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3D printed versus spherical adsorbents for gas sweetening

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HIGHLIGHTS

● 3D printing of carbon and 13X zeolite monoliths for the removal of H2S and CO2.
● 3D printed monoliths stacked in a reactor were compared to packed-bed counterparts.
● Highest H2S adsorption capacity of 3.5 mmol g⁻¹ was obtained for 13X zeolite beads.
● Adsorption & desorption rates of monoliths are markedly faster than those for beads.
● 3D printed monoliths present a scalable alternative to randomly packed-bed design.

GRAPHICAL ABSTRACT

ARTICLE INFO

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Structured (packed-bed) reactor
3D printed monolithic adsorbents
13X zeolite
Carbon

ABSTRACT

A range of adsorbent structures were examined for sour gas removal over a number of conditions by utilising the choice of materials as well as packing geometry as critical factors for the efficient design of the sorbent bed systems. A comparison was made between 13X zeolite and carbon model structures and their conventional equivalents: beads. They were examined for CO2 and H2S adsorption, using thermogravimetric analysis (TGA) and breakthrough measurements in a packed bed reactor (PBR) system. 13X beads exhibited the highest adsorption capacity and longest breakthrough, followed by the printed 13X structures. The adsorption and desorption rates of the 3D printed structures were found to be significantly faster than that of beads. 3D printed adsorbent beds with their highly defined three-dimensional networks are considered advantageous for both temperature swing and pressure swing adsorption allowing for increased mass and heat transfer efficiency and lower pressure drop. The results demonstrate that the 3D printed adsorbents are a promising alternative, ready to assemble in gas sweetening units, exhibiting high adsorption capacity and fast kinetics.

1. Introduction

One of the main trends in natural gas exploration and production in recent year has been the exploitation of an increasing variety of natural gas sources and new wells that require the development of innovative, reliable and cost-effective technologies to remove impurities from natural gas streams.

Natural gas sources primarily consist of methane and are
predominantly sour, both at conventional oil refineries and natural gas plants, as well as at unconventional sour-gas fields (shale gas, tight gas), containing a high level of impurities varying greatly between different sources, such as CO\(_2\) along with higher hydrocarbons and low (> 5) ppmv to high volume percentages of H\(_2\)S, which makes it less viable and desirable on the market [1].

The work presented herein is focused on the key steps of gas treating known as the sweetening of natural gas that relies on the principle of physical adsorption to remove these particular impurities (H\(_2\)S and CO\(_2\)). The adsorption and desorption performance of the two most common commercially available types of sorbents, 13X zeolite and activated carbon in the structured form (beads and monoliths), have been studied.

While chemical solvents (such as advanced liquid amine solutions in the so-called amine sweetening process) are still considered the workhorse of the commercial-scale sour gas processing, the reason for selecting the physical adsorption-based systems as an alternative or complimentary technology is that there are still some operating drawbacks that have been associated with chemical sorption through liquid amines such as energy-consuming regeneration, their oxidative and thermal degradation during regeneration and amine foaming and corrosion that make the sorption process deteriorate [2-5].

There is a variety of H\(_2\)S and CO\(_2\) recovery systems that can pursue solid sorbent-based design (e.g. packed beds, fluidised beds, transport reactors and other systems). Currently, packed beds of sorbent pellets are mostly used in sorption systems. Among the commercially available sorbents activated carbon has been reported to show low H\(_2\)S selectivity, while zeolites and alkali-alumina showed good H\(_2\)S sorption performance, and adsorbed water vapour well [6]. One of the main disadvantages with each of these granulated/pelletised sorbents is that they can be easily fluidised and/or eroded in the treated gas, due to both thermal cycling and mechanical vibration, which can generate fine particulates that bypass the downstream mesh filters. Furthermore, these packed beds of granules create a large pressure drop across the sorption system.

The ordered packing with parallel channels of adsorbent beds has found wide application in environmental management (such as coated honeycomb monoliths and extruded carbon monoliths for exhaust gas cleaning). It has been demonstrated that an activated carbon monolith that has a dynamic mass transfer performance for n-butane sorption from air equal to that of the packed bed of the equivalent mass of granules and a pressure drop less than 6% of that of the bed of carbon granules [7]. A similar comparison study of packed beds of 5A beads and of 5A monoliths showed the role the parallel channels in the monoliths play in the reduction of mass transfer resistance and the enhancement of diffusivity including the pressure drop across the monoliths which was 1.3 times lower than that for beds [8]. Another study on a hybrid packed bed (composed of an activated carbon honeycomb monolith filled with 13X zeolite particles) pointed to a significant localised mass transfer limitations due to preferential flow pathways created by the uneven packing of zeolite within the monolithic channels [9].

