sp²-coordinated boron were observed (Fig. S6). Interestingly, ¹H-¹³C HETCOR spectrum with moderate contact time of 500 μs suggested a proximity of aliphatic signals of the polymers with the methylene (CH) resonances of BDO (Fig. S8).

Another phenylboronate-functionalized polymer obtained via cross-linking of protected *p*-vinylphenylboronic acid with EDMA was also tested. The results were similar to those obtained for the polymer cross-linked with DVB reaching ca. 240 mg_{BDO} g_{Polymer}⁻¹ loading of BDO (Fig. S9). However, the polymer cross-linked with EDMA exhibited a higher boron leaching under the adsorption conditions, with up to 18% loss of boron.

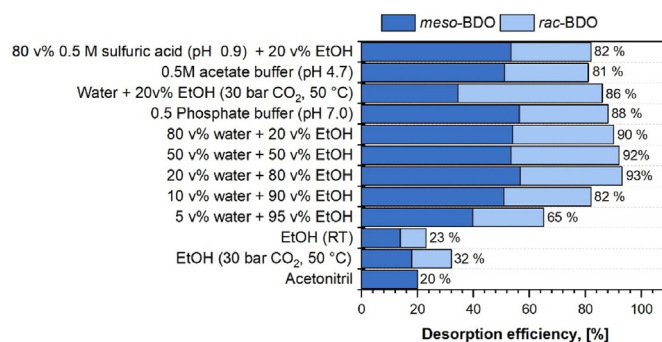


Fig. 3. Results of BDO desorption in different solvents. Conditions: 100 mg dried polymer after adsorption and 2.63 mL solvent were stirred for 4 h at RT.

3.2. Desorption of BDO

As Scheme 1 suggests, complexation of BDO with phenylboronate moieties is favorable in alkaline medium, whereas complex cleavage occurs in acidic medium. We previously showed that application of acidified solutions is required for desorption of saccharides and sugar alcohols [63]. Diols form less stable complexes with phenylboronate and can, therefore, be desorbed using neutral 20 vol% H₂O-80 vol% EtOH mixture [63].

In this work, we screened various solvents for desorption of commercial BDO. The results are summarized in Fig. 3. As expected, a high desorption efficiency of 82–86% was observed in acidic solutions such as sulfuric acid, acetate buffer at pH 4.7 or a mixture of 80% water-20% ethanol saturated with CO₂ under pressure. Interestingly, a very high efficiency of 88% was observed by using of such a mild acid as phosphate buffer at pH 7. This indicates that the complex can be cleaved even under neutral conditions. This is in agreement with the results on cleavage of molecular BDO-phenylboronate complexes, which we obtained in the previous study on BDO extraction [51]. We examined desorption in mixtures of water and ethanol with different ratios of the components. High content of ethanol is desirable due to its much lower heat of vaporization compared to water. However, addition of at least 20 vol% water is required for an efficient ester cleavage, resulting in a desorption efficiency above 90%. Upon decrease of the water content below 20%, the desorption efficiency dramatically diminished. Nevertheless, heat of vaporization of 20 vol% water-80 vol% EtOH equals 858 kJ L⁻¹, which is much less than 2254 kJ L⁻¹ for pure water [70]. Thus, less energy would be required for vaporization of the solvent after desorption than for

Table 1
Composition of fermentation broths FB1 and FB2.

| Entry | Compound | Concentration [g L ⁻¹] | |
|-------|------------------|------------------------------------|-------|
| | | FB1 | FB2 |
| 1 | <i>rac</i> -BDO | 12.19 | 38.43 |
| | <i>meso</i> -BDO | 22.57 | 30.08 |
| 2 | Acetoin | 51.50 | 25.56 |
| 3 | Glycerol | n.a. | 1.60 |
| 4 | Citrate | 9.59 | n.a. |
| 5 | Succinate | n.a. | 0.97 |
| 6 | Glucose | n.a. | n.a. |

n.a. corresponds to "not available".

aqueous-phase fermentation broths. In addition, desorption into the solution without any acidic components is of great interest for the practical application due to economic benefits, better corrosion properties, and an easier workup of the obtained effluent. Desorption efficiency using pure ethanol and acetonitrile was rather low. No desorption occurred when aprotic organic solvents such as propylene carbonate, ethyl acetate, or toluene were used. Only minor leaching of boron of ca. 2% was detected for acidified solutions and no boron loss was observed after desorption in neutral aqueous-ethanolic mixtures.

Meso-BDO is desorbed more easily than *rac*-BDO, which relates to a lower complex stability of the *meso*-isomer with phenylboronate. Thermodynamics plays the central role not only for the adsorption but also for the desorption processes. The obtained mixture of the stereoisomers contained more *meso*- than *rac*-BDO (Fig. 3).

