Towards Sustainable Lactic Acid Production: Avoiding Gypsum as By-Product by Selective Liquid Phase Adsorption

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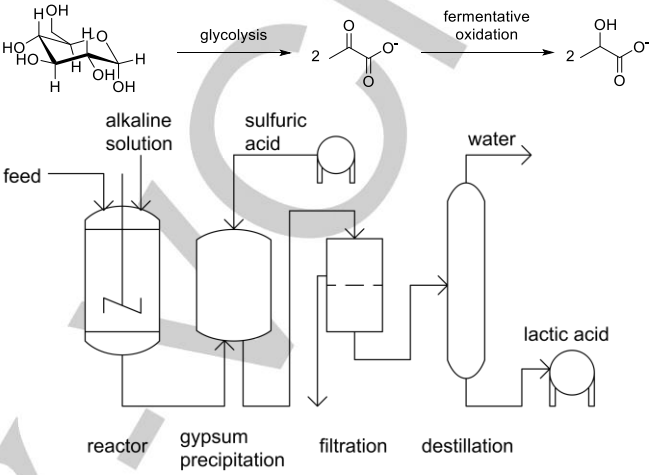
Abstract: The utilization of biomass is one of the major challenges for the transition from fossil to renewable resources. Often, the separation of the desired product from the reaction mixture is the most energy intensive step. Liquid phase adsorption is a promising separation technology that could significantly improve downstream processing in biorefineries. We applied highly hydrophobic adsorbents for the separation of lactic acid (LA) from aqueous solution and to avoid the formation of gypsum as by-product. Single solute and co-adsorption experiments exhibited high uptakes and selectivity. Porous hypercrosslinked polymers (HCP) and polymer-based spherical activated carbon (PBSAC) performed best and showed excellent selectivity for the selective removal of LA. Desorption experiments revealed that HCP is the ideal adsorbent for the separation of LA from aqueous solution. Hence, the development of a gypsum-free LA production is enabled.

Introduction

The separation units in chemical and biotechnological processes require a great amount of the total process energy.[1] Considering the transition from fossil to renewable energy, the need to reduce the total energy consumption increases. To do so, either new separation methods have to be developed, or existing technologies need to be improved. Liquid phase adsorption is a technology with the potential to be one of these low energy consuming processes. Its application is especially suitable for the development and improvement of biorefineries as often energy-intensive thermal separation is not an option. The physical adsorption, based on weak van der Waals interactions, was already successfully proven for different biogenic platform chemicals such as itaconic acid[2], 5-hydroxymethylfurfural[3,4] and levulinic acid[5]. Typical commercially available adsorbents are porous materials such as zeolites or activated carbons. In general, the adsorption capacity strongly depends on the surface properties and the available surface area. When it comes to process efficiency, selectivity is the most dominant factor, especially in case of *in situ* product recovery. Feasible adsorbents exhibit a low surface polarity and are therefore highly hydrophobic. Besides commercially available adsorbents, particularly tailored porous polymers with a highly hydrophobic surface exhibited great performance in the liquid phase adsorption of biogenic compounds.[2,3,6]



Scheme 1. Conventional fermentative production of lactic acid/lactate via glycolysis of glucose and consecutive oxidation, typically by *lactobacillus* bacteria. Calcium lactate is precipitated and finally the lactic acid is regenerated using sulfuric acid

Lactic acid (LA) is one of these promising platform chemicals for which liquid phase adsorption might be an alternative to current separation methods, as the industrially established process produces a stoichiometric amount of salt waste as by-product.[7] LA is produced by microbial fermentation converting starch-based substrates. It is mainly used as monomer for the production of polylactic acid (PLA), but has also great potential for the production of various substances, such as acetaldehyde, propylene glycol or acrylic acid.[8] PLA is a bio-based and bio-degradable polymer which can replace petrochemical-based plastics. With its high chemical resistance and good processability it is a bio-based alternative for fibers, films and many more.[9] The downstream processing in fermentation processes often poses the major challenge, as these steps can add up to 40 % of total production costs.[10] Currently, calcium hydroxide precipitation is the most often applied method to adjust the pH value for a higher productivity and separate LA from the fermentation solution (Scheme 1).[10] By regeneration of the LA from its calcium salt with sulfuric acid stoichiometric amounts of gypsum ($CaSO_4$) are produced, which is considered to be a major drawback for economic and environmental impact of LA production. Alternative methods proposed for the LA recovery are extraction, ion exchange, membrane separation or reactive distillation, amongst others.[11] Besides these techniques, liquid phase adsorption was already envisioned to be suitable in the separation of LA from the fermentation mixtures.[12,6] In these studies mainly conventional activated carbons or polymeric resins were investigated, showing strongly varying adsorption capacities and rather low selectivity. Besides these commercially available materials, recently also a porous covalent organic framework (COF) was used in the LA adsorption that showed

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rather promising performance although an in-depth investigation was not carried out.[6]

Hence, in this study we investigated in detail the selective separation of lactic acid and glucose from aqueous solution by liquid phase adsorption using highly hydrophobic adsorbents such as porous hyper-crosslinked polymers and various commercially available materials. We focused on the temperature, concentration and pH dependence of uptake and selectivity as well as the desorption properties. Overall, a high potential of liquid phase adsorption for an enhanced LA production process is demonstrated.