New methods for materials fabrication and components design by means of additive manufacturing and 3D printing such as the 3D fibre deposition technique (3DFD) developed at VITO, have emerged at the forefront of scientific and technological advances across multidisciplinary boundaries, offering the potential to construct tailor-made 3D patterned structures composed of suitable sorbent materials [10-17]. 3D printing technology of adsorbent (and in parallel catalyst) monoliths is still in its infancy in terms of up-scaling efforts and commercial application. However, it has been gaining the momentum in the last two years. A few very recent noteworthy attempts were made to develop and apply 3D printed structures (of polymer MOF and polymer zeolite composites) to gas separation processes (e.g CO\(_2\)/CH\(_4\), CO\(_2\)/N\(_2\), and CO\(_2\)/H\(_2\) separation) [18,19].

A number of activated carbon and zeolite extruded monoliths, including 3D printed 13X and 5A zeolites, have been investigated for CO\(_2\) adsorption, but to the authors’ best knowledge there are no reports on printed or honeycomb monolithic adsorbent systems for gas sweetening thus far [20]. The aim of this work was to take the sorption bed design for gas sweetening a decisive step further by developing patterned lattice packing into structured beds of 13X zeolite and carbon. The rationale behind this is that it will enable greater control of the flow pattern with minimal pressure drops and improved mass (and heat) transfer efficiency, including the improved attrition resistance of the material. This will in turn allow for process performance in the packed bed to be optimised, i.e. purification productivity and operations to be greater than those used in typical beaded sorption systems [21].

2. Experimental

2.1. Materials

The appropriate 13X (SW and SU series) and 5A-DP zeolite materials in the shape of spheres were supplied by N-Wissen GmbH. SYLO- BEAD® (molecular sieve material) obtained from GRACE Davison was selected for benchmark comparison for CO\(_2\) adsorption. For the printing process, the 13X-SU spheres were subjected to grinding in a ball mill and subsequent sieving through 45\(\mu\)m mesh to obtain below finer particle size fractions to prevent the particles blocking the nozzle. Highly spherical bead-shaped activated carbon (A-BAC LP grade) samples were obtained from Kureha GmbH. Activated carbon Norit® powder for printing the monolithic structures was purchased from Sigma Aldrich.

Matrix-like structures were directly printed and built up, layer by layer, in regular periodic patterns using the aforementioned highly adaptable in-house 3D printing system, 3DFD. This involved the direct fibre extrusion (‘direct writing’) of a low viscosity 13X zeolite or carbon containing paste through a nozzle of a syringe while the position of the sample was defined via a computer numerically controlled (CNC) x–y–z stage operated through a control panel, its own native operating system and menu-guided graphical user interface. The preparation of printing paste relied on conventional ceramic powder processing and paste mixing techniques. The paste formulations and the control of the viscosity of the printing pastes are crucial for obtaining defect-free, mechanically stable adsorbent structures. The binder system used in the paste (ink) formulations can play a critical role in the composition and properties of the end adsorbent product [23]. Typical ink/paste formulations specially adapted for printing zeolites and carbon in this work consisted of the following components: milled and sieved powder, 45–55 wt% polymer binder (in this case methyl cellulose) containing water as a solvent and inorganic binders (such as colloidal silica and bentonite each of up to 10 wt% the solids content/dry mass after calcination) and additives (up to 5%) to tune the viscosity of the paste (in this specific case this was achieved by adding water).

Along with the paste formulation and viscosity, further consideration should be given to the choice of optimised printing settings such as the nozzle opening, nozzle height, pump pressure, the speed of the stage, the stacking of the layers and fibre dimensions. These settings play a key role in helping to define the architecture of the adsorbent. As soon the layers are being laid down, another crucial moment comes for defining the final print. At this stage the water evaporation is underway and the printed structures starts to solidify in air. The fresh structures were stored in a climate chamber (at room temperature and 90% relative humidity) to aid a slow drying process for as long as realistically possible. The resulting dry structures were subsequently fired at 470–500 °C (with a dwell period of 2 h) in order to remove the organics (methyl cellulose polymer) and obtain homogeneous and rigid fibre networks. The structures were cut to fit into 1 cm and 2.6 cm diameter reactor tubes. Fig. 1 shows photographs of the activated carbon and 13X zeolite beads as well as printed carbon and 13X structures used for
the experiments presented herein.

