Study of CO₂ Sorption Kinetics on Electrospun Polyacrylonitrile-Based Carbon Nanofibers

Electrospun carbon nanofibers (CNFs) exhibit a decent CO₂ sorption capacity and outstanding CO₂/N₂ selectivity. In this work, the sorption rate as another practically relevant parameter for CO₂ adsorption is analyzed for different carbonization temperatures. Equilibration curves obtained from different CO₂ sorption isotherms are discussed qualitatively and quantitatively, employing empirical models for pseudo-first- and second-order reactions. The sorption rate constants are found to be highly dependent on the carbonization temperature of the CNFs and the applied pressure during the measurement. Furthermore, two distinct processes of sorption are observed, which are attributed to different sorption sites on the surface and the inner volume of the CNFs.

Keywords: Adsorption, Carbon dioxide sorption, Electrospun carbon nanofibers, Molecular sieve

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1 Introduction

The anthropogenic climate change is one of the greatest challenges of our time. The atmospheric CO₂ content has risen from 280 ppm to more than 400 ppm and is still climbing [1]. A possible way to lower the amount of the greenhouse gas CO₂ is to separate it from the atmosphere or flue gas and to reuse it as a chemical feedstock.

Common ways to separate CO₂ from a gas mixture include membrane separation processes [2], amine adsorption [3], and physisorption-based methods such as pressure swing adsorption (PSA) [4, 5], temperature swing adsorption (TSA) [6], and special cases like vacuum (VSA) [6, 7] or electric swing adsorption (ESA) [8, 9].

For a successful separation by physisorption, suitable materials with a high CO₂ adsorption capacity, high selectivity towards CO₂ adsorption, and high adsorption and desorption rates are required, e.g., zeolites [10], metal organic frameworks (MOFs) [11, 12], surface-modified polymers [13], silica [14], or carbons [15, 16]. Of these materials, carbons offer many advantages since they are cheap, comparatively stable, and insensitive towards impurities [17, 18].

Electrospun polyacrylonitrile (PAN)-based carbon nanofibers (CNFs) have been presented, which feature CO₂ adsorption capacities of up to 2.8 mmol g⁻¹ and an outstanding CO₂/N₂ ideal adsorbed solution theory (IAST) selectivity [19] of up to 350. Both the adsorption selectivity and capacity were higher for a lower carbonization temperature of the CNFs during the preparation process. The excellent adsorption selectivity was attributed to a molecular sieve effect in narrow ultramicropores, which, however, can induce kinetic limitations. For example, the CO₂ sorption isotherms showed an increasing pseudo irreversibility with increasing carbonization temperature at constant equilibration parameters [19]. This effect may be attributed to a drastically reduced sorption rate in narrowing pores, as diffusion takes a long time in pores, which are in the size range of the adsorptive molecules. This type of diffusion is called configurational diffusion [20] and is characterized by diffusion coefficients which can be several orders of magnitude lower than for molecular diffusion [21].

In general, the diffusion and adsorption of gases is a comparatively fast process. Thus, most studies on adsorption kinetics on carbons focus on pollutant removal from aqueous solutions [22, 23], where kinetic hindrance is more commonly found. In the fewer gas adsorption-related studies, the focus lies mainly on kinetic limitations in fixed-bed reactors [24], which is close to application but allows only for an indirect measurement of the adsorption kinetics.

In contrast, the study of the adsorption kinetics in a static physisorption setup is not as close to application as the dynamic method but allows a direct measurement of the sorption rate at a specific temperature and pressure. In these studies, the
adsorption rate is most frequently measured with a single adsorption point from 0 bar to a pressure of 1 bar or more [12, 25], but rarely with intermediate steps as shown here. For static setups, a gravimetric determination of the adsorbed amount is usually employed [14, 26, 27], but volumetric approaches have been reported as well [28].

To obtain quantitative information on sorption rates and to give insights into diffusion and sorption mechanisms, various models have been developed to analyze and predict the change of the amount of adsorbate over time. These models range from simple empirical equations to sophisticated and physically consistent theories. In this study, an empirical approach is chosen to estimate and quantitatively compare sorption rates at different measurement pressures of samples prepared at various carbonization temperatures.

1.1 Lagergren/Pseudo-First-Order Model

One of the most commonly applied empirical models for adsorption modeling is the pseudo-first-order (PFO) model by Lagergren [29], which is in similar form also found in classical chemical reaction kinetics for first-order reactions [30]. The model assumes that the sorption rate linearly depends on the difference between the adsorbed amount \( q_t \) and the adsorbed amount in equilibrium \( q_e \).

\[
\frac{dq_t}{dt} = k_{PFO}(q_e - q_t) \quad (1)
\]

\[
q_t = q_e(1 - \exp(-k_{PFO}t)) \quad (2)
\]

Defining \( q'_t \) as partial loading \( (q(t=0) = 0, q_e = 1) \), Eq. (2) becomes

\[
q'_t = 1 - \exp(-k_{PFO}t) \quad (3)
\]

Azizian [31] gave a derivation of the PFO model from the Langmuir isotherm model [32], which introduces a physical base. A general rate equation for the Langmuir model was developed and solved for two different cases [31]. For the first case, a very high initial adsorptive concentration compared to the capacity of the adsorbent was assumed, which allowed to simplify the rate equation and integrate it to yield the PFO equation [31]. For the second case, however, this simplification was not valid. Integration with appropriate mathematical approximations resulted in the pseudo-second-order (PSO) approach [31] as defined in the next section.