Results and Discussion

Adsorbent screening

An initial adsorbent screening was carried out based on a broad range of different porous materials that exhibit a rather high hydrophobicity. Besides commercially established materials such as polymer-based spherical activated carbon (PBSAC)[13], zeolite or polymeric resins, also a zeolitic imidazolate framework (ZIF) and a hyper-cross-linked polymer (HCP) were investigated. Not only their textural properties (see Table S1) were of importance for the adsorption capacity, but also the surface polarity and hydrophobicity have a major influence on the selectivity.

Single solute experiments at 30 °C (Figure 1a) showed that the PBSAC (2.2 mmol g^{-1}) and the HCP (1.5 mmol g^{-1}) exhibit the highest adsorption capacities for LA, respectively. The polymeric resins Amberlite 458 Cl and Purosorb PAD 400 show no or only very minor adsorption, probably due to pore blocking in the aqueous environment. Interestingly, ZIF-8 does not show a very high uptake of LA (1.02 mmol g^{-1}), despite its hydrophobic surface and crystalline pore structure. The zeolite HCZP has a ratio of 800:1 Si:Al and therefore, also a highly hydrophobic surface. Compared to ZIF-8, HCZP exhibits a similar uptake (0.88 mmol g^{-1}) even though the specific surface area is significantly smaller.

No material except for the PBSAC showed a measurable adsorption of glucose (Figure 1a) from single solute solution. It exhibited an uptake of 0.87 mmol g^{-1}, a quite significant amount compared to the LA uptake. For the HCP the glucose uptake is expected to be low, as shown before for the competitive adsorption of itaconic acid and glucose[2], as the material consists only of aromatic building blocks resulting in its very hydrophobic nature.

Of greater importance is the competitive adsorption of LA and glucose from aqueous solution as this provides direct information on the selectivity and hence, the expected separation performance of different materials (Figure 1b). For the application of liquid phase adsorption in the separation of lactic acid, the adsorption of LA should be strongly favored. As the resins did not show any uptake of either LA or glucose, they were not used in further adsorption screenings. All adsorbents show a small decrease in the LA adsorbed amount, while only ZIF-8 exhibits an increased glucose adsorption resulting in a very low selectivity. A significant difference is observed for the PBSAC. It shows a significantly decreased glucose adsorption, and hence, an outstanding high selectivity for LA. A very similar performance is observed for HCP as it adsorbs a similar amount of LA and also no glucose within the error of measurement. This outstanding performance of HCP and PBSAC, based on their hydrophobic surface with large specific surface areas and permanent pore volume, motivated us for a more detailed investigation of the adsorption performance of both adsorbents.