2.2. Methods

Porosimetry analysis was performed using a Quantachrome Autosorb-iQ–MP. XRD measurements on small amounts of the powder form of the samples were carried out with a PANalytical X’Pert Pro Powder diffractometer operating with a Cu anode operated at a 40 kV voltage and 30 mA current. Phase identification was carried out by the X’Pert PANalytical High Score Plus software and using the ICDD Powder Diffraction database. The microstructures of selected samples were examined by SEM using a FEI Nova NanoSEM 450. The physical properties (mass loss due to water and polymer release and thermal stabilities to up to 500 °C in nitrogen) of the printed samples were examined by using a TGA-DTG Netsch analyser.

Preliminary screening for CO2 and H2S adsorption and desorption capacity and kinetics screening of the samples were carried out using an in-house designed experimental setup (see a schematic diagram in Fig. 2) for gravimetric analysis (TGA) and packed bed reactor (PBR) experiments. Bronkhorst MFCs were used to accurately deliver the feed flow of CO2 or H2S (up to 5% in N2 carrier gas) into the packed bed or TGA reactors. To test packed bed configurations a small 27 mm inner diameter stainless steel tube reactor was used of a total length of 350 mm (made in AISI 316L stainless steel). A distributor plate with a pore size of 40 µm was placed at a height of 50 mm from the bottom edge. The sorbent structures were weighed out and loaded into the reactor. A SICK GMS800 gas analyser was used for the analysis of H2S breakthrough measurements. The amount of adsorbate held in the reactor can be calculated in order to determine the cyclic adsorption capacity of the different sorbent materials. For TGA experiments a microbalance (Sartorius M25D) with a sensitivity of a 1 µg to 200 mg operating range was used. About 100 mg of sample was typically used. The sample was placed into a small porous basket which was connected to the balance when inserted in the TGA reactor. Once the analysis had started the balance and the reactor heating environment was purged with nitrogen to ensure no other gas species were present and were likely to be absorbed. All experiments conducted in the TGA apparatus were corrected with blank measurements in order to eliminate weight changes occurring due to thermal and species (gas density) variations and in the reactor. Prior to the TGA and PBR experiments, the sorbent was pre-treated at 350 °C for 180 min under N2 to remove adsorbed CO2 and H2O from the atmosphere.

After the pre-treatment the samples were cooled down to 30 °C and adsorption of CO2 (at 1 bar CO2 pressure) and H2S (at 0.05 bar H2S pressure) were carried out at atmospheric pressure for 30 min. After the adsorption was completed N2 was introduced to the reactor, and the samples were heated to 300 °C (10 °C/min) to allow complete desorption of adsorbed CO2 or H2S. The effect of the adsorption temperature has been studied by adsorption experiments at 50 and 70 °C.

Packed bed reactor experiments were carried out with commercially available 13X beads as well as 3D-printed monolith structures. The 3D-printed monolith structures were stacked onto a thermocouple (d = 6 mm) and carefully inserted into the tubular reactor (Fig. 3). Total sorbent mass and resulting bed height are listed in Table 1. Blank tests were performed regularly before each type of measurement including the blank pressure swing adsorption of H2S. The experimental conditions under which both the TGA and PBR experiments were carried out are listed in Table 3.

3. Results and discussion

3.1. Characterisation

Data derived from the nitrogen adsorption–desorption isotherms of the samples recorded at −196 °C were surface area, average pore diameter and total pore volume calculated using the Brunauer-Emmett-Teller (BET) method and the micropore surface area and volume calculated using t-plot method from the isotherm profile (see Table 2). The micropore volume of the 13X beads was 0.26 m3/g which is in agreement with the values typically found in the literature [24,25]. The results obtained indicate that the 3D printed structures have undergone changes in morphological characteristics. The isotherms for the studied materials are presented in Supplementary Material Fig. S4. The adsorption isotherm of both the carbon and 13X beads were clearly of Type I (typical isotherms for microporous adsorbents such as carbon and zeolites) according to the IUPAC classification, while the 3D printed carbon and 13X materials were a combination of Type I and Type II isotherms. The predominantly microporous characteristics of the beads are evidenced by the fairly large nitrogen volume adsorbed within a very low relative pressure range. In contrast, at a relative pressure (P/P0) of about 0.40 for the 3D printed Carbon monoliths and at about 0.80 for the 3D printed 13X-SU monoliths, Type II isotherms were obtained that indicate the presence of macropores. It should be noted that both (pseudo) Type II isotherms (of the 3D printed materials) feature an H4 hysteresis loop (a difference in adsorption and desorption isotherms) that is associated with the capillary condensation of the adsorbate in the mesopores. The average pore diameters of the 3D printed samples were found to be 2.75 and 3.5 nm for 13X and carbon respectively, showing that the structures were mesopores per definition, although close to the microporous range. It can be concluded that 3D printing, and more accurately, the post-printing thermal treatment, has brought about the formation of mesopores accompanied by an increase in the total pore volume, while the surface area has been reduced. According to the calculation methods for macro-porosity (%) described by Danaci [26] the macroporosity of the structures printed for this work was calculated to be at ca. 65–70%.