3.3. Adsorption of BDO from fermentation broths

Fermentation broths present very complex mixtures containing not only the products of fermentation but also inorganic salts, yeast, enzymes, and compounds originated from cell lysis. All these components can potentially influence not only the sorption capacity, but also the selectivity of adsorption. We tested two fermentation broths FB1 and FB2, which contained both *meso*- and *rac*-BDO in different concentrations and ratios. The broths were obtained by fermentation of *D*-glucose by *Bacillus licheniformis* DSM 8785. The major low-molecular weight organic components of the broths are listed in Table 1.

In our first screening, the fermentations broths were mixed with 4 M NaOH solutions to achieve various ratios of BDO-to-NaOH. Moderate to low loadings of the polymer were obtained with the highest value of ca. 0.7 mol_{BDO} mol_B⁻¹ (Fig. 4). The more NaOH solution was added to the broths, the lower was the observed loading. According to the results

obtained with the model solutions reported in Section 3.1, this effect refers to the dilution of the broths leading to disfavored adsorption. For this purpose, we applied more concentrated 10 M NaOH to avoid high dilution factors upon adjusting desirable OH⁻-to-BDO ratios. Fig. 5 shows that utilization of 2 or 2.5 equivalents of NaOH and keeping initial BDO concentration in the range of 25–27 g L⁻¹ indeed results in a nearly quantitative boron complexation. Lower BDO uptakes for the conditions with 5 or 10 NaOH equivalents can be explained by the dilution leading to low initial concentrations of BDO. Interestingly, the *rac*-BDO isomer is preferably adsorbed from both FB1 and FB2, although the fermentation broths exhibit different ratios of the isomers (Table 1, Figs. 4 and 5).

Co-adsorption of other components of the fermentation broths is not desirable, since it results in contamination of the BDO streams after desorption and a potential decrease of the adsorption capacity. As adsorption takes place by complexation with the phenylboronate groups according to Scheme 1, co-adsorption of other molecules bearing vic-diol

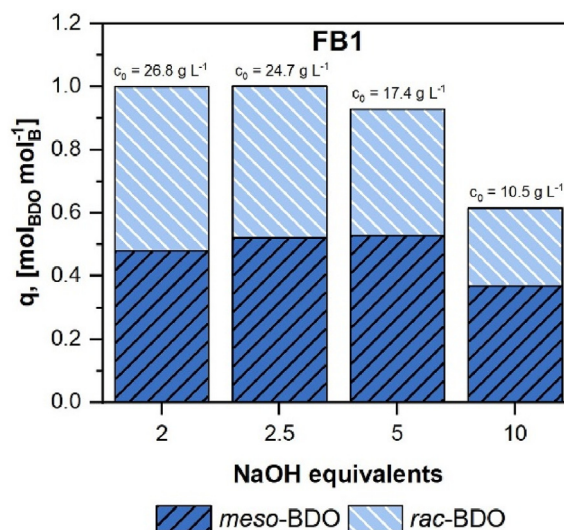


Fig. 5. Results of the BDO adsorption from the fermentation broth FB1 under the optimized conditions. FB1 was diluted due to addition of 10 M NaOH. The concentrations of BDO c_0 in the obtained solutions are provided on the graphs, the NaOH concentrations can be derived from the NaOH equivalents referring to the molar ratio of NaOH-to-BDO. Conditions: 2.63 mL solution were stirred with 200 mg polymer for 3 h at RT.

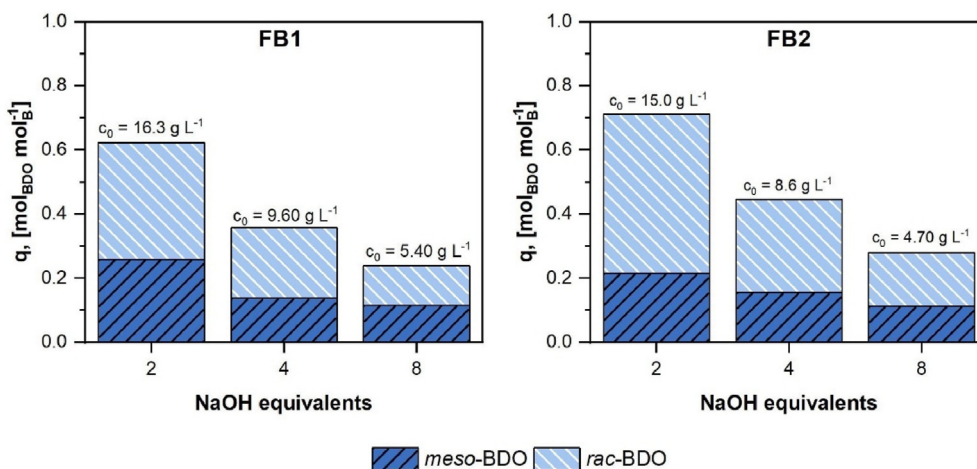


Fig. 4. Results of the BDO adsorption from the fermentation broths FB1 (left) and FB2 (right). FB1 and FB2 were diluted due to addition of 4 M NaOH. The concentrations of BDO c_0 in the obtained solutions are provided on the graphs, the NaOH concentrations can be derived from the NaOH equivalents referring to the molar ratio of NaOH-to-BDO. Conditions: 2.63 mL solution were stirred with 200 mg polymer for 3 h at RT.