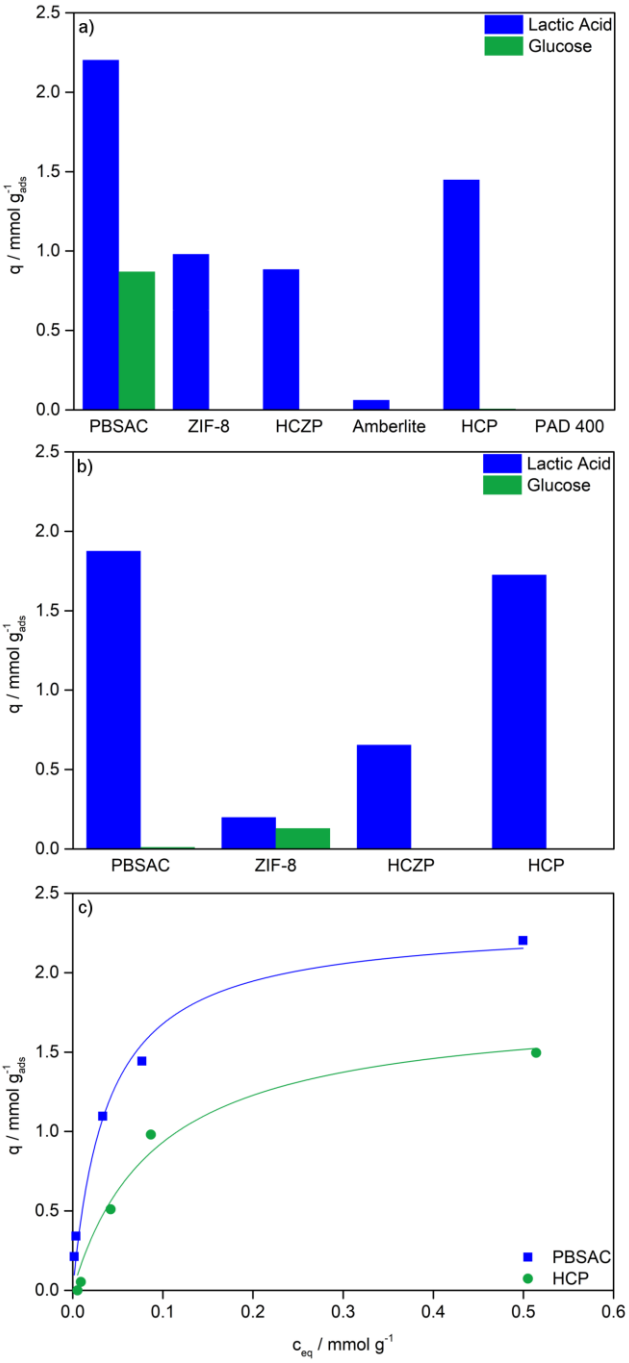

Figure 1. a) Adsorbent screening with single solute solutions (4.8 wt.-%), b) Competitive adsorption with selected adsorbents (4.5 wt.-% each component), c) Comparison of adsorption isotherms of LA from aqueous solution (0.05 – 4.8 wt.-%), fitted by a Langmuir adsorption isotherm model.

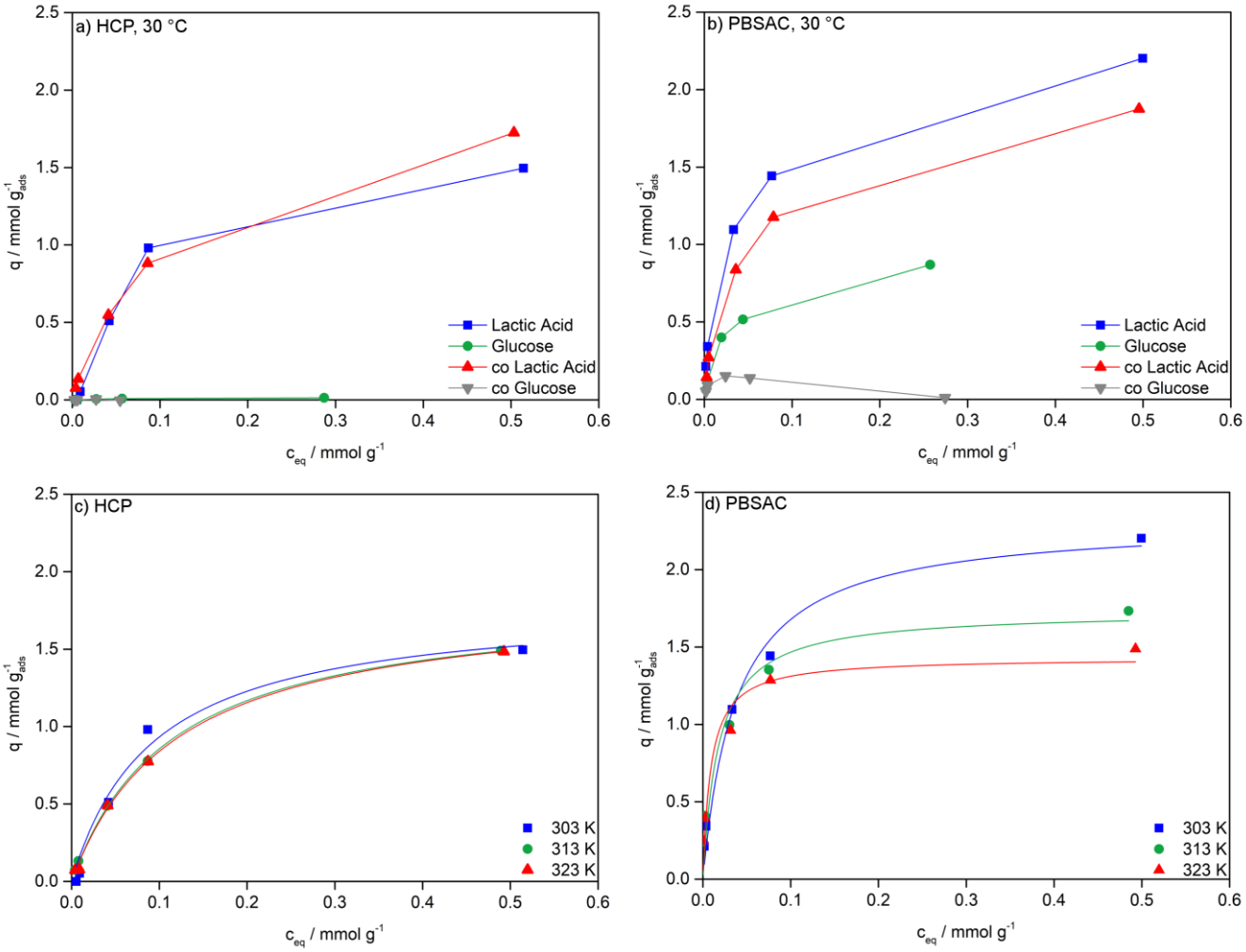

Figure 2. a) Competitive adsorption of LA and glucose, compared to the single solute adsorption measurements at 30 °C on HCP; b) Competitive adsorption of LA and glucose, compared to the single solute adsorption measurements at 30 °C on PBSAC (measured points are connected with a straight line for clarity); c) Temperature influence on the adsorption of LA from aqueous solution on HCP; d) Temperature influence on the adsorption of LA from aqueous solution on PBSAC.