In conclusion, the porosity of the structures remained post calcination. In general, it is important to ensure a complete burn out of the organic binder while leaving significant residual porosity behind. Binder residue may lead to reduced performance; the adsorption may...
decrease due to reduced porosity. Porosity may weaken the overall mechanical strength of the printed structures. Because of this trade-off, the calcination temperature in this study was chosen to be between 470 and 500 °C (with a dwell time of 2 h). It is well-established from numerous reports in the literature on organic-binder based printing inks (for various applications) that the TGA analysis can quantify the amount of water/solvent, binder (due to thermal decomposition) and the amount of remaining solid components. In addition, it has been confirmed by TGA results that methyl cellulose decomposition and burn off temperature is below 450–500 °C [13,24,27]. Further treatment at a higher temperature should result in a small amount of binder residue being completely removed. From the TGA curves (presenting repeated heat treatment of pre-calcined 3D printed 13-SU) provided in Fig. S5a–c in the Supplementary material, it can be seen that at 500 °C none of the methyl cellulose remains. After heating to 450 °C it showed a small amount of the organic binder or gaseous residue remaining.

The obtained XRD results on the samples pre and post operation under H2S are in accordance with those found in the literature on
during the experiment. In addition, the H2S desorption kinetics for the is a key observation regarding the e
hardly any evolution of the material. The main re
mechanism occurs: the adsorption of H2S takes place at a slower rate
comparison of CO2 and H2S adsorption kinetics suggests that a di
5A-DP sample di
beads while the 13X materials need a greater rise temperature to desorb
Sylobeads. When compared to CO2 adsorption-desorption experiments,
similar adsorption and desorption capacity and kinetics was observed for all materials except for carbon beads. 13X-SU and 13X-SW beads
curves obtained are based on four adsorption
3D printed carbon monoliths
3D printed 13X zeolite monoliths
3D printed 13X zeolite beads
3D printed 13X zeolite monoliths
3D printed carbon monoliths

Fig. 4. XRD patterns for 13X-SW and 13X-SU materials before and after H2S adsorption. Diffraction patterns are almost identical for the four samples and show hardly any evolution of the material. The main reflections in the diffraction patterns are indexed.

typical 13X zeolite structures [13]. Characteristic peaks are assigned to cubic Sodium aluminum silicate hydrate phases (Fd3m space group) and the same strongest reflections were indexed for both before and after adsorption. The XRD data show that no phase change occurred during the H2S adsorption (see Fig. 4).

3.2. Cyclic working capacity of CO2 of different sorbents

Fig. 5 compares the CO2 and H2S adsorption and desorption profiles of different sorbents in the form of beads. The results confirm the 13X zeolite beads to be the best performing adsorbents with capacity close to or even higher than other standard commercially used zeolites (see a direct comparison of H2S and CO2 adsorption and desorption kinetics of 13X zeolite beads in Supplementary Material, Fig. S7). The experimental conditions are summarised in Table 3.

Fig. 5 shows the dynamic mass uptake curves of different samples with 100% CO2 at constant temperature and atmospheric pressure. The curves obtained are based on four adsorption-regeneration cycles. Similar adsorption and desorption capacity and kinetics was observed for all materials except for carbon beads. 13X-SU and 13X-SW beads showed a slightly higher adsorption capacity compared to 5A-DP and Sylobeads. When compared to CO2 adsorption-desorption experiments, H2S adsorption kinetics were much slower which can be due to the lower partial pressure of the H2S (compared to CO2) sorbate during the experiment. In addition, the H2S desorption kinetics for the 5A-DP sample differs from that of the other materials starting at lower temperatures compared to 13X-SW, 13X-SU and Sylobeads. A direct comparison of CO2 and H2S adsorption kinetics suggests that a different mechanism occurs: the adsorption of H2S takes place at a slower rate but it is stronger since a higher temperature is required to desorb it from the material. It is evident that even a much lower temperature increase (120 °C) would be sufficient to desorb all adsorbed CO2, which is a key observation regarding the efficiency of the TSA cycle. Interestingly, the H2S desorption is completed faster for carbon and SDP beads while the 13X materials need a greater rise temperature to desorb H2S completely. For more detail on 13X beads see Fig. S6 – the adsorption and desorption kinetics of H2S and CO2 on 13X are observed to be dissimilar. Note that a direct comparison between H2S and CO2 adsorption kinetics should not be considered since the partial pressure of H2S and therefore the mass flow of the active component is much lower compared to CO2.