1.2 Pseudo-Second-Order Model

Kinetics obeying the PSO model are frequently found for chemisorption processes [33].

\[
dq_t \over dt = k_{PSO}(q_e - q_t)^2 \quad (4)
\]

\[
q_t = \frac{tq_e^2}{k_{PSO} + q_et} \quad (5)
\]

Defining \( q'_t \) as partial loading \( (q_0 = 0, q_e = 1) \), Eq. (5) becomes

\[
q'_t = \frac{t}{k_{PSO} + t} \quad (6)
\]

1.3 Fractal Models

More generalized versions of the PFO and PSO models are the fractal PFO (f-PFO) and fractal PSO (f-PSO) models proposed by Haerifar and Azizian [34], which may provide deeper insights into the presence of different diffusion paths [34], adsorption sites [35], or pore systems [36]. For these models, the sorption rate constant is considered to depend on time, when for example different sorption sites are filled consecutively. With respect to the time dependency, a fractional time index \( \alpha \) is introduced, leading to the following form of Eqs. (2) and (5):

\[
q_t = q_e(1 - \exp(-k_{f-PFO}t^\alpha)) \quad (7)
\]

\[
q_t = \frac{t^{1/\alpha}q_e^2}{k_{f-PSO} + q_et^\alpha} \quad (8)
\]

For \( \alpha = 1 \), the fractal models turn into their non-fractal counterparts. A more detailed derivation of the fractal models can be found in literature [34–36].

1.4 Other Models

Alongside the first- and second-order models, a vast number of mixed-order models has been proposed to study sorption kinetics [22, 37–39]. However, the nature of mixed-order models hampers the comparison of sorption rate constants within the model, as they are not independent of the reaction order. Furthermore, the lack of a physical meaning of the obtained parameters is a drawback for any mechanistic interpretation.

To study sorption kinetics in a physically consistent way and receive true physical parameters, diffusion equation-based models, including Boyd’s internal and external diffusion models [14, 22], have been proposed. The complexity of real adsorption systems and the associated physically consistent models require numerous assumptions on adsorbent geometry and thermodynamic properties, whose applicability is very demanding to assess. The development and application of such a model is, therefore, beyond the scope of this work.

\[\text{List of symbols at the end of the paper.}\]
2 Analysis Method

To assess the sorption kinetics of CO₂, isotherms have been measured in a static volumetric setup. In the most common procedure for static volumetric gas adsorption, certain relative pressures are defined prior to the measurement. During isotherm acquisition, for each point, gas is carefully added in various dose steps until the predefined equilibrium pressure is reached.

In contrast, in the present approach, the VectorDose™ mode of the Quantachrome measurement device was used, which applies only one dose for each isotherm point and records the approach of the pressure towards equilibrium over time.

Fig. 1 illustrates the relationship between the individual isotherms and the underlying equilibration curves, which are analyzed in this work. As an example, a CO₂ adsorption isotherm at 273 K with rather low resolution of the sample carbonized at 600 °C is shown in Fig. 1a. For each point, a predefined amount of CO₂ is dosed into the sample cell and starts to adsorb, which is indicated by a pressure drop in the sample cell that is converted into an increase in the adsorbed amount of gas (Figs. 1b, c). When the equilibrium pressure is reached, i.e., no significant pressure change is observed anymore, the isotherm point is recorded, and another dose step will be performed.

For the quantitative analysis of the obtained equilibration curves, it is indicated to normalize these to limit the number of free parameters. For each isotherm point, the starting time is set to 0 s and the adsorbed amount is set to 0 for the first data point. With the normalization, the CO₂ uptake \( q_t \) at the time \( t \) is divided by the experimental equilibrium uptake \( q_e \), which implies that \( q_t/q_e \) is set to 1 at \( t_e \); see Fig. 1c (linear) and 1d (logarithmic). By performing this normalization, both models applied in this study depend on one free parameter only. In the standard PSO model, \( k_{PSO} \) is independent of \( q_e \), which is changed by normalization. On comparing Eqs. (5) and (6), it becomes apparent that for the conversion of the normalized PSO rate constant into the non-normalized one it must be multiplied with \( q_e \).

3 Results and Discussion

For the evaluation of their sorption kinetics, various CO₂ adsorption and desorption isotherms were recorded aiming for high-resolution data in different pressure regimes (see Supporting Information (SI) for experimental details). The resulting isotherms for the electrospun carbon nanofibers (CNFs) carbonized at different temperatures ranging from 600 °C to 1100 °C are depicted in Fig. 2. Fig. 2a shows high-resolution isotherms for low pressures up to 100 mbar. For higher pressures up to 1000 mbar the resolution was lowered (Fig. 2b), since the amount of gas adsorbed at higher pressures is lower and the pressure transducers used for higher pressures are less precise.