Single solute isotherms

Single solute adsorptions isotherms of LA and glucose were measured for HCP and the PBSAC (Figure 1c). As glucose adsorption was only observed for the activated carbon this will not be discussed in this chapter in detail. The LA adsorption data were fitted with the Langmuir adsorption isotherm model. This model assumes only monolayer formation and a saturation within a given concentration range.[14] As the Langmuir isotherms fit the data very good, the general assumptions for this model seem to be feasible in the investigated concentration ranges. The parameters and correlation coefficients are shown in the Table S2. Due to the high affinity of adsorbate and adsorbent the obtained values for the dimensionless equilibrium factor R_L are between zero and one and indicate that the adsorption for LA is favored for both adsorbents in the evaluated concentration range. Comparing the Langmuir constant K_L of PBSAC and HCP, the value for the activated carbon was more than twice as high as for the porous polymer. This indicates a higher affinity of LA towards the PBSAC and is fortified by a higher LA adsorption at small concentrations for this activated carbon material compared to HCP. The maximum adsorption of LA is different for the two screened materials, but shows in both cases a saturation uptake under equilibrium conditions. PBSAC shows a higher uptake (2.2 mmol g^{-1}) than the HCP (1.5 mmol g^{-1}), which is also reflected in the calculated saturation uptake Q_{sat} as it is higher for the PBSAC. The different uptake is even more dominant when the adsorption is normalized to the specific surface area (PBSAC: $1.58 \cdot 10^{-3}$ mmol m^{-2}; HCP: $0.8 \cdot 10^{-3}$ mmol m^{-2}). These varying adsorption capacities can be attributed to the hydrophobicity of the materials. As HCP is far more hydrophobic than PBSAC the wettability might be reduced, lowering the contact surface area between the polymer particles and the aqueous solution. Thus, resulting in a lower adsorption for HCP even though it exhibits a higher specific surface area.

Competitive adsorption of lactic acid and glucose

Knowledge of single solute equilibrium adsorption is useful for the comparison of different adsorbents, but it is more important to investigate the co-adsorption from mixed solute solutions as it provides information about the selectivity of the adsorbents.

Therefore, adsorption isotherms of glucose and LA in binary mixtures were measured (Figure 2a, b). No modelling of the isotherms was carried out as the Langmuir model is only suitable to describe the adsorption of single adsorptives.

In case of the HCP adsorbent the results of the competitive adsorption do not differ significantly compared to the single solute adsorption (Figure 2a). In both cases no glucose adsorption is observed in the investigated concentration range of 0.05-4.8 wt.-%. Regarding the adsorption of LA, no significant differences between the single solute and the co-adsorption can be observed. These results further prove the great selectivity of HCP towards the adsorption of LA over a broad concentration range. Through the addition of glucose to the aqueous LA solution, the total polarity of the solution is increased. This effect does not show an influence on the adsorption behavior of HCP, but causes a significantly different adsorption behavior of PBSAC (Figure 2b). There, the adsorption for LA as well as for the glucose decreases. For glucose the effect is much more pronounced, as the adsorption drops even to zero for the highest concentration. In general, the selectivity for PBSAC increased significantly from single solute adsorption to competitive adsorption.

Temperature dependence of the lactic acid adsorption

Both investigated adsorbents show a high selectivity and capacities for LA at 30 °C. Since fermentative production of LA often is also performed at higher temperatures, the adsorption behavior was investigated also at 40 and 50 °C in order to evaluate the temperature influence on the uptake under equilibrium conditions (Figure 2c, d). As HCP showed no adsorption of glucose, only aqueous LA isotherms are discussed. Again, the Langmuir model was applied for the adsorption isotherms and showed excellent convergence. With the consideration of an exothermic adsorption mechanism, the Langmuir constant K_L and the adsorption capacity Q_{sat} are expected to decrease with increasing temperature. The calculated values for HCP showed this trend for K_L, but the effect was smaller than expected (Table S2). Additionally, only a negligible decrease of the adsorption capacity at the higher concentration is observed. On the other hand, even a small increase of the saturation uptake (Q_{sat}) is found. This effect is unexpected when considering the conventional exothermic adsorption mechanism. However, the HCP is known to exhibit a high flexibility of the framework despite its permanent porosity.[15] Hence, upon temperature increase the accessible surface area can be increased by an enhanced surface wetting due to a reduced surface tension of water and swelling of the framework structure. As this effect occurs only in the liquid phase as an artefact of great polarity differences of fluid and solid phase in combination with the framework flexibility it cannot be easily quantified by conventional analytical methods. The investigation of this behavior is a topic of our current research.

