Synthesis of Nitrogen and Sulfur Codoped Nanoporous Carbons from Algae: Role in CO₂ Separation

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ABSTRACT: Nitrogen and sulfur codoped and completely renewable carbons were synthesized from two types of algae, Spirulina Platensis and Chlorella Vulgaris, without any additional nitrogen fixation reaction. The type of activation agents, char-forming temperature, activation agent-to-char ratio, and activation temperature were all varied to optimize the reaction conditions for this synthesis. The maximum Brunauer–Emmett–Teller surface area and total pore volumes of the carbons were 2685 m²/g and 1.4 cm³/g, respectively. The nitrogen and sulfur contents of the carbons were in the range of 0.9–5.69 at. % and 0.05–0.2 at. %, respectively. The key nitrogen functionalities were pyridinic, amino, and pyridonic/pyrrolic groups, whereas the key sulfur functionalities were S–C, O–S–C, and SO₃ groups. CO₂ adsorption isotherms were measured at 273, 298, and 313 K, and the ideal adsorbed solution theory was employed to calculate the selectivity of adsorption of CO₂ over N₂ and simulate binary adsorption isotherms. The adsorption results demonstrated that the CO₂ adsorption amount and the heat of CO₂ adsorption were higher for carbons with higher nitrogen content, confirming the influence of nitrogen functionality in CO₂ adsorption. The overall results suggested that these algae-derived renewable carbons can serve as potential adsorbents for CO₂ separation from N₂.

1. INTRODUCTION

Heteroatom-doped carbons have gained significant attention for their remarkable properties that are not manifested by pure carbons. Although oxygen is commonly present in most kinds of carbons, boron (B), nitrogen (N), sulfur (S), and phosphorous (P) are considered as the key heteroatoms. These elements can improve the electronic properties, including tunable band gap of host carbon, easy availability of lone pairs of electrons, thermal stability and durability, higher charging and polarizability, and superior conductivity. These properties can be harnessed into better metal-free oxygen reduction reaction catalysts, ultracapacitor electrodes, drug delivery, and selective separation of few important species, including isolation of greenhouse gases, acid gases, or environmental remediation of heavy metals from the water stream. More details of these usages can be found elsewhere.1–3

Among all of the heteroatom-doped carbons, nitrogen- and sulfur-doped carbons were most commonly synthesized and applied for different specific applications.4 As carbon precedes nitrogen in the periodic table, it is easier to incorporate nitrogen into the carbon matrix. Although the catalytic role of nitrogen-doped carbons may originate from the variation of the electronic charge profile of a carbon atom from the more electronegative nitrogen atom and the interactions of the lone pair of electrons from the pyridinic nitrogen site,4 the exact nature of interactions between adsorbate molecules and nitrogen-doped carbons could be far more complex. It was shown that nitrogen-doped porous carbons could adsorb up to 5.48 and 8.6 mmol/g CO₂ at 298 and 273 K, respectively, and at an ambient pressure. This was probably the highest ever CO₂ adsorbed amount reported for carbon-based materials under similar conditions.5

Sulfur doping, on the other hand, creates another unique type of configuration on the parent carbon surface. Unlike nitrogen, sulfur atoms are much larger and protrude out of the graphene plane, creating an uneven surface with some unique properties. These properties include superconductivity, polarizability, or other unique interactions with neighboring atoms.6–10 For CO₂ adsorption in sulfur-doped porous carbons, it was demonstrated that the heat of adsorption was as high as 59–65 kJ/mol at zero loading,11,12 which was higher...
than any other carbon material reported so far. Oxidized sulfur functionalities are more prone to interact with CO2, thus increasing its overall adsorption capacity. Although different types of B–N, P–N, or even B–P–N doped carbons were reported in the literature, synthesis of N–S dual-doped carbons is relatively rare, and in those cases, two types of raw proteins were employed as the carbon precursor.