Fig. 6 presents a comparison of CO2 and H2S cyclic adsorption capacities of different beads. As it can be observed from adsorption and desorption profiles there are some distinct differences between carbon beads on the one hand and Sylobeads, 5A beads and 13X on the other hand. The same trend was observed for all tested materials – all exhibited higher capacities of CO2 than of H2S. 13X zeolite beads displayed the highest adsorption capacity of both CO2 as well as H2S, while carbon beads displayed the lowest adsorption capacity of both components, which makes 13X zeolite a promising candidate for the gas sweetening process. The observed trends are in agreement with the previously reported data [28–30]. The CO2 adsorption capacity of 13X zeolite beads with a capacity of 3.4 mol/kg falls in the upper part of the range of values reported in the literature (e.g. this can be compared to up to 4 mol/kg at 1 bar and 35 °C reported in a review of CO2 capture materials for 13X as a benchmark material by Gibson et al. [31]; structured adsorbents made of 13X have been reported by Akhtar et al. to have a CO2 working capacity of 1.5–3.5 mol/kg, while 13X powder shows a CO2 adsorption capacity of 4 mol/kg [32]). The result of about 3.0 mol/kg for the H2S adsorption capacity of 13X measured in this study is higher than the values reported in the literature for 13X (e.g. 1.17 mol/kg of adsorbed H2S by a 13X modified by ion-exchange) [34].

Adsorption kinetic data of adsorbents is a key prerequisite to understanding the overall mass transfer of both sorbate species, and design parameters of the adsorber (such as its volume/size and the duration of the adsorption process). To study the influence of operating temperature of the adsorber and sorbate partial pressure, H2S partial pressure and operating temperature were varied for selected samples (13X-SU zeolite and carbon beads).

From comparing all the adsorption capacity values (in Fig. 8) it is clear that the operating temperature and partial pressure determined the adsorption capacity to a great extent. Two distinct trends were
Fig. 5. Gravimetric analysis of CO\textsubscript{2} (PCO\textsubscript{2} = 1 bar) adsorption and desorption (a and b) and H\textsubscript{2}S (PH\textsubscript{2}S = 0.05 bar) (c and d) adsorption and desorption curves for different beads based on dynamic mass uptake during four adsorption–regeneration cycles at a constant temperature of 30 °C for adsorption and a temperature increase from 30 °C to 300 °C (10 °C/min) for desorption at atmospheric pressure.

Table 3
List of CO\textsubscript{2} and H\textsubscript{2}S adsorption and desorption experiments carried out with selected beads and printed structures (CO\textsubscript{2} adsorption was mainly performed at 30 °C and desorption at 300 °C). The pressure was 1 bar unless otherwise specified. Runs number 5 and 6 were performed at different temperatures and partial pressures for H\textsubscript{2}S.