In contrast, PBSAC shows a temperature dependence as expected for LA (Figure 2d). The saturation adsorption capacity (Q_{sat}, Table S2) clearly decreases with increasing temperature, in maximum up to 34 % from 30 to 50 °C. As this material consists of rigid spherical particles, no changes of the material textural properties with rising temperature is expected. Additionally, even though the material is hydrophobic, the wettability of the spheres is at 30 °C already much better than for the small HCP particles. Besides the LA adsorption, also the influence of the temperature on the glucose adsorption was investigated and shows the expected behavior (Figure S1).

More importantly, the temperature dependence of the co-adsorption was investigated for HCP and PBSAC, respectively (Figure S2). Again, HCP showed no changes in adsorption capacity or selectivity, underlining its unique adsorption properties over a broad temperature and concentration range. Also for PBSAC the temperature seemed to have less influence on the performance in competitive adsorption, displaying a very similar performance as HCP.

Desorption experiments

Considering a technical application of LA adsorption on porous materials, an easy recovery of the adsorbed species is required and was therefore tested to confirm the applicability of this separation method. Both, the HCP and PBSAC, were in a first step loaded with LA from aqueous solution under equilibrium conditions, filtered off and then washed for one hour in acetone to ensure quantitative desorption under equilibrium conditions. An excellent desorption was observed for HCP as 98 % of the adsorbed LA could be recovered with only one washing step (Figure 3). The reason for this is, on one hand, the greater affinity of LA towards acetone. On the other hand, swelling might play an important role. When exposed to organic media, the volume of the polymer increases up to 100%.[16] Therefore, the contact area between acetone and HCP is significantly increased and LA can be easily desorbed. For PBSAC only 75% were desorbed in a single washing step. Therefore, multiple washing steps or continuous washing with much more desorption solvent or longer residence times are required to achieve full recovery. Technically, the HCP would be the better choice or, alternatively, the working capacity of the PBSAC would be significantly reduced per adsorption/desorption cycle as the remaining adsorbed species after one cycle can be considered constant for subsequent cycles.

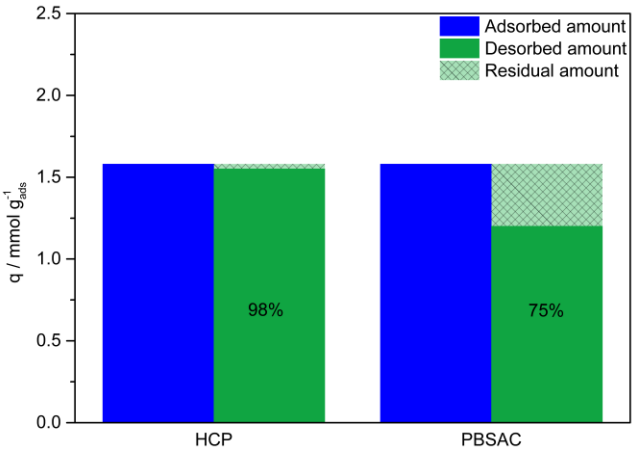

Figure 3. Adsorption from aqueous LA solution (4.8 wt.-%) on HCP and PBSAC with consecutive desorption with acetone.

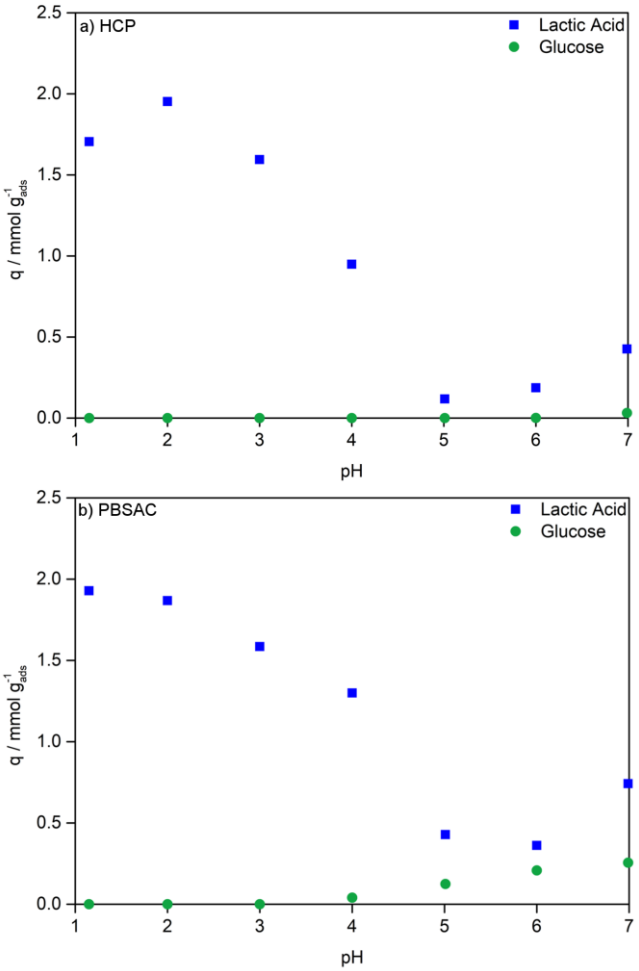

Figure 4. Influence of pH value on the adsorption of LA and glucose from model fermentation mixture (LA:glucose 7:1) on a) HCP and b) PBSAC.