Although there is an increased interest in heteroatom-doped carbon materials worldwide, the precursors of those carbons are limited to synthetic precursors, including heteroatom-containing carbon polymers, ionic liquids, proteins, and nanocarbons such as graphene and carbon nanotubes. Low availability, high cost, and hazardous synthesis conditions limit the universal use of these precursors. In this work, algae is used as a natural, inexpensive, and environmentally benign precursor. Several species of algae can accumulate a large amount of protein within their cellular biomass, and this protein can serve as a source of nitrogen and sulfur heteroatoms. Algae is naturally highly abundant and grows very fast by rapid photosynthesis, thereby utilizing the atmospheric CO2. Utilizing algae as a natural precursor for carbon instead of synthetic precursors will help maintain the carbon cycle by limiting the emission of additional CO2 to the atmosphere in the course of synthesis. Glucose and algae mass (Spirulina Platensis) have been used together in the synthesis via a hydrothermal reaction that provided low CO2 emission during carbonization and higher nitrogen fixation with a Maillard type of reaction between the algae protein and glucose. A similar approach to synthesize porous carbon from another type of algae (Nannochloropsis Salina) resulted in a nitrogen content of 0.84–4.5% with a BET surface area of 284–1538 m²/g. Furthermore, past research work did not report the sulfur content of the resultant carbon because it may also originate from the protein content of the algae.

In this work, we have employed two species of algae, S. Platensis and Chlorella Vulgaris, which have a high protein content of 70 and 65%, respectively, as specified by the commercial vendor. No nitrogen-fixing Maillard type of reaction was employed in the course of synthesis. In a two-step synthesis to produce heteroatom-doped porous carbons, a char is obtained followed by its activation with KOH and CO2. In the course of synthesis, the parameters that were varied were the char-forming temperature, the activation temperature, and the char-to-KOH ratio. A large set of carbons synthesized in this process was examined with CO2 and N2 adsorption to investigate their role in carbon capture. Furthermore, we have also elaborated the correlation between the nitrogen content and adsorbed amount of CO2 and the heat of CO2 adsorption.

2. RESULTS AND DISCUSSION

2.1. Pore Textural Properties. Results of thermogravimetric analysis (TGA) of raw spirulina and chlorella under a nitrogen atmosphere are given in Figure S1 of the Supporting Information. The nitrogen adsorption–desorption plots at 77 K for spirulina- and chlorella-derived carbons are shown in Figure 1a,b. The sharp rise in the adsorption isotherm indicates microporosity, but the presence of small hysteresis loops for few carbons signifies the possible presence of mesoporosity as well. The hysteresis loops were more prominent for chlorella-derived carbons. The BET specific surface area, micropore volume, and total pore volume were calculated from the N2 adsorption data and are shown in Table 1a,b. As observed in Figure 1b, there is a presence of a small amount of
mesoporosity in chlorella-derived carbons that are not observed in spirulina-derived ones. Although the exact reason may be difficult to establish because of the heterogeneous nature of the algal cells, the possible reason may be attributed to the dissolving of mineral matters (ash) from the carbon mass during the washing of the carbons, thereby generating an empty space (mesopores) in the carbon matrix. The BET specific surface area (SSA) for KOH-activated carbons varies within 1217−2613 m²/g for spirulina-derived carbons and from 1027 to 2685 m²/g for chlorella-derived carbons. The maximum micropore volume and the total pore volume of these sets of carbons were 0.92 and 1.40 cm³/g, respectively, and they were obtained from chlorella. Upon increasing the KOH-to-char ratio from 2 to 4 at the same temperature of 700 °C, the BET SSA increased monotonically for chlorella-derived carbons, but it turned lower for spirulina-derived carbons at the highest KOH content. Most likely, a relatively weaker cell wall of spirulina was susceptible to over-burning, giving rise to lowering of the available surface area. The high activation temperature of 850 °C yielded the highest BET SSA and pore volume in all of the carbons that were activated by KOH. The BET SSA as well as the pore volume of the carbons that were produced from low temperature char (300 °C) is the lowest among all of the KOH-activated carbons, and the BET SSA is within 1027−1299 m²/g. As Table 1 reveals, increasing the KOH content during the activation for this type of char did not change the pore textural properties significantly in the resultant carbons. It is also quite imperative to mention that we tried to synthesize porous carbons by one-step activation of the algae by directly carbonizing the pristine algae and KOH mixtures. However, the entire product was converted to liquid tar without any solid (carbon) residue. CO₂ activation of the char at 850 °C revealed the lowest BET SSA (147−326 m²/g) as well as the pore volume. The BET surface area, micropore volume, and total pore volume of our algae-derived carbons were higher than that of KOH-activated carbons from N. Salina²⁰ and spirulina-derived carbons¹⁹ reported in the literature. The maximum BET SSA and total pore volume of the carbons obtained from spirulina were 2390 m²/g and 1.15 cm³/g, respectively, as observed in the literature.¹⁹ The pore textural properties of KOH-activated N. salina-derived char were even lower; the maximum BET SSA and total pore volume were 1538 m²/g and 0.69 cm³/g, respectively.¹⁸ It is worth mentioning that both types of carbons were obtained via a hydrothermal reaction between algal biomass and glucose, and hence over 50% of the carbon mass might have originated from glucose itself.¹⁹ The low porosity of the carbons activated by CO₂ may have contributed to the presence of a hard and resistive cell wall of algae that could not be fully broken by a weaker oxidizing agent such as CO₂. The burn-off level for