Both low- and high-resolution isotherms were recorded at the instrument’s highest possible equilibration parameters.

Fig. 2c displays isotherms with lower equilibration parameters and medium resolution from our previous work [19], which are included here for reference purposes. An overview over the equilibration parameters can be found in Tab. S1 in SI.

Figure 1. Exemplary representation of the correlation of a CO₂ adsorption isotherm (a), time-dependent equilibration data (b), and the normalization for quantitative analysis in linear (c) and logarithmic scale (d) for the sample carbonized at 600 °C (low resolution isotherm, second point).
For all three isotherm measurement routines, the CNFs carbonized at low temperatures of 600°C to 700°C show a high initial slope and a CO₂ uptake of about 2.8 mmol g⁻¹ at 1 bar for low resolution and standard isotherm and 1.5 mmol g⁻¹ at 100 mbar. For 800°C and 900°C the initial slope and the low-pressure CO₂ uptake are slightly lower. For the isotherm obtained with short equilibration time (Fig. 2c), the sample carbonized at 900°C presents a significantly lower isotherm slope and lower total uptake of CO₂ than in the isotherms obtained with higher equilibration times, which indicates slow sorption kinetics.

The CNFs carbonized at temperatures from 1000°C to 1100°C exhibit linear isotherms with a pronounced pseudo-irreversibility, which is a hint that the sorption of CO₂ is kinetically hindered as well.

3.1 Qualitative Discussion

As a qualitative comparison of adsorption kinetics at different pressures, equilibration curves for various CNFs carbonized at different temperatures ranging from 600°C to 1100°C are depicted in Fig. 3 for 10 mbar. The curves for 0.1, 1, 100, and 500 mbar as well as the desorption equilibration curves are shown in Figs. S1 to S3 in the Supporting Information (SI). The plots are shown as absolute data and as normalized plots for improved qualitative discussion. In the absolute data plot the equilibrium uptake \( q_e/m_{\text{sample}} \) is set to 0 wt% for all samples to facilitate the comparison of different curves. The CO₂ uptake over time \( q_t \) is given as a weight difference to \( q_e \) and is therefore negative. In the normalized plot, \( q_e \) is set to 1 and the first measurement point is set to 0 s; 0. The time axis of the normalized plots is displayed logarithmically to allow for easier observation of long-term changes during the adsorption process.

In Figs. S1a and b (in SI) it can be observed that at a low pressure of 0.1 mbar the shape of the equilibration curves for the samples carbonized from 600°C to 900°C is close to an exponential saturation curve. With the same amount of dosed gas, the CO₂ uptake (quantified by the \( y \)-axis intercept) shrinks with the carbonization temperature. This observation can easily be understood since the CO₂ uptake of a single point directly corresponds to the isotherm slope, which is decreasing for an increasing pressure. Furthermore, it is found that the approach to the equilibrium loading occurs faster for the samples, which were carbonized at lower temperatures. For example, at 0.1 mbar the samples carbonized at 600°C, 700°C, and 800°C equilibrate within 2–3 min, while the sample carbonized at 900°C takes about 20 min for equilibration.

At a higher pressure of 10 mbar (Fig. 3), the approach to equilibrium for the samples carbonized at 600°C and 700°C appears to be slightly faster, as the equilibrium is reached in less than 2 min. In contrast, the adsorption rate for the sample carbonized at 900°C is again much lower. For the samples carbonized at 1000°C and 1100°C, the adsorption mechanism is divided into two processes, which is visible in two distinct ranges with a significant difference in sorption rates. Firstly, a very fast process is observed, which takes place in the first few seconds of recording and which is responsible for about 80% of the CO₂ uptake of this specific isotherm point. Secondly, an extremely slow process is found, which is not finished after the instrument’s limiting equilibration time of 80 min.

In contrast to 10 mbar, at a higher pressure of 500 mbar (Figs. S2c and d in SI) all samples exhibit a two-step adsorption mechanism. The samples carbonized from 600°C to 900°C...
show a fast process within the first minute of adsorption, which is followed by a second, significantly slower process. In addition, the differences in adsorption rate between the samples carbonized at 900°C and 600°C to 800°C become much less significant. Since the slow process is not finished within the total recording time, none of the samples is fully equilibrated at this isotherm point.

In our previous work we have demonstrated that the changing CO₂ adsorption properties can be explained by a shrinkage of the ultramicropore width with higher carbonization temperature [19]. In accordance with this model, the first, comparatively fast process could be attributed to the CO₂ adsorption in narrow ultramicropores between carbon layers on the fiber surface. Further diffusion into the inner part of the fiber is kinetically hindered and does not take place in any significant extent when adsorption sites close to the surface are still available. Upon pressure increase, CO₂ molecules are forced to further migrate into the inner part of the fiber, which constitutes the second, much slower adsorption process. A more detailed discussion of a possible diffusion limitation can be found in the SI.