pH influence on the adsorption of lactic acid

Typically, bacteria that produce LA in fermentative processes like *Lactobacillus acidophilus* are able to grow even at rather low pH values.[17] Many of these bacteria grow best at a pH 5-6. Hence, often the fermentation mixture is buffered at this value.[18] In some cases, even a pH of 4 is found after the fermentation.[19] Below such pH the growth of *lactobacillus* strain is strongly inhibited and leads to a fast decrease of the number of viable cells.[20] As the pH is a crucial factor in the LA fermentation, its influence on the adsorption behavior of HCP and PBSAC was investigated. The typical adsorption experiments described above with no buffer solution applied were carried out at approximately pH 1. Hence, to investigate the pH dependence a sodium hydroxide solution was used to adjust the pH value in the range 1-7.

For both adsorbents, a drastic influence of the pH value on the adsorption capacity at equilibrium conditions is observed due to the formation of more polar lactate ions that exhibit a significantly decreased adsorption at increasing pH (Figure 4). HCP shows a LA adsorption maximum at pH 2 with a significant decrease with increasing pH. At pH 5 the adsorption is close to zero, whereas the glucose adsorption remains constantly low for the whole measured range. PBSAC exhibits, comparable to HCP, a decrease of adsorption capacity with increasing pH.

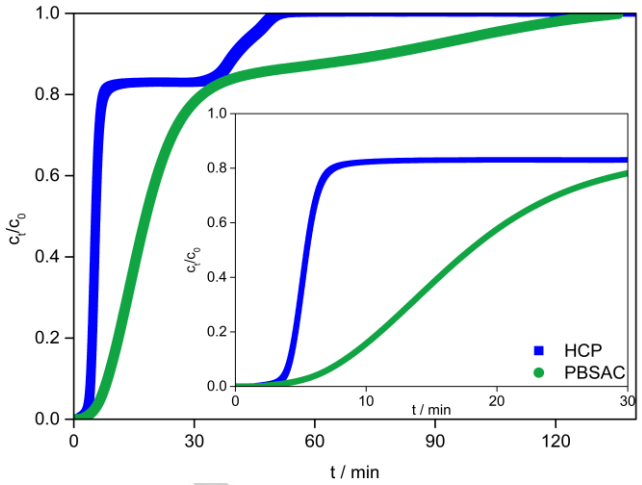

Figure 5. Breakthrough curves of lactic acid from continuous adsorption of an aqueous lactic acid solution (0.044 mmol g^{-1}) on a 300 mg fixed-bed of HCP and PBSAC at 30 °C. The inset show the zoom in for t = 0-30 min.

Additionally, both adsorbents show at pH 7 a slightly increased adsorption than at pH 5-6, but especially for PBSAC the selectivity was rather low as glucose adsorption increases with the pH.

To control the pH value of the mixture in the current technical process between 5.0 and 6.5 calcium hydroxide, calcium carbonate, ammonium hydroxide and sodium hydroxide are typically added, resulting in the formation of the corresponding lactate salts. Thereby, stoichiometric amounts of salts are produced as by-products as the addition of sulfuric acid is necessary to regenerate the free lactic acid. Hence, to apply the adsorption-desorption process for LA separation to avoid salt formation the fermentation has to be carried out at a trade-off of a slightly decreased pH value to enable sufficient productivity of the microorganisms but also to allow for a sufficient adsorption uptake for an overall efficient separation process.

Continuous adsorption in a fixed-bed adsorber

Considering the technical application of lactic acid adsorption, continuous separation with a fixed-bed adsorber has to be evaluated in order to confirm its applicability. Both materials exhibit strong mass transfer limitations, as they show a first plateau at around 80 % c_t/c_0 (Figure 5). The reason for this are the surface properties of the materials. Both have a high amount of micropore surface area and pore volume (Table S1) which generally limits the mass transport in the pores. Until the first breakthrough, all adsorption sites that are easily accessible seem to be occupied. The adsorption in the smaller share of micropores, however, is not completed at that point. Transport into the micropores takes a significant longer time, resulting in the observable plateau. Interestingly, the HCP fixed-bed shows a fast and very steep breakthrough, already after 200 seconds. Whereas in the case of PBSAC the breakthrough after 280 s takes more than 25 minutes to reach the first plateau. The resulting adsorption capacities before the first breakthrough are 0.37 mmol g^{-1} for PBSAC and 0.3 mmol g^{-1}for HCP, respectively.