<table>
<thead>
<tr>
<th>No.</th>
<th>Technique</th>
<th>Sorbent</th>
<th>Adsorption</th>
<th>Regeneration</th>
<th>cycles</th>
<th>Figure</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>TGA</td>
<td>13X-SW beads</td>
<td>30 °C 100% CO\textsubscript{2}</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>5a, 5b</td>
</tr>
<tr>
<td>2</td>
<td>TGA</td>
<td>13X-SU beads</td>
<td>30 °C 100% CO\textsubscript{2}</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>5a, 5b</td>
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<tr>
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<td>TGA</td>
<td>Carbon beads</td>
<td>30 °C 100% CO\textsubscript{2}</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>5a, 5b</td>
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<td>4</td>
<td>TGA</td>
<td>5A-DP beads</td>
<td>30 °C 100% CO\textsubscript{2}</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>5a, 5b</td>
</tr>
<tr>
<td>5</td>
<td>TGA</td>
<td>13X-SW beads</td>
<td>30 °C 5% H\textsubscript{2}S</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>5c, 5d</td>
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<td>TGA</td>
<td>13X-SU beads</td>
<td>30 °C 5% H\textsubscript{2}S</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>5c, 5d</td>
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<td>Carbon beads</td>
<td>30 °C 5% H\textsubscript{2}S</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>5c, 5d</td>
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<tr>
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<td>TGA</td>
<td>5A-DP beads</td>
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<td>300 °C in N\textsubscript{2}</td>
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<tr>
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<td>TGA</td>
<td>13X-SU beads</td>
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<td>7a, 7b</td>
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<td>3</td>
<td>7a, 7b</td>
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<td>3</td>
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<td>7c, 7d</td>
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<td>13X-SU</td>
<td>1 bar, 4 bar and 8 bar at 30 °C</td>
<td>300 °C in N\textsubscript{2} (PSA and NON PSA)</td>
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<td>9a, 9b</td>
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<td>13X-SU beads and monolith structures</td>
<td>30 °C 5% H\textsubscript{2}S</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>10a</td>
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<td>Carbon beads and monolith structures</td>
<td>30 °C 5% H\textsubscript{2}S</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
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<td>30 °C 5% H\textsubscript{2}S</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>11a, 11b</td>
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<td>17</td>
<td>PBR</td>
<td>13X-SU monolith structure</td>
<td>30 °C 5% H\textsubscript{2}S</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td>11e, 11f</td>
</tr>
<tr>
<td>18</td>
<td>PBR</td>
<td>Carbon monolith structure</td>
<td>30 °C 5% H\textsubscript{2}S</td>
<td>300 °C in N\textsubscript{2}</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>
observed:

(1) a significant capacity loss with an increase in operating temperature
(2) lower partial pressure of H₂S leading to a significantly reduced adsorption capacity.

Weight change (H₂S intake) profiles in Fig. 7, (a) and (c) for both materials when subjected to 5% H₂S showed the initial adsorption rate to be similar at all three different temperatures (during the first 500 and 100 s respectively). This was followed by a slower adsorption rate dependent on operating temperature and material. At 30 °C and 5% H₂S the profiles showed adsorption to be more rapid on carbon beads with approximately 90% of the equilibrium uptake being achieved twice as fast as that of 13X-SU beads. At higher operating temperatures for 5% H₂S and 1% H₂S for 13X-SU zeolite, adsorption was completed only after 1 h of adsorption process. In particular for the latter it is indicative that the low H₂S content in the feed stream is limiting the adsorption rate (mass transfer). In contrast, adsorption for carbon beads at 1% H₂S was completed sooner than in any of the other cases.

Since the partial pressure is a rate determining constant in the adsorption expression considering Langmuir Hinshelwood adsorption expression, the observed results can be explained. However for 13X-SU beads the low nearly constant adsorption rate could be explained with mass transfer limitations at this low H₂S content. This would explain the fact that, for the carbon beads (due to a way lower maximum adsorption capacity), equilibrium is reached quite fast. The possible occurrence of external mass transfer limitation in previous experiments was excluded by increasing the total flow rate from 480 ml/min to 1000 ml/min (see Fig. S7 showing H₂S adsorption profiles of 13X-SW for three different feed flow rates).

The adsorption rate varies at different operating temperatures: the slower adsorption rate is more prominent for the samples at 70 °C being governed by diffusive transport. Where the desorption rate usually increases at high temperatures leading to a lower adsorption equilibrium, the increase in diffusive transport at high temperatures could be the
reason for the slow mass increase for experiments (at higher temperatures of 50 °C and 70 °C).

The highest \( \text{H}_2\text{S} \) adsorption capacity of up to 3.5 mmol g\(^{-1}\) was obtained for the 13X-SU zeolite beads at 30 °C and 5% partial pressure for \( \text{H}_2\text{S} \). The carbon beads showed very poor performance compared to 13X, with up to 10 times lower adsorption capacity for 1% partial pressure at a feed rate of 480 ml/min for \( \text{H}_2\text{S} \) at 30 °C. Note that during these tests, all sorbents showed a nearly constant adsorption capacity and no significant capacity loss.