The desorption behavior (see Fig. S3 in SI) is closely comparable to the discussed findings for the adsorption. Whereas at higher pressures two sorption processes can clearly be distinguished, the second process vanishes at low pressures.

### 3.2 Quantitative Discussion of Individual Equilibration Curves

For a quantitative discussion of adsorption rates, the normalized equilibration curves in Fig. 3 and Figs. S1–S3 were fitted using two simple models for chemical reactions, namely the pseudo-first-order model (PFO, see Eqs. (1)–(3)) and the pseudo-second-order model (PSO, see Eqs. (4)–(6)). When applied to a normalized curve, both models exhibit only one free parameter and predict the curve shape well, given their simplicity. Thus, a quantitative comparison of adsorption kinetics within a specific model at different pressure for various carbonization temperatures is possible.

Figs. S4 to S9 present the normalized equilibration curves with the fit of the PFO and the PSO models. The resulting sorption rate constants and the corresponding $R^2$ values are given in Tab. 1 for adsorption and Tab. S2 (in SI) for desorption. The time span used for the fit was limited to 3 min after the dosing step to reduce the influence of data points in equilibrium, except the sample carbonized at 900°C, here about 10 min are necessary as the adsorption is much slower than for the other samples.

![Graph showing adsorption kinetics](image)

#### Table 1. Adsorption rate constants for CO₂ sorption on electrospun carbon nanofibers obtained by PFO and PSO fits. Desorption rate constants are listed in Tab. S2.

| Carbon. temp. [°C] | $k$(PFO) [s⁻¹] | $R^2$ | $k$(PSO) [s⁻¹] | $R^2$ |
|-------------------|----------------|-------|----------------|-------|
| **0.1 mbar**      |                |       |                |       |
| 600               | 0.065          | 0.994 | 0.168          | 0.883 |
| 700               | 0.052          | 0.996 | 0.129          | 0.901 |
| 800               | 0.044          | 0.965 | 0.107          | 0.950 |
| 900               | 0.012          | 0.855 | 0.028          | 0.992 |
| **1 mbar**        |                |       |                |       |
| 600               | 0.083          | 0.958 | 0.194          | 0.953 |
| 700               | 0.076          | 0.991 | 0.184          | 0.915 |
| 800               | 0.042          | 0.879 | 0.096          | 0.991 |
| 900               | 0.011          | 0.636 | 0.024          | 0.974 |
| **10 mbar**       |                |       |                |       |
| 600               | 0.216          | 0.834 | 0.455          | 0.947 |
| 700               | 0.150          | 0.907 | 0.328          | 0.956 |
| 800               | 0.054          | 0.897 | 0.123          | 0.986 |
| 900               | 0.009          | 0.518 | 0.020          | 0.950 |
| **100 mbar**      |                |       |                |       |
| 600               | 0.089          | 0.930 | 0.203          | 0.951 |
| 700               | 0.076          | 0.882 | 0.179          | 0.983 |
| 800               | 0.059          | 0.877 | 0.129          | 0.976 |
| 900               | 0.008          | 0.743 | 0.018          | 0.991 |
The experimental data was fitted with the fractal f-PFO and f-PSO models as well, which may provide deeper insights into the presence of different diffusion paths [34], adsorption sites [35] or pore systems [36]. The fit results for these models are listed in Tab. S3 in SI.

At a very low pressure of 0.1 mbar (see Fig. S4) and low carbonization temperatures of 600°C and 700°C, the PFO model predicts the adsorption data very well with \( R^2 > 0.99 \). For higher carbonization temperatures of 900°C, the adsorption behavior slightly changes towards the PSO model, indicated by an \( R^2 \) value of 0.855 for PFO and 0.992 for PSO.

At 1 mbar (see Fig. S5), a comparable transition from PFO to PSO behavior is observed in the carbonization temperature range between 600°C and 900°C. However, the PSO model works better for lower carbonization temperatures than at 0.1 mbar. For carbonization temperatures of 1000°C and 1100°C both models do not satisfactorily describe the data since the sorption process seems to be split into two independent processes as described in the qualitative discussion.

At higher pressures of 10 mbar (Fig S6) and 100 mbar (Fig S7), the PSO model fits best for all carbonization temperatures from 600°C to 900°C. As is visible in Fig. 2, at 500 mbar all samples exhibit a two-step adsorption process, which is not sufficiently described by the discussed models and therefore not further discussed here since a quantitative evaluation is not possible.

For the desorption, similar results are obtained at all studied carbonization temperatures and gas pressures (see Figs. S8 and S9), which yield no additional information on the sorption mechanism.

All in all, the PFO model best represents the data obtained at low pressures for the samples carbonized at low temperatures, whereas the PSO model works best for higher pressures and carbonization temperatures of 800°C and 900°C.