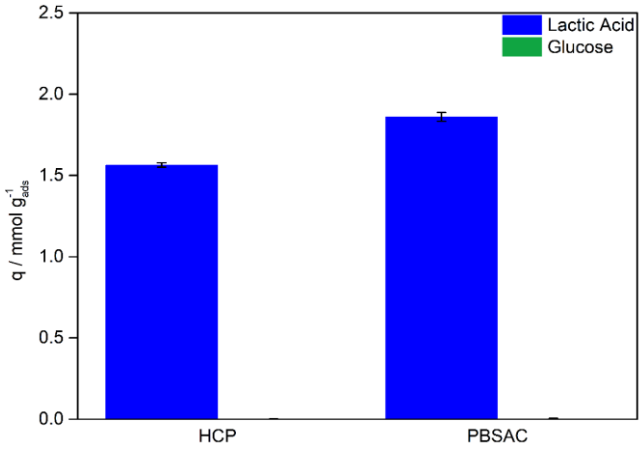

Figure 6. Adsorption of LA and glucose from aqueous model fermentation mixture with a ratio of 12.1 : 1.7 wt.-% (LA:glucose) on PBSAC and HCP. Error bars indicate the standard deviation of three independently performed adsorption experiments. The pH was not adjusted to an actual fermentation broth.

The adsorbed amount until the first plateau is much higher for PBSAC (1.65 mmol g^{-1}) than for HCP (0.53 mmol g^{-1}), resulting from the different nature of the breakthrough slope. These different slopes can be attributed to the unequal particle size of the materials. HCP has significant smaller particles (<100 nm), compared to the PBSAC (0.315-0.58 mm). The obtained adsorption values at the beginning of the plateau are equivalent compared to the adsorbed amount from the batch adsorption experiments at an equilibrium concentration of 0.044 mol g^{-1} LA (see Figure 1). The additional uptake after the plateau is caused by the elevated pressure inside the fixed-bed adsorber (0.6-2 bar). Thereby, small pores have to be taken into account that weren't accessible at normal pressure during the batch experiments, resulting in an overall more effective wetting of the particles. This leads to a total uptake (at c/c_0 =1) on HCP of 1 mmol g^{-1} and 2.25 mmol g^{-1} for PBSAC, respectively. In contrast to the two steps of the lactic acid breakthrough, aqueous glucose solution only shows plateau at initial concentration after 53 minutes on PBSAC (Figure S7). The adsorbed amount of glucose is 0.54 mmol g^{-1} which again is in the range of the results from the batch adsorption (compare Figure 2b) at an equilibrium concentration of 0.022 mmol g^{-1}. Bearing in mind that glucose has double the molecular mass of lactic acid and is consequently larger no adsorption in the small micropores is expected, leading to the observable single plateau.

These first tests for the continuous adsorption revealed that a technical application on both investigated materials is only feasible at a partial loading based on the fast mass transfer while part of the capacity remains unused. Both materials show severe mass transport limitations for a certain fraction of smaller pores and the additional uptake only occurs after multiple initial breakthrough times. Further studies with aqueous solutions of both glucose and lactic acid need to be carried out to determine the working capacity and selectivity of the fixed-bed columns in competitive adsorption.

Model fermentation solution

Normally, lactic acid fermentation mixture does not contain equal amounts of LA and glucose as applied for most experiments described above, but rather a high concentration of LA and just residual amount of glucose.[21] Therefore, the HCP and the PBSAC were tested in a more realistic fermentation model solution with a ratio of 7:1 LA to glucose (Figure 6), without adjusting the pH to that of an actual fermentation broth. The results show no significant change compared to the 1:1 mixture at 4.5 wt.-% each. This indicates on the one hand, that the materials retain their high selectivity independently of the glucose concentration and on the other hand, that their maximum adsorption capacity does not exceed 2 mmol g^{-1}. The same experiments were used to determine the overall error of the typical adsorption experiments by three independently performed runs. It shows that the standard deviation for each adsorption experiment is negligibly low and proves the high accuracy of all conducted experiments.

Conclusion

This study provides a comprehensive investigation on the separation of lactic acid from glucose and aqueous solutions by selective liquid phase adsorption. A variety of adsorbents were tested and the screening showed the necessity of a combination of high specific surface areas and a highly hydrophobic surface, as an activated carbon (PBSAC) and a nanoporous hyper-cross-linked polymer (HCP) showed an outstanding performance. Single solute and competitive adsorption experiments at equilibrium conditions and on a broad concentration range were carried out, modeled and compared. It was shown that both, HCP and PBSAC, had comparable adsorption capacities, whereas PBSAC showed a major temperature dependence, which was not found for HCP as it is probably compensated by an enhanced swelling and wettability at increased temperature. Desorption experiments demonstrated the excellent reversibility of LA adsorption on the HCP, as lactic acid was quantitatively recovered after one washing step. Both materials exhibited a great influence of the pH value on the adsorption properties, with a maximum adsorption between pH 1-3. Regarding the outstanding performance of the porous HCP, continuous breakthrough experiments in a fixed-bed adsorber were performed. Both, HCP and PBSAC showed a pronounced mass transfer limitation as the breakthrough curves showed a plateau at around 80 % c_t/c_0. The obtained adsorption capacities at the beginning of the plateau fit with the adsorbed amounts from batch adsorption isotherms. Further adsorption that occurs much slower is induced through elevated pressure and hence, either an improved wetting of the particles or a much slower mass transfer by pore or even surface diffusion.

