

Application of Amine-Functionalized Cellulose Foam for CO₂ Capture and Storage in the Brewing Industry

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ABSTRACT Due to a lack of technology, smaller breweries simply dump excess CO₂ into the atmosphere, fueling the greenhouse effect and global warming. State-of-the-art CO₂ capture technologies using nanofibrillated cellulose are expensive and require laborious freeze-drying. Consequently, there is a high demand for affordable alternatives in order to reduce the environmental impact in this industry sector. This work describes a novel route for a quick and cost-efficient synthesis of amine-functionalized cellulose pellets by a surfactant-assisted steam explosion process. Typical values with this method were porosity of 92% and density of 67 g/cm³. Investigations on polyethylenimine (PEI) content and distribution revealed a maximum PEI concentration of 20 wt% with decreasing concentration to the core of a pellet. Sufficient stability against brewery exhaust gas was determined and CO₂ release at ~ 120 °C could be confirmed. Capacity tests under simulated working conditions with a novel laboratory reactor yielded a CO₂ capacity of 1.0 mmol/g or 67 mol/m³, which is comparable to values known from the literature for other cellulose-based adsorbents.

KEYWORDS: CO₂ capture, carbon capture, poly(ethylenimine), cellulose, adsorption

1 INTRODUCTION

Anthropologic climate change is an ever-growing problem for the planet, nature and the human population. One of the major factors influencing global warming is the emission of CO₂ into the atmosphere [1]. Besides direct fossil fuel combustion, industrial production processes also release greenhouse gases. In breweries, the fermentation during the brewing process generates large amounts of CO₂. Additionally, it is used as flushing and pressurization gas that has to be purchased and afterwards directly released into the environment. Since current techniques for the recovery of the CO₂ gas are too expensive for small- and medium-sized companies (i.e., < 200,000 hl/a) [2], around 70,000 t/a of the gas are emitted into the atmosphere in Germany [3].

Therefore, materials that can capture and release CO₂ on demand are required in order to reduce industrial CO₂ emissions. Especially techniques that change environmental conditions, like temperature or pressure, are

of high interest [4–10]. For the manufacturing of such materials, freeze-drying of amine-functionalized nanofibrillated cellulose (NFC) is widely reported in the literature for CO₂ capture and storage [11–13]. However, there are two challenging disadvantages regarding this type of CO₂ adsorbent, which highly limit its further application. First, the process of NFC production is still not industrialized. Therefore, the costs for NFC as a support material are reported to be up to 2000 €/kg [14]. Second, a time-consuming and energy inefficient freeze-dry process further increases the cost of functionalized NFC. Since NFC solutions contain more than 90 wt% water before freeze-drying, the energy consumption could be evaluated similar to industrial freeze-dried fruit with approximately 40 €/kg [15].

In this study, we introduce a novel, economically advantageous fabrication process of amine-functionalized cellulose foam based on cellulose microfibrils. Instead of freeze-drying, a violent hot press process at 140 °C is used to produce porous adsorbent material. Structure and stability of the novel material are investigated along with CO₂ capacity measurements in a novel laboratory test platform simulating working conditions in breweries.

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2 EXPERIMENTAL SECTION

Cellulose fibers (Arbocel BC 1000) were purchased from J. Rettenmaier & Söhne GmbH + Co KG (Germany). Branched Polyethylenimine (PEI) with an average molecular weight of 25,000 g/mol and Lugol Solution (KI/I₂) were purchased from Sigma-Aldrich. Water-free sodium hydroxide (NaOH) was purchased from Merck. Sodium n-dodecyl sulfate (SDS) was supplied by Alfa Aesar. The potato starch was supplied by RUF KG (Germany). All experiments used deionized (DI) water.

2.1 Adsorbent Fabrication with Hot Press Process

First, 10 g of BC 1000, 1 g of starch powder and 0.16 g of SDS were weighed in a beaker and mixed with an aqueous solution of 10 g of PEI. The amount of water was adapted to enable proper stirring and pH was adjusted to 11.5 with NaOH. Subsequent stirring with a high-performance dispersing instrument for 5 min led to a volume increase of around 300% by the generation of air bubbles in the mixture and yielded a stable pulp foam. Excess water in the system was removed by mild vacuum filtration in order to preserve the foam structure. In a next step, the pulp foam was transferred into an aluminum mold with cylindrical cavities of 27 mm diameter and 11 mm height, each filled with 3 g of pulp foam. The mold was placed in a laboratory hot press at a temperature of 140 °C and an initial pressure of 0.4 MPa, leading to water vapor explosion in the cavities. The pressure was reduced to normal after 3 min and the samples were fully dried for about 10 min at 140 °C in the cavities, yielding porous adsorbent pellets.