Looking at these trends in detail, firstly the transition from PFO to PSO with increasing pressure could be explained by assuming the gas pressure or the number of available surface sites to be constant or to be changing simultaneously during the adsorption process. Proposing a mechanism, where a gas molecule has to hit a free surface site to adsorb, the adsorption rate would depend on both parameters. In general, the availability of gas molecules and the availability of surface sites are pressure-dependent. Nevertheless, at very low pressures the number of surface sites could be assumed constant since the number of adsorbing molecules is comparatively low at low pressure, which makes the adsorption rate solely dependent on the gas pressure. This behavior would be described with a (pseudo) first-order model. At higher pressures, the number of available surface sites starts to change significantly during the adsorption process and influences the adsorption rate as well. The adsorption rate can now be explained with a second-order model. A similar transition from PFO to PSO with increasing loading has been found for CO\(_2\) adsorption on platinum [25] and mesoporous silica [40] and has been discussed in general [37]. As described above, Azizian provided a theoretical derivation based on the Langmuir isotherm model for this behavior [31].

For the fractal f-PFO and f-PSO fits a drop of the fractional time index \( \alpha \) with higher pressures can be observed (see Tab. S3). In literature, a higher initial concentration of adsorptive leads to a lower value of \( \alpha \) [35]. At a given adsorption capacity, a higher gas pressure is equivalent to a higher concentration in liquid adsorption systems. Hence, the results obtained by the fractal models support that the transition from PFO to PSO can be explained by changing relations of the numbers of free adsorptive molecules and adsorption sites.

Secondly, however, the influence of the carbonization temperature on the adsorption mechanism appears to be more complex. Some authors suggest that a change from PFO to PSO may be explained with an increase in binding strength [28]. Whereas PFO is assigned to physisorption [14], PSO is more frequently found for chemisorption-like binding [33]. The assumption that an increase in binding strength is responsible for a PSO-like adsorption mechanism would be in accordance with the model of a shrinking pore width for an increasing carbonization temperature. A shrinkage of ultramicropore width could indeed induce a higher energy of adsorption due to overlapping pore wall potentials. However, the correlation to isosteric heats of adsorption [19] is not unambiguous.

Another possible explanation for the change from PFO to PSO with higher carbonization temperatures could be the fact that the adsorption capacity at a specific pressure, i.e., the isotherm slope, decreases for an increasing carbonization temperature. A decreasing sorption capacity would induce an earlier transition from PFO to PSO due to the same effects for the transition from PFO to PSO with higher pressures as explained above.

Furthermore, this effect would explain that the fractional time index \( \alpha \) derived from the f-PFO and f-PSO models drops for higher carbonization temperatures (see Tab. S3). On reducing the adsorption capacity at a given adsorption pressure, the “initial concentration” of adsorptive in relation to the adsorption capacity would effectively increase, leading to a rise in \( \alpha \) due to a higher heterogeneity of adsorption paths. All in all, any trend for the value of \( \alpha \) corresponds well to the transitions from PFO to PSO (see also Fig. S10).

For a quantitative comparison, the sorption rates obtained from the PFO and PSO fits in Fig. S4–S9 are shown in Fig. 4 at different carbonization temperatures ranging from 600°C to 900°C for different pressures.

In Fig. 4 it can be observed that the sorption rate is highly dependent on the carbonization temperature and the applied pressure. In fact, regardless the model, the sorption rate constants slightly decrease from 600°C to 800°C and are much slower for 900°C. For example, the PFO adsorption rate at 1 mbar is about 0.08 s\(^{-1}\) for 600°C and 700°C, 0.04 s\(^{-1}\) for 800°C and 0.01 s\(^{-1}\) for 900°C. This finding can be explained by the fact that the ultramicropore width in the electrospun carbon fibers shrinks with increasing carbonization temperature [19]. Thus, at higher temperatures, especially at 900°C, the pores become extremely narrow and the CO\(_2\) adsorption takes a longer time.

Nevertheless, despite the narrow ultramicroporosity, these PFO adsorption rates are still comparatively high compared to literature values, which implies that the narrow ultramicroporosity of the CNFs is not a drawback for the obtainable sorption rates in a practical application. For example, Nasri et al. measured 0.059 s\(^{-1}\) at 303.15 K and 0.5 bar on palm shell-based
Please note: For 1000 °C and 1100 °C reasonable sorption rate constants could not be obtained by the PFO and PSO model. Moreover, due to the different assumptions on the mechanism, the absolute values of PFO and PSO models must not be compared directly.

Activated carbon [28], whereas Loganathan et al. found 0.003 s⁻¹ at 303 K and 0.2 bar on mesoporous silica [14].

Moreover, interestingly, the sorption rate is also highly pressure-dependent. In fact, it is comparable at 0.1, 1, and 100 mbar, but significantly higher for 10 mbar. This effect is strongest for lower carbonization temperatures. In literature, a decline of the sorption rate with increasing pressure is frequently found, but for different pressure ranges. For example, Loganathan et al. [14] observed a decrease in sorption rate when increasing the pressure from 0.2 to 11 bar, which was assigned to repulsive interactions of CO₂ molecules. Nasri et al. found a decrease in a range from 0.5 to 4 bar [28].

In addition to the pressure dependence of the sorption rate, the desorption rate at 10 mbar is significantly higher than the adsorption rate. For the higher pressure of 100 mbar, the difference between adsorption and desorption rate is far less significant.