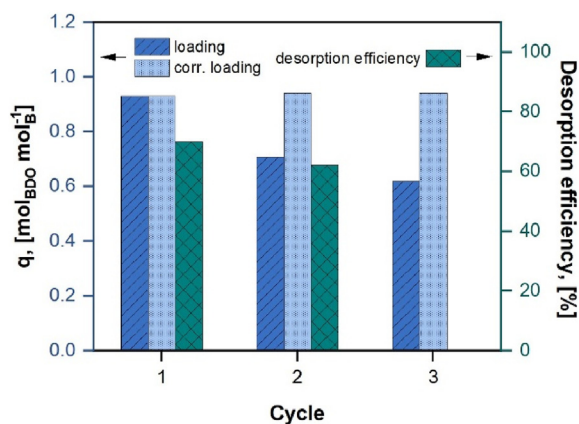


Fig. 6. Recycling of the polymer for BDO recovery in three adsorption-desorption cycles. Adsorption conditions: in the first adsorption cycle, 7.88 mL of FB2 with 2 equivalents of NaOH were allowed to stir with 300 mg polymer for 4 h at RT. Desorption was performed by stirring the loaded polymer in 20 vol% water-80 vol%EtOH solution for 4h at RT. “Corrected loading” refers to a total loading after a cycle, considering BDO adsorbed during the previous cycles.

motifs can be envisaged. This work and the previous studies [63,64] show that thermodynamics determines the loading, i.e. uptake of the compounds with high complexation constants is preferable. Consequently, the explored separation method is exceptionally suitable for fermentation broths, which are free from D-glucose and other saccharides (Table 1). Saccharides form more stable complexes than BDO ($K^{B-S} = 1.81$ for D-glucose vs. $K^{B-S} = 0.54$ for BDO). Moreover, saccharides can undergo different degradation and transformation reactions in the presence of NaOH [71,72]. Glycerol shows a somewhat higher complexation constant than BDO ($K^{B-S} = 1.2$ for glycerol). Noteworthy, glycerol concentration was controlled by selecting sufficiently high maximum oxygen transfer capacities (low filling volumes) during the fermentation resulting in no or only little glycerol concentration in FB1 and FB2 [67]. Due to the rather low concentration of glycerol in the fermentation broth, its only negligible uptake during adsorption was observed. We monitored the concentration changes of acetoin and carboxylic acids upon adsorption. Only slight changes of 1–6% were detected, the details are provided in the ESI.

Potential adsorption of the components of the fermentation broths was explored by MAS NMR. In accordance with the HPLC data, the spectra of the loaded materials exhibited only the signals of the polymer and BDO. No signals of glycerol were observed. Moreover, no characteristic resonances in the range of 180–210 ppm which would correspond to a carbonyl group of acetoin were detected. Based on this data, we conclude that adsorption of BDO from the fermentation broths takes place selectively.

In order to explore recyclability of the polymer, it was used in three adsorption and two desorption cycles of BDO from FB2. The results are shown in Fig. 6. In the first cycle, a very high loading of the material of $0.93 \text{ mol}_{\text{BDO}} \text{ mol}_{\text{B}}^{-1}$ was obtained. The 20 vol% water-80 vol% EtOH solution was used for desorption, and the desorption efficiency was ca. 70%. The lower desorption efficiency for FB2 than for the model solution can be attested to a higher fraction of *rac*-BDO, which were 56% and 25% for FB2 and the model solution, respectively. In the second and the third cycle, the uptake of BDO exhibited a monotonous decrease. This can be explained by an incomplete desorption as well as a minor boron leaching (Section 3.1), though MAS NMR data suggested no degradation of polymer backbone under adsorption conditions. The total loading considering the uptakes of the previous adsorption cycles referred to as “corrected loading”, remains as high as 93–94% in all three cycles. This suggests a high robustness and recyclability of the material.

4. Conclusion

This work shows a high efficiency of phenylboronate-functional polymers for adsorption of BDO from fermentation broths. The careful optimization of the reaction conditions regarding the concentration of NaOH and dilution factors enabled quantitative loadings of the polymers of $250 \text{ mg}_{\text{BDO}} \text{ g}_{\text{polymer}}^{-1}$ or ca. $1 \text{ mol}_{\text{BDO}} \text{ mol}_{\text{B}}^{-1}$. Efficient desorption was possible in a 20 vol% water-80 vol%EtOH solution, which suggests a significant gain in energy efficiency upon solvent vaporization compared to aqueous fermentation broths. An excellent selectivity for BDO adsorption compared to other components of the fermentation broths makes the adsorption an attractive recovery technique. The presented results can serve as a basis for development of novel sustainable and energy-efficient methods for separation of highly commercially relevant BDO from fermentation broths.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Irina Delidovich reports financial support was provided by Deutsche Forschungsgemeinschaft. Guido Schroer reports financial support was provided by German Federal Environmental Foundation (DBU).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.crgsc.2022.100297>.

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