2.2 Physico-Chemical Characterization

Microstructural investigations of the adsorbent were performed with scanning electron microscopy (SEM) in a Zeiss REM EVO MA15 microscope. An integrated EDX/EBSD sensor was used for energy dispersive X-ray analysis. Prior to the analysis, the samples were placed on a sample holder with conductive carbon stickers and subsequently were sputtered with gold for 100 s under argon atmosphere at 0.05 mbar in a Cressington 108 Auto Sputter Coater.

Analysis of starch particles in the adsorbent was done by coloring the starch with diluted Lugol Solution (1:10 v/v with DI water) and subsequent optical microscopy (OM) using a Zeiss Axioskop 2 MAT. A complex of intense color can be formed by the intercalation of polyiodide chains into the amylose helix of starch [16].

X-ray microtomography (μ -CT) of pellets was performed with a directional X-ray tube (110 kV, 150 μ A). Exposure time was 999 ms with one averaging step and an angular resolution of 0.225°. Use of helix scan pattern enabled a resolution of 19.2 μ m. Scan data evaluation with VGStudio MAX 3.0 yielded porosity and surface area of the specimen.

The density of the pellets was calculated as the ratio between weight and volume of the dried samples.

Thermal stability of the adsorbent was investigated by means of thermogravimetric analysis (TGA). Experiments were carried out by heating the samples from 25 to 800 °C in a Mettler Toledo TGA/SDTA 851e under nitrogen at a heating rate of 10 K/min.

Fourier transform infrared spectroscopy (FTIR) was used for qualitative analysis of PEI concentration at different positions of the adsorbent pellets. A Nicolet Nexus 40 spectroscope equipped with ATR measuring was used to record spectra with 64 scans in a range from 4000 to 800 cm⁻¹ and a resolution of 1.93 cm⁻¹.

Nitrogen content of the adsorbent was determined by means of elemental analysis (HEKAtech EA 3000). Prior to the analysis, the samples were dried at 105 °C. With known nitrogen content in the PEI, the PEI content in the adsorbent was calculated [17].

The temperature range for CO₂ release was investigated by coupling TGA (Mettler Toledo TGA/SDTA 851e) and FTIR (Nicolet Nexus 40) with a tempered interface. Prior to the measurements, adsorbent material was stored in pure CO₂ atmosphere at ambient pressure for 24 h. The specimen was then heated in the TGA from 25 to 200 °C under a nitrogen atmosphere employing a heating rate of 10 K/min. Simultaneously, the composition of the gas flow was analyzed every 10 s by FTIR, recording spectra between 4000 and 500 cm⁻¹ with a resolution of 1.93 cm⁻¹ processing 64 scans.

2.3 CO₂ Capacity Measurements at Simulated Operational Conditions

A laboratory setup to determine CO₂ adsorption capacity of the adsorbent with different gas compositions was invented. A schematic diagram on the setup can be found in Figure 1. The setup is equipped with a gas mixing unit for O₂, N₂ and CO₂, a gas humidifier, an adsorption column, as well as with sensors for pressure, temperature, relative humidity (RH) and oxygen content. The adsorption was carried out at room temperature. A gas stream of 600 ml/min containing 90 vol% CO₂ and 10 vol% O₂ was used for adsorption as well as desorption processes. Therefore, the gas was flushed through the adsorption column filled with cellulose material as adsorption bed. The CO₂ capacity was determined by