Fig. 7b and d show that desorption is also slower for 13X-SU beads compared to carbon beads. This indicates that external mass transfer limitations are not necessarily the reason for the described phenomena above. Hence, a difference in the nature of the adsorption sites on both components seems to be different. Stronger basic sites present on 13X-SU would explain the difference in adsorption rate and also the somewhat higher temperature required to desorb all \( \text{H}_2\text{S} \). The presence of different adsorption sites can be determined with temperature programmed desorption (TPD) where the temperature at which a certain amount of sorbate is released, can give an indication of the strength of the basic sites on the adsorbent. The results for desorption of \( \text{CO}_2 \) as a function of temperature based on the experiments shown in Fig. 5, revealed that for the carbon-containing samples a temperature of 30 °C was sufficient to desorb nearly all of the adsorbed \( \text{CO}_2 \). In other words, the desorption of \( \text{CO}_2 \) completed within the isothermal part at adsorption temperature. All other (non carbon-containing) materials exhibit similar trends with rapid weight change taking place at 30 °C (easily desorbing \( \text{CO}_2 \)). Upon an increase in temperature, within the temperature range of 75 °C and 100 °C, a clear increase in desorption rate (i.e. an increase in weight loss) can be observed indicative of at least two different adsorption sites with different basic strengths. Note that Fig. 59 in the Supplementary material shows the weight loss of adsorbed \( \text{CO}_2 \) as a function of temperature (TPD data). The figure is indicative of \( \text{CO}_2 \) desorption and the underlying bonding mechanisms with the heterogeneous distribution of adsorption sites on different types of adsorbents, where the different basic sites can be distinguished depending on the temperature \( \text{CO}_2 \) is released at.

The effect of the pressure has been investigated for \( \text{H}_2\text{S} \) adsorption and desorption on 13X-SU monoliths at three different pressures (see Fig. 9 for comparison). An increase of 25% in \( \text{H}_2\text{S} \) intake is observed at slightly elevated pressure (the values of 4 and 8 bar do not vary as much compared to 1 bar). It should be noted that even though there is no substantial difference, a slightly higher weight change is observed at 4 bar pressure compared to 8 bar pressure (the average results are presented for repeated experiments). The results for desorption indicate that whether or not desorption is carried out under pressure swing (PSA) conditions at 8 bar, the weight changes are not distinctly different as expected if partial pressure of the sorbate is determining adsorption/desorption rate.

The effect of the geometrical structure (and packing arrangement) on the adsorption/desorption kinetics is shown in Fig. 10. For both monolithic structures, it can be observed that adsorption and desorption rates are significantly faster than that for beads. This indicates that in both cases the internal mass transfer limitation hinders the adsorption and desorption of \( \text{H}_2\text{S} \) in beads. This is a very important observation in terms of the suitability of the printed structure. The thickness of the printed structures (as well as the thickness of the particles used) are shown to have a major influence on the kinetic behavior during the sorption process.

Both printed structures show a reduced total capacity which could be attributed to closure of certain fraction of pores during the post printing calcination process. In fact, as presented in Table 2, the surface area, which is one of the key parameters for the adsorption capacity, is reduced in both cases of the printed structures.

The experiments on the “prototype PBR” with an inner diameter of 27 mm were performed on 13X-SU beads and printed structures (both 13X-SU and carbon) according to the applied conditions specified in the overview in Table 3. Cyclic working capacities were determined based on breakthrough experiments using feed concentrations of 5% \( \text{H}_2\text{S} \) in \( \text{N}_2 \) at adsorption conditions. Fig. 11 shows the breakthrough curves for the first two adsorption/regeneration cycles for the different sorbents and structures. The breakthrough time of \( \text{H}_2\text{S} \) was determined both by the mass of sorbent used in the experiment (see Table 1) and the adsorption capacity (tested with TGA experiments previously). Due to the different bulk density of the sorbent, there were significant differences in the used sorbent mass, as shown in Fig. 11 (with adsorption of \( \text{H}_2\text{S} \) marked in green, and desorption in red). The highest adsorption capacity and the longest breakthrough were found for 13X-SU beads (Fig. 11a and b) followed by the printed 13X-SU structures (Fig. 11c and d). The printed carbon structures (Fig. 11c and e) showed lower adsorption capacities, with \( \text{H}_2\text{S} \) continuously present in the outlet stream. A significant temperature rise of 15 °C (for 13X-SU beads) and 13 °C (for 13X-SU structures) is shown during \( \text{H}_2\text{S} \) adsorption due to the exothermic adsorption of \( \text{H}_2\text{S} \). It is apparent that the heat front is moving along the sorbent bed with time in Fig. 11a–d. Note that measuring points T1, T3 and T5 represent the temperature at 0, 4 and 8 cm respectively. For the printed carbon structures no significant temperature rise could be detected.