Although the fit quality of each particular model changes with carbonization temperature and pressure, both PFO and PSO models show consistent results. However, the absolute values for the sorption rate constants of both models must not be compared since they assume different sorption mechanisms.

3.3 Quantitative Discussion of Batchwise Processed Equilibration Curves

In order to further elucidate the pressure dependence of the sorption rate, Fig. 5 depicts four plots of the PSO rate constants vs. the equilibrium pressure on a logarithmic scale for those samples carbonized at temperatures ranging from 600 °C to 900 °C. The results for the PFO model as well as the desorption rate constants can be found in Figs. S11–S13. Unlike the previous discussion, where specific isotherm points close to a predefined equilibrium pressure were chosen for comparison, Fig. 5 presents the results of all isotherm points.

To cover a wide range of pressures within the experimental limits of the instrument, three different isotherms have been measured; the isotherms are depicted in Fig. 2. First, a high-resolution isotherm at low pressures was determined (blue). Secondly, a low-resolution isotherm at higher pressures was recorded (red) using higher dose amounts. The third isotherm (green) is a standard isotherm with lower equilibration parameters as depicted in our previous publication [19] which is included here for consistency checks, as the usable ranges of high- and low-resolution isotherms do not overlap significantly. To be able to fit all equilibration curves with the same parameters and to avoid an excessive influence of the above-mentioned second adsorption process, the value of \( q_e \) was set to \( q_e \) at 150 s for the samples carbonized at 600 °C to 800 °C and to \( q_e \) at 600 s for the sample carbonized at 900 °C.

Inspecting the results in Fig. 5, it is clearly visible that the sorption rate constants obtained from the three different isotherms for each plot are mostly consistent within their overlapping pressure range. As described above, the PSO adsorption rate shows a maximum at around 10 mbar for the samples carbonized in a temperature range from 600 °C to 700 °C. For example, the PSO adsorption rate for the sample carbonized at 600 °C below 1 mbar is about 0.2 s⁻¹ and increases to 0.8 s⁻¹ at 10–50 mbar. The maximum in adsorption rate of the low-pressure isotherm is slightly shifted compared to the values obtained from the reference isotherm. For all the isotherms, on approaching 1 bar, the adsorption rate drops below 0.2 s⁻¹.

For a carbonization temperature of 700 °C, the pressure dependency is similar like for 600 °C. As for 600 °C, the maximum at 10 mbar is very pronounced. A slower adsorption at lower pressures below 10 mbar can easily be understood since the adsorption in smaller pores is thermodynamically favored at lower pressures due to overlapping pore wall potentials. Still, the accessibility of pores declines with decreasing size and implies a lower rate of adsorption. On increasing the pressure to medium pressures of about 10–100 mbar, larger pores are filled. A subsequent decrease in sorption rate constants at higher pressures can be assigned to repulsive interactions between CO₂ molecules, leading to additional collisions with the pore walls and reducing the overall diffusivity [14]. As explained above, this trend is consistent with literature results [14]. In contrast, for carbonization temperatures of 800 °C and 900 °C a small, a continuous increase of the sorption rate without a maximum can be observed.

The results for the PFO sorption rate constants (see Fig. S11) are consistent with the results for PSO. As already described...
and discussed in the previous section, the fit accuracy especially at higher pressures and for the samples carbonized at higher temperatures is higher for PSO than for PFO.

Compared to the adsorption rate constants, the desorption rate constants (see Figs. S12 and S13) indicate a similar trend with a maximum in sorption rate at about 10 mbar, which disappears for higher carbonization temperatures of 800°C and 900°C. However, as described in the previous section, for an unknown reason the desorption rate constants are slightly higher than the adsorption rate constants, especially at high pressures above 100 mbar.

4 Conclusion

In this work, sorption kinetics of CO₂ on electrospun PAN-based carbon nanofibers have been analyzed. For low pressures and low carbonization temperatures of 600°C and 700°C, the sorption kinetics followed a pseudo-first-order kinetics, with a transition towards pseudo-second-order kinetics for higher carbonization temperatures and pressures. Furthermore, two distinct adsorption steps could be observed. The first one – more dominant at lower pressures – was comparatively fast and was attributed to adsorption in ultramicropores close to the fiber surface. The second process dominates at higher pressures and carbonization temperatures of 1000°C and 1100°C and is very slow. This process was ascribed to additional adsorption in the inner part of the fiber, which is diffusion-limited.