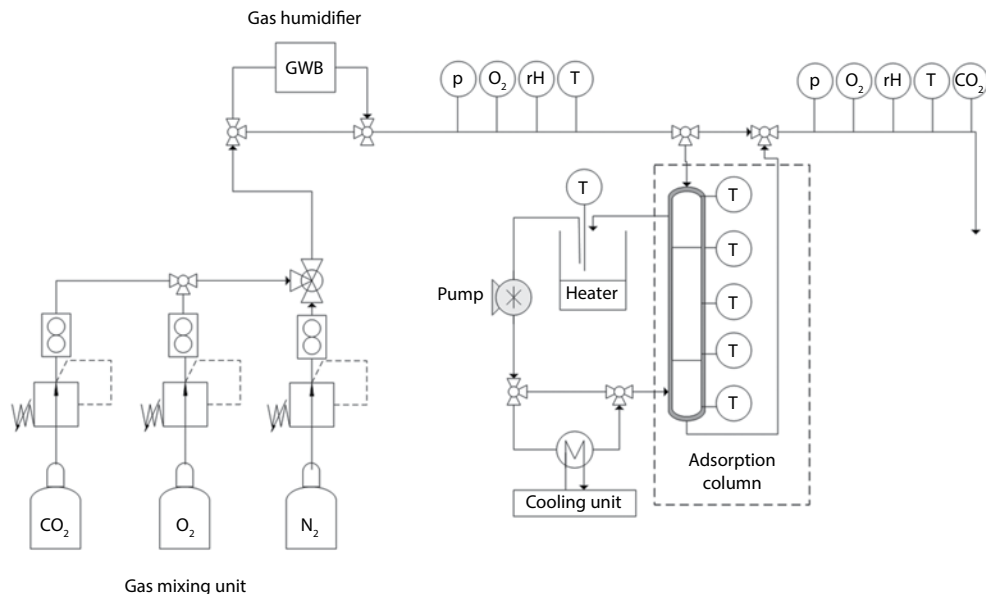


Figure 1 Schematic drawing of the laboratory setup of capacity measurements.

simultaneous measuring of temperature, pressure, RH and O₂ concentration of the incoming and outgoing gas stream from the adsorption column. For the capacity calculation it was assumed that O₂ does not interact with the adsorbents, thus the incoming and outgoing molar flow rate of O₂ are equal. This way the measured difference of O₂ partial pressure in the gas was used to calculate the change of CO₂ partial pressure indirectly. The CO₂ capacity was calculated from the difference between the incoming and outgoing molar flow rate of CO₂ over time. The CO₂ capacity correlates to the adsorbed amount of CO₂ per mass of the adsorbent. For the CO₂ desorption and recovery process of the adsorbent the double-shell column was heated to 120 °C with an oil-based heating system equipped with a pump and a heater. A cooling unit was used to cool down the reactor system for the next adsorption.

2.4 Brewery Gas Composition

The gas composition of brewery exhaustion gas was analyzed using pressure-, temperature-, humidity-, and oxygen-sensor as well as CO₂ sensor.

3 RESULTS AND DISCUSSION

3.1 Textural and Structural Features of the Adsorbent Material

In order to tailor a novel CO₂ adsorbent material and to establish an economically efficient production technique for this material, a hot press processing approach

is used. Initial trials (data not shown) indicated low mechanical stability of the cellulose-PEI composites. Therefore, starch was added to improve the mechanical properties of the fabricated pellets. Starch is a well-known additive in the paper industry to enhance the mechanical stability by the formation of a high number of hydrogen bonds [18, 19]. Due to the identical chemical structure of starch and cellulose, starch features the same functionalization potential as the fiber matrix.

The photographs of the resulting cellulose/starch/PEI pellets are shown in Figure 2a,b. Large voids in the μ -CT (Arrows in Figure 2c,d) and separated fibers in the SEM micrograph (Figure 2e) indicate high porosity of the adsorbent and depict the violence of the vapor explosion during the hot press processing. The vapor pushes some material from the core to the sides, causing an agglomeration of material at the walls (side effect). However, the use of surfactant as well as the vapor explosion successfully prevents fiber agglomeration on a small scale, which is caused by capillary forces during the drying of the adsorbent pellets. Distribution of starch in the sorbent material visualized by means of an iodine/starch complex could be imaged with optical microscopy (Figure 2f). The starch granules are homogeneously dispersed in the cellulose matrix, forming a network of junctures between the fibers. These connections improve the distribution of forces within the pellet and, consequently, increase its mechanical stability. The density of the cellulose/starch/PEI pellets was determined to be around 70 kg/m³. This correlates with a porosity of 92% and a surface area of 7,120 mm², both calculated from μ -CT measurements.