| Table 1. Pore Textural Properties of Carbons Derived from (a) S. platensis and (b) C. vulgaris |
|---|
| algae | carbon name | BET SSA (m²/g) | micropore volume (cm³/g) | total pore volume (cm³/g) |
| S. Platensis | S(1/2):(700/700) | 1217 | 0.54 | 0.65 |
| | S(1/3):(700/700) | 2095 | 0.79 | 1.06 |
| | S(1/4):(700/700) | 1979 | 0.75 | 1.04 |
| | S(1/3):(700/850) | 2613 | 0.90 | 1.35 |
| | S(1/1):(300/700) | 1299 | 0.60 | 0.62 |
| | S(1/2):(300/700) | 1228 | 0.56 | 0.60 |
| | S(CO₂):(700/850) | 326 | 0.13 | 0.19 |
| C. Vulgaris | C(1/2):(700/700) | 1550 | 0.66 | 0.75 |
| | C(1/3):(700/700) | 2056 | 0.77 | 0.98 |
| | C(1/4):(700/700) | 2418 | 0.84 | 1.16 |
| | C(1/3):(700/850) | 2685 | 0.92 | 1.40 |
| | C(1/1):(300/700) | 1027 | 0.46 | 0.47 |
| | C(1/2):(300/700) | 1034 | 0.46 | 0.47 |
| | C(CO₂):(700/850) | 147 | 0.06 | 0.09 |

Figure 2. (a) Schematic of a possible N, S, and O functionality on graphitic carbon. XPS peak fitting of (b) nitrogen functionality, (c) sulfur functionality, and (d) oxygen functionality in S(1/1):(300/700) and C(1/1):(300/700).
CO₂ activation is around 50%. We did not try to further optimize the CO₂ activation level owing to the poor pore textural properties of the resultant carbons.

The nonlocal density functional theory (NLDFT)-based pore size distribution plots for all the carbons are calculated from N₂ adsorption at 77 K and CO₂ adsorption at 273 K²⁰,²¹ (Figure 1c,d). From these plots, it is clear that both spirulina- and chlorella-derived carbons have similar pores that were synthesized under similar conditions. All KOH-activated carbons have similar pores that were optimized the CO₂ activation level owing to the poor pore textural properties of the resultant carbons.