Overall, HCP seems to be an ideal adsorbent as it shows excellent adsorption/desorption properties in combination with an exceptional high selectivity. The application of this material in the liquid phase adsorption offers a promising opportunity to improve the separation of lactic acid towards a more sustainable process. Also, a transfer of this technology to the production of

other high value chemicals from aqueous reaction mixtures and fermentation broths seems feasible as the liquid phase adsorption demonstrates great potential to solve one of the major challenges in biorefineries.

Experimental Section

Materials

D-Glucose (>99%) and Lactic acid (90%) were purchased from Carl Roth. 4,4'-Bis(chloromethyl)-1,1'-biphenyl (BCMBP, 95%) and 1,2-dichlorethane (DCE, 99,8%) were purchased from Sigma-Aldrich. Trifluoromethylsulfonic acid (TFMSA, >99%) was supplied from Fluorochem. The zeolite HCZP 800 was provided by Clariant, ZIF-8 was purchased from Material Center Dresden and the polymer-based spherical activated carbon was provided by Blücher GmbH (particle size: 0.315-0.580 mm). The resin PAD-400 was provided by Purolite and Amberlite IRA 458 Cl from Rohm and Haas France S.A.S. Purified water (>18.2 MΩ·cm) from a Millipore simplicity® UV system was used to prepare aqueous solutions. All chemicals were used without further purification.

Methods

Synthesis of Hyper-Cross-Linked Polymer (HCP). The synthesis of the hyper-cross-linked polymer (HCP) was carried out as described recently by Schute et al.[16] SEM images showed a strong aggregation of the small primary particles (<100 nm) to particles of 5-10 µm (Figure S6).

Adsorption Experiments. All adsorption experiments were carried out in a sand bath under isothermal conditions. Except for the resins, the adsorbents were dried in vacuum at 60°C for at least 24 h. In a typical adsorption experiment 2 g of adsorbate solution with 40 mg of adsorbent were stirred at isothermal conditions for 1 h. The time of adsorption was held constant to ensure equilibrium conditions, which was confirmed by prior time-resolved adsorption experiments. After the designated adsorption time, the loaded materials were filtered off, and the resulting solutions were analysed by HPLC. Single solute adsorption isotherms were measured in a concentration range from 0.05 to 4.8 wt.-% and at 30, 40 and 50 °C, respectively. Competitive adsorption isotherms were also measured at a concentration of 0.05 to 4.5 wt.-% for each compound, at the same temperatures. Further adsorption experiments were performed at a model fermentation solution with a concentration of lactic acid of 12.1 wt.-% and glucose of 1.7 wt.-%. To investigate the influence of the pH value, different solutions of the model fermentation mixture were prepared using a 3M sodium hydroxide solution. The total uptake q_{eq} of the materials in the equilibrium is calculated as ratio to the specific applied mass of the adsorbent according to eq. 1.

$$q_{eq} = \frac{(c_0 - c_{eq}) \cdot m}{W} \quad (1)$$

The uptake is calculated on the basis of the concentration change of the single components, whereas volume changes were not considered. c_0 and c_{eq} are the concentrations of the substances at initial conditions and at the equilibrium. m is the total mass of the adsorbate solution and W is the mass of the dry adsorbent.

Desorption Experiments. Prior to the desorption tests, a typical adsorption experiment with a 4.8 wt% aqueous solution of lactic acid was performed. Afterwards, the adsorbent was filtered off, transferred to a small vial and stirred with 2 mL of the corresponding desorption solvent at isothermal conditions for 1 h. The resulting solutions were analysed by HPLC.

Continuous Adsorption Experiments. For the continuous adsorption on a fixed-bed adsorber two different stainless steel columns were used (PBSAC: 5.65 x 60 mm, HCP: 4 x 41 mm). The lactic acid solution with a concentration of 0.044 mmol g^{-1} was pumped through the fixed-bed by a HPLC pump at a flow rate of 0.6 mL min^{-1}. The adsorber column was kept under isothermal conditions at 30 °C in a water bath. The output of the column was analysed online by a refractive index detector. Typically, 300 mg of adsorbate was used for the fixed-bed adsorber.

HPLC Analysis. After filtration the solutions were analysed using an Agilent 1260 high performance liquid chromatography (HPLC) system equipped with a refractive index detector as well as an organic acid analysis column (Aminex© HPX-87H, BIO RAD) maintained at 60°C. 10 µL injections were made, and a mobile phase of 0.1 N sulphuric acid in water with a flow of 0.475 mL min^{-1} was used.

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Keywords: Biomass • Lactic Acid • Adsorption • Separation • Downstream processing

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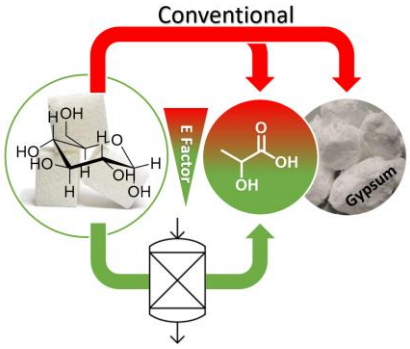

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