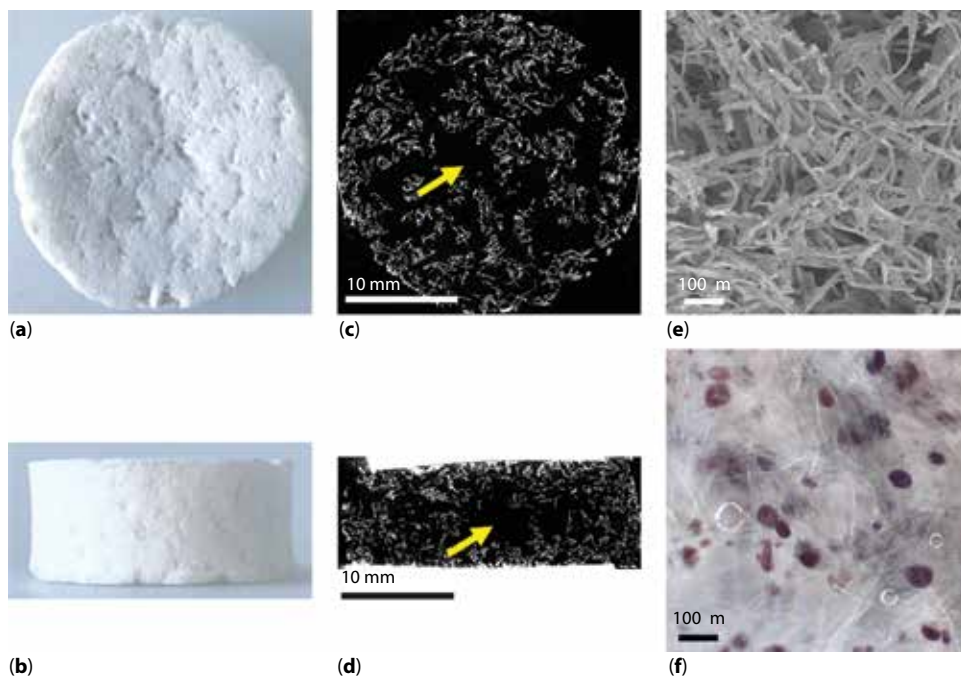


Figure 2 Photographs (a,b), μ -CT images showing x-z cross section (c) and x-y cross section (d) through a pellet; cross section SEM micrograph (e) of the cellulose/starch/PEI adsorbent and optical microscopy image after marking starch with Lugol Solution to form iodine/starch complex (dark regions) (f).

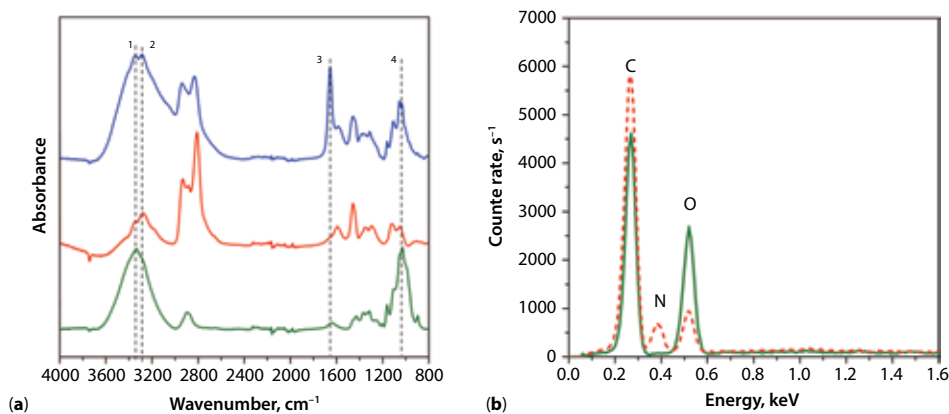


Figure 3 FTIR spectra (a) of reference cellulose (bottom), cellulose/starch/PEI (middle) and PEI (top) and EDX-spectra (b) of cellulose/starch/PEI (---) and neat cellulose fibers (-). The peak labels represent the elements that emit characteristic radiation at the distinct energy.

3.2 PEI Content and Distribution

As the concentration of amine groups directly correlates with the adsorbents' capability to bind CO₂, the reaction conditions for the physisorption of PEI on cellulose have to be adjusted thoroughly. According to the literature, basic conditions (i.e., pH > 11) promote PEI adsorption due to reduced charge density of the PEI molecules and the so-called effect of screening enhanced adsorption [20–22]. This pH-dependent behavior has been reported to be independent of average molecular weight of the

PEI [23]. Besides, with the novel hot press process introducing SDS surfactant to that system, influence of the detergent on PEI physisorption should be negligible in the used pH range [24].