The sorption rate was found to depend on the carbonization temperature as well as on the pressure. Whereas for the sample carbonized at 600°C the sorption rate was comparatively high, it decreased by one order of magnitude for higher carbonization temperatures of 900°C. This effect was explained by a shrinking pore size. In addition, the sorption rate showed a maximum at about 10 mbar, which was less pronounced for higher carbonization temperatures. Moreover, the adsorption and desorption behavior were found to be similar for all samples, despite an increased desorption rate at higher pressures. Despite the small pore size of the studied carbon nanofibers, a comparison with literature values demonstrated that the sorption rate is – for carbonization temperatures of 600°C to 800°C – in the order of magnitude of other carbon materials, which is important for the practical relevance of the material.
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Symbols used

| Symbol | Definition |
|--------|------------|
| $k_{id}$ | [s^{-0.5}] Weber-Morris diffusion constant |
| $k_{PSO}$ | [s^{-1}] pseudo-second-order rate constant |
| $k_{PFO}$ | [s^{-1}] pseudo-first-order rate constant |
| $m_{sample}$ | [mg] sample weight |
| $q_e$ | [mg] adsorbed weight in equilibrium |
| $q_i$ | [mg] adsorbed weight at time $t$ |
| $q'$ | [–] partial loading |
| $t$ | [s] time |
| $t_e$ | [s] time at equilibration |

Greek letter

| Symbol | Definition |
|--------|------------|
| $\alpha$ | [–] fractional time index |

Abbreviations

- f-PFO: fractal pseudo-first-order
- f-PSO: fractal pseudo-second-order
- IAST: ideal adsorbed solution theory
- PAN: polyacrylonitrile
- PFO: pseudo-first-order
- PSO: pseudo-second-order