Breakthrough experiments confirm that the printed 13X-SU structures exhibit somewhat (ca. 23%) lower cyclic working capacity for \( \text{H}_2\text{S} \) under the measured conditions than that of 13X-SU beads (Fig. 12).
This decrease in capacity can be attributed to a great extent to a loss in available surface area (and related porosity) for adsorption and the change in porosity due to the post printing thermal treatment (calcination at 470–500 °C with a dwell period of 2 h for binder removal). There is a decrease of around 30% in the BET value and 15% in total pore volume for the printed structures in comparison to the beads (both as received and milled into powder for printing). As previously confirmed during the TGA experiments, the carbon printed structures showed a similar low cyclic working capacity of 0.5 mol/kg. It has been reported that chemical modification of activated carbon (such as by NaOH, KOH, KI or Na2CO3, K2CO3 solutions) or impregnation or doping can greatly enhance H2S adsorption capacity.

Another issue encountered during dismantling the reactor filled in with printed carbon structures is the significant lower mechanical stability compared to that of the printed 13X-SU monoliths. Whereas the 13X-SU monoliths were mostly intact after removal of the thermocouple (onto which the monoliths were stacked) from the reactor, the carbon monoliths were almost entirely destroyed. To prevent this damage from occurring, an improved test reactor design would be necessary to ensure the successful insertion and removal of the monoliths to and from the reactor. While the printed 13X-SU monoliths tended to form granulates upon breaking, the destroyed printed carbon structures showed a high degree of brittleness resulting in forming powder which needed to be filtered and as such requiring an additional separation step in a future process application (OPEX). Lower bulk density of printed carbon structures would result in the need for larger-sized equipment (CAPEX) compared to the printed 13X-SU monoliths, making 13X monoliths the preferable sorbent for possible use in H2S separation by adsorption.

4. Conclusions

The study investigated CO2 and H2S adsorption of several commercially available, state-of-the-art adsorbents in the form of beads, typically used for CO2 capture from flue gas, such as zeolite 13X, 5A and carbon. 13X and carbon were structured into monoliths and investigated as 3D printed adsorption beds for a model gas sweetening process. To our knowledge, 3D printed adsorbents have not been commercialised and this study presents the first attempt to investigate the comparative performance of model 3D printed adsorbents for gas sweetening (sour gas removal). If only low concentrations (in terms of ppm) of sour gas have to be removed, physisorption-based, structured solid sorbent removal systems could be an attractive add-on to the large scale commercial gas sweetening (scrubbing) processes, depending on the concentration of the undesired sour gas components and the requirements for the downstream gas concentrations.

3D printed monolith structures of both 13X-SU and activated carbon have been successfully implemented and tested in a model packed bed reactor. The carbon printed structures did not yield suitable results for this application. Due to higher bulk density, higher mechanical stability
and generally higher adsorption capacity of the 13X-SU compared to the activated carbon printed structures, it was evident that this sorbent exhibits promising performance for the removal of sour contaminants from gas streams in TSA processes.

It can be seen from the results of TGA and PBR of beads as well as of the 3D printed bed experiments that 13X-SU in either shape has a high cyclic working capacity for H$_2$S under the tested conditions compared to other sorbent materials. In a PSA process, 13X-SU monolith structures yielded a similar increase of 25% in H$_2$S intake at both 4 bar and 8 bar. By employing the printed monolithic structures the internal mass transfer limitations observed in 13X-SU beads can be eliminated resulting in enhanced adsorption and desorption rates. It was found that the cyclic working capacity of the sorbent is reduced for the 3D printed 13X-SU structures compared to conventional 13X-SU beads due to its lower surface area and a change in porosity which was a result of calcination at 470–500 °C (2 h dwell) necessary to remove the polymer.
Fig. 12. Cyclic working capacities for H2S for different sorbent materials (13X-SU beads, 3D printed 13X-SU monolith structures and 3D printed carbon monolith structures). Experiments at 30 °C for adsorption (PH2S = 0.05 bar) and 300 °C for desorption (P N2 = 1 bar). Cyclic working capacities were determined by integration of the outlet analyser signal as per Fig. 11 legend with respect to the mass of sorbent used during the tests in the reactor.

binder used for printing.

The loss of the specific surface area observed in the printed structures can be avoided by using a low temperature binder or a polymer with adsorption capacity (i.e. by functionalising the adsorbent with a polymer) which does not need to be removed from the structure.

Even though the adsorber design used here is not yet fully optimised it has been demonstrated in this work that 3D printing in different adsorbent materials offers a practical edge towards the production of novel, high quality, on-demand, scalable structures for bespoke design and improvement of the adsorption beds.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2018.09.130.

References