Successful functionalization of the cellulose could be confirmed by means of FTIR spectroscopy and EDX measurements (Figure 3). The reference material shows typical bonds for cellulose in the FTIR (e.g., δ_1 : OH stretching at 3 340 cm⁻¹, δ_4 : COC skeletal vibrations at 1 035 cm⁻¹) and the cellulose/starch/PEI material features characteristic bonds for PEI (e.g., δ_2 :

NH stretching at 3 280 cm⁻¹, δ_3 : primary NH bending at 1 655 cm⁻¹). In the complementary EDX spectra of cellulose prior to and post processing, characteristic X-rays for nitrogen (N) from the PEI in the adsorbent could be detected. Besides, signals from carbon (C) and oxygen (O), both present in cellulose and starch, were detected.

With elemental analysis of cellulose/starch/PEI, concentrations of up to 20 wt% PEI could be determined. FTIR spectroscopy indicated higher concentration at the pellets' surface (data not shown). This phenomenon can be explained with excess PEI in the pulp foam being flushed from core to surface caused by the intense vapor explosion in the hot press process. However, homogeneity is not an obligatory prerequisite for the adsorbent to function as intended but the availability and accessibility of amine groups for CO₂ molecules.

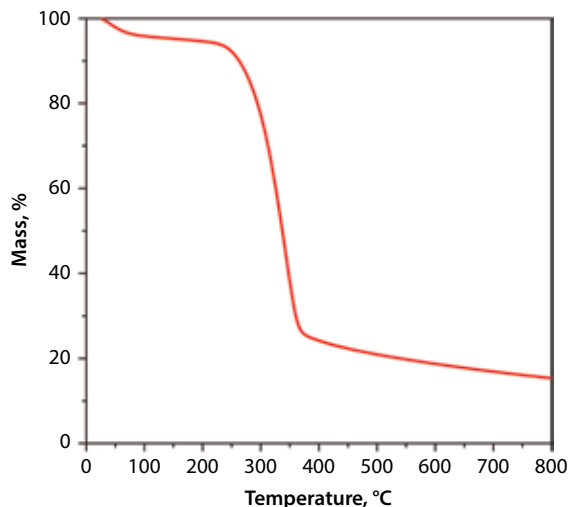


Figure 4 Thermal stability of cellulose/starch/PEI acquired by TGA.

3.3 Adsorbent Stability, Desorption Temperature Range and CO₂ Capacity

Of importance for the industrial application are factors like material stability and CO₂ capacity. The thermal stability of the adsorbent could be verified by means of TGA, displayed in Figure 4. Besides initial mass loss due to gas release (water, CO₂), the cellulose/starch/PEI is thermally stable up to ~ 250 °C.

Coupled TGA/FTIR measurements allowed determination of the temperature range of CO₂ release. The according spectral evolution with rising temperature is shown in Figure 5a. Spectra of CO₂ given in the literature feature a clear peak at 660 cm⁻¹, consequently allowing the qualitative identification of CO₂ in the FTIR [25]. Figure 5b shows the evolution of extinction at 660 cm⁻¹ with the temperature and reveals CO₂ being released between ~ 100 and 150 °C with a peak maximum at ~ 120 °C. This result is in good agreement with values reported in the literature ranging from 85 to 170 °C for various amine-based adsorbents [6, 8, 13, 17]. Together with the results from TGA, CO₂ release can be induced far below decomposition temperature of the adsorbent.