References

[1] Climate Change 2014: Synthesis report: Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (Eds: R. K. Pachauri, L. Mayer), Intergovernmental Panel on Climate Change, Geneva, Switzerland 2015.
[2] A. Brunetti, F. Scura, G. Barbieri, E. Drioli, J. Membr. Sci. 2010, 359 (1-2), 115–125. DOI: https://doi.org/10.1016/j.memsci.2009.11.040
[3] B. Dutcher, M. Fan, A. G. Russell, ACS Appl. Mater. Interfaces 2015, 7 (4), 2137–2148. DOI: https://doi.org/10.1021/ am507465f
[4] C. A. Grande, ISRN Chem. Eng. 2012, 2012, 1–13. DOI: https://doi.org/10.5402/2012/982934
[5] A. D. Wiheeb, Z. Helwani, J. Kim, M. R. Othman, Sep. Purif. Rev. 2016, 45 (2), 108–121. DOI: https://doi.org/10.1080/15422119.2015.1047958
[6] N. Hedin, L. Andersson, L. Bergström, J. Yan, Appl. Energy 2013, 104, 418–433. DOI: https://doi.org/10.1016/j.apenergy.2012.11.034
[7] A. Andersen, S. Divatekar, S. Dasgupta, J. H. Cava, Aarti, A. Nanoti, A. Spjelkavik, A. N. Goswami, M. O. Garg, R. Blom, Energy Procedia 2013, 37, 33–39. DOI: https://doi.org/10.1016/j.egypro.2013.05.082
[8] C. A. Grande, R. P. L. Ribeiro, E. L. G. Oliveira, A. E. Rodrigues, Energy Procedia 2009, 1 (1), 1219–1225. DOI: https://doi.org/10.1016/j.egypro.2009.01.160
[9] R. P. P. L. Ribeiro, C. A. Grande, A. E. Rodrigues, Sep. Sci. Technol. 2014, 49 (13), 1985–2002. DOI: https://doi.org/10.1080/01496395.2014.915854
[10] O. Cheung, Z. Bacsik, Q. Liu, A. Mace, N. Hedin, Appl. Energy 2013, 112, 1326–1336. DOI: https://doi.org/10.1016/j.apenergy.2013.01.017
[11] C. Landaverde-Alvarado, A. J. Morris, S. M. Martin, J. CO2 Util. 2017, 19, 40–48. DOI: https://doi.org/10.1016/j.jcou.2017.01.029
[12] Z. Zhang, S. Huang, S. Xian, H. Xi, Z. Li, Energy Fuels 2011, 25 (2), 835–842. DOI: https://doi.org/10.1021/ef101548g
[13] Y. Zhang, J. Guan, X. Wang, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2017, 9 (46), 41087–41098. DOI: https://doi.org/10.1021/acsami.7b14635
[14] S. Loganathan, M. Tikmani, S. Eduballi, A. Mishra, A. K. Ghoshal, Chem. Eng. J. 2014, 256, 1–8. DOI: https://doi.org/10.1016/j.cej.2014.06.091
[15] N. A. Rashidi, S. Yusup, M. M. Ahmad, N. M. Mohamed, B. H. Hameed, ACPREE Procedia 2012, 3, 84–92. DOI: https://doi.org/10.1016/j.acpree.2012.06.051
[16] H. Zhao, X. Luo, H. Zhang, N. Sun, W. Wei, Y. Sun, Greenhouse Gas Sci. Technol. 2018, 8 (1), 11–36. DOI: https://doi.org/10.1002/ghg.1758
[17] J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, Y. Gao, Q. Wang, D. O’Hare, Z. Zhong, Energy Environ. Sci. 2014, 7 (11), 3478–3518. DOI:https://doi.org/10.1039/C4EE01647E
[18] S.-Y. Lee, S.-J. Park, J. Ind. Eng. Chem. 2015, 23, 1–11. DOI:https://doi.org/10.1016/j.jiec.2014.09.001
[19] A. Kretzschmar, V. Selmert, H. Weinrich, H. Kunigl, H. Tempel, R.-A. Eichel, ChemSusChem 2020, 13 (12), 3180–3191. DOI:https://doi.org/10.1002/cssc.202000520
[20] V. Vattipalli, X. Qi, P. J. Dauenhauer, W. Fan, Chem. Mater. 2016, 28 (21), 7852–7863. DOI:https://doi.org/10.1021/acs.chemmater.6b03308
[21] F. Keil, Diffusion und Chemische Reaktionen in der Gas/Feststoff-Katalyse, VDI-Buch, Springer, Berlin 1999.
[22] J. Wang, X. Guo, J. Hazard. Mater. 2020, 390, 122156. DOI:https://doi.org/10.1016/j.jhazmat.2020.122156
[23] V. Fierro, V. Torné-Fernández, D. Montané, A. Celzard, Microporous Mesoporous Mater. 2008, 111 (1-3), 276–284. DOI:https://doi.org/10.1016/j.micromeso.2007.08.002
[24] J. Mugge, H. Bosch, T. O. M. Reith, in Adsorption Science and Technology, Proc. of the Second Pacific Basin Conf. (Ed. D. D. Do), World Scientific, Brisbane 2000, 451–455.
[25] J. Sobkowski, A. Czerwiński, J. Electroanal. Chem. Interfacial Electrochem. 1974, 55 (3), 391–397. DOI:https://doi.org/10.1016/S0022-0728(74)80433-X
[26] N. A. Rashidi, S. Yusup, L. H. Loong, Chem. Eng. Trans. 2013, 35, 361–366.
[27] S. Jribi, T. Miyazaki, B. B. Saha, A. Pal, M. M. Younes, S. Koyama, A. Maalej, Int. J. Heat Mass Transfer 2017, 108, 1941–1946. DOI: https://doi.org/10.1016/j.ijheatmasstransfer.2016.12.114
[28] N. S. Nasri, U. D. Hamza, N. A. Saidina Amin, J. Mohammed, M. M. Ahmed, H. Mohd Zain, AMR 2014, 1043, 224–228. DOI: https://doi.org/10.4028/www.scientific.net/AMR.1043.224
[29] S. Lagergren, Kungliga Svenska Vetenskapsakademiens Handlingar 1898, 24, 1–39.
[30] G. Wedler, H.-J. Freund, Lehrbuch der physikalischen Chemie, 6th ed., Wiley VCH Lehrbuchkollektion 1, Wiley-VCH, Weinheim 2012.
[31] S. Azizian, J. Colloid Interface Sci. 2004, 276 (1), 47–52. DOI: https://doi.org/10.1016/j.jcis.2004.03.048
[32] I. Langmuir, J. Am. Chem. Soc. 1918, 40 (9), 1361–1403. DOI: https://doi.org/10.1021/ja02242a004
[33] G. Song, X. Zhu, R. Chen, Q. Liao, Y.-D. Ding, L. Chen, Chem. Eng. J. 2016, 283, 175–183. DOI: https://doi.org/10.1016/j.cej.2015.07.055
[34] M. Haerifar, S. Azizian, J. Phys. Chem. C 2012, 116 (24), 13111–13119. DOI: https://doi.org/10.1021/jp301261h
[35] M. Haerifar, S. Azizian, J. Phys. Chem. C 2014, 118 (2), 1129–1134. DOI: https://doi.org/10.1021/jp4110882
[36] M. Khosravi, S. Azizian, Microporous Mesoporous Mater. 2016, 230, 25–29. DOI: https://doi.org/10.1016/j.micromeso.2016.04.039
[37] X. Guo, J. Wang, J. Mol. Liquids 2019, 288, 111100. DOI: https://doi.org/10.1016/j.molliq.2019.111100
[38] B. Guo, Y. Wang, X. Shen, X. Qiao, L. Jia, J. Xiang, Y. Jin, Materials 2020, 13 (4), 877. DOI: https://doi.org/10.3390/ma13040877
[39] A. G. Ritchie, J. Chem. Soc. Faraday Trans. 1 1977, 73, 1650. DOI: https://doi.org/10.1039/F19777301650
[40] R. Serna-Guerrero, A. Sayari, Chem. Eng. J. 2010, 161 (1-2), 182–190. DOI: https://doi.org/10.1016/j.cej.2010.04.042
[41] R. Schierholz, D. Kröger, H. Weinrich, M. Gehring, H. Tempel, H. Kungl, J. Mayer, R.-A. Eichel, RSC Adv. 2019, 9 (11), 6267–6277. DOI: https://doi.org/10.1039/C9RA10491c
[42] M. Gehring, H. Tempel, A. Merlen, R. Schierholz, R.-A. Eichel, H. Kungl, RSC Adv. 2019, 9 (47), 27231–27241. DOI: https://doi.org/10.1039/C9RA03805A
[43] W. J. Weber, C. Morris, J. Sanitary Eng. Div. 1963, 89 (2), 31–60.
[44] M. Alhassan, I. Andrew, M. Auta, M. Umaru, M. U. Garba, A. G. Isah, B. Alhassan, Biofuels 2018, 9 (6), 719–728. DOI: https://doi.org/10.1080/17597269.2017.1306680