Besides thermal stability of the adsorbent in inert atmosphere, stability against CO₂ and O₂ at elevated temperatures is important for the application in the brewing process. In consideration of different types of beer, the exhaust gas in a reference brewery has been determined to be 65 to 99 vol% CO₂ and 0.1 to 8 vol% O₂. Significant performance loss for amine-based adsorbents in the presence of CO₂ (urea formation) [26] and O₂ (C=O formation) has been published [27]. With an inherent relative humidity in the brewery of 60 ± 3% not only urea formation is prevented [28, 29] but also a positive influence on CO₂ capacity is reported [9, 17, 30]. Besides, the measured O₂ concentrations in the brewery prove that the gas should

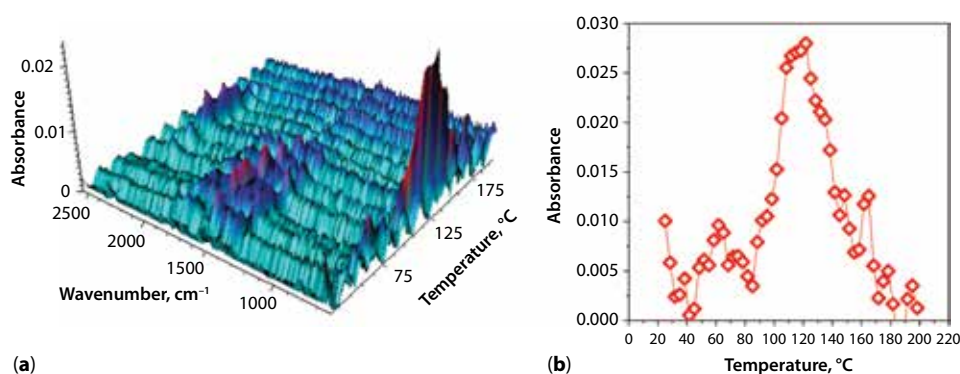


Figure 5 Spectral evolution between 2500 and 500 cm⁻¹ with rising temperature from coupled TGA/FTIR measurement of the cellulose/starch/PEI adsorbent (a) and evolution of the extinction with increasing temperature at a wavenumber of 660 cm⁻¹ (O-C-O bending) as determined by *in-situ* TGA-FTIR (b). The dashed line serves the purpose of clarity only.

Table 1 Comparison of published data on cellulose-based adsorbents with the novel cellulose/starch/PEI adsorbent.

Type	Synthesis	T _{Ads} (K)	RH (%)	Density (kg/m ³)	Gravimetric Capacity (mmol/g)	Volumetric Capacity ^b (mol/m ³)	Reference
NFC/AEAPDMS ^a	Freeze-dry	298	40	61	1.39	85	[32]
NFC/PEI	Freeze-dry	298	80	12.3	2.2	27	[17]
cellulose/starch/PEI	Hot press	293	60	67	1.0	67	-

^a N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane; ^b Calculated from Density and Gravimetric Capacity

not be problematic regarding long-term stability of the adsorbent [29].

First tests in the laboratory reactor confirmed CO₂ capacity of the novel adsorbent of 1.0 mmol/g. Table 1 compares the result with published data on other cellulose-based CO₂ adsorbents. Materials fabricated with freeze-drying feature higher capacity per weight compared to the novel cellulose/starch/PEI adsorbent. This is mainly due to the microporous structure that is only achievable by combining NFC and lyophilization. The inner surface area of these materials exceeds the possibilities of the hot press processing. Considering material density, however, hot press processing delivers a capacity of 67 mol/m³, which is comparable to that of adsorbents that are more laborious. Especially versus NFC/PEI, the cellulose/starch/PEI shows a far better volumetric capacity. A first attempt to explain these proportions is the presence of inaccessible amine groups in the NFC/PEI. This phenomenon has been reported in the literature and is caused by the amine-containing material blocking pores in the microporous substrate and consequently the pathway of CO₂ [31]. For non-microporous cellulose/starch/PEI, however, this effect should be not as severe, resulting in higher amine efficiency.

4 CONCLUSION

Using a novel fabrication method, an alternative route to fabricate amine-functionalized cellulose-based adsorbents for CO₂ recovery application has been developed. Compared to the state-of-the-art freeze-drying process with NFC, the novel method uses less expensive cellulose microfibers and features a quick hot press process, reducing the fabrication time drastically. A smart combination of surfactant and heat-induced vapor explosion allows preservation of the adsorbents' shape and porous structure during drying. Surface functionalization with PEI was successful with remaining challenges regarding absolute content and distribution. In consideration of future application, the literature indicates stability of the adsorbent at operational conditions in breweries [9, 17, 28–30]. In addition, CO₂ release was shown to occur at moderate

temperatures below 120 °C, which is favorable regarding energy consumption of adsorbent regeneration. Finally, tests in the novel laboratory reactor revealed a capacity that is comparable to more laborious and expensive NFC-based adsorbents.

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