Table 2. Results of Surface Functionality of (a) Spirulina- and (b) Chlorella-Derived Carbons by XPS (All at %)

| elements          | functionality | (a) Spirulina | (b) Chlorella |
|-------------------|---------------|---------------|---------------|
|                   |               | S(1/2):(700/700) | C(1/2):(700/700) | S(1/3):(700/700) | C(1/3):(700/700) | S(1/4):(700/700) | C(1/4):(700/700) | S(1/1):(700/850) | C(1/1):(700/850) | S(1/1):(300/700) | C(1/1):(300/700) |
| C                 | sp³           | 71.91         | 18595         | 71.69         | 64.2 | 71.69 | 56.9 | 73.0 | 58.0 | 71.5 | 62.1 | 74.7 |
|                   | sp²           | 4.82          | 79.76         | 7.2 | 80.8 | 7.7 | 7.4 | 8.3 |
| C−O/C−S          | 0.85          | 0.8           | 0.8           | 0.1 | 0.8 | 0.1 | 0.8 | 0.1 | 0.8 | 0.1 | 0.8 |
| O−C≡O, C≡O, COOH, CO₂ | 2.18 | 2.19 | 2.6 | 7.35 |
| N                 | pyridinic     | 0.78          | 0.3 | 0.3 | 1.1 | 0.3 | 1.65 | 0.2 | 0.9 | 1.82 | 5.69 |
|                  | amino         | 0.99          | 0.5 | 0.5 | 0.68 | 0.4 | 0.4 | 3.09 |
|                  | pyrrolic/pyridonic | 0.62     | 0.1 | 0.1 | 0.31 | 0.2 | <0.05 |
|                  | graphitic     | 0.18          | <0.1 | 0.17 | 0.1 | 0.1 | 0.51 |
|                  | NO₃           | 0.15          | 0.2 | 0.12 | 0.1 | 0.27 |
| S                 | S−C           | <0.05         | 0.12 | <0.1 | <0.05 | <0.1 | 0.04 | 0.17 |
|                  | O−S−C         | <0.05         | 0.07 | 0.07 | 0.1 | 0.11 |
|                  | SO₃           | 0.07          | 0.07 | 0.12 | 0.07 | 0.17 |
| O                 | O=O=S, C−O/O−H | 9.06         | 15.60 | 9.2 | 15.5 | 9.46 | 15.98 | 4.6 | 10.5 | 8.08 | 13.98 |
|                  | −COH          | 6.54          | 6.3 | 6.52 | 5.9 | 5.9 | 5.9 |
| minerals          |               | 1.86          | 3.6 | 1.41 | 0.7 | 1.52 |

CO₂ functionalities that may be detected by XPS are shown in Figure 2a. Peak fitting results for nitrogen, sulfur, and oxygen functionalities are shown in Figure 2b−d, respectively. Detailed quantifications of the functional groups obtained from XPS results are shown in Table 2a,b for spirulina- and chlorella-derived carbons, respectively. The nitrogen contents lie within 0.9−5.69 and 0.7−5.0 at. % for spirulina- and chlorella-derived carbons, respectively. Different nitrogen functionalities that were detected through XPS are pyridinic, amino, pyrrolic/pyridonic, graphitic, and nitro/nitroso (NO₂) groups. The largest three nitrogen functionalities that dominate these carbons are pyridinic, amino, and pyrrolic/pyridinic. They are also the key contributors in CO₂ capture, as discussed in the Introduction. Although both nitrogen and sulfur contents of these carbons originated from the protein components of the algae cells, the sulfur content is much smaller compared to nitrogen because of the lower sulfur content of the protein itself and the higher tendency of the sulfur atom to be dissociated from the carbon matrix owing to its larger size. The largest quantitative contribution of sulfur is within 0.1−0.5 at. % and that can be successfully distributed to S−C, O−S−C, and SO₃ functionalities only. It is quite intuitive to notice that the severe synthesis conditions, including larger dose of KOH or exposure to higher temperature in the course of synthesis, lowered the nitrogen and sulfur functionalities, and therefore,
the carbons that were produced from the 300 °C char or only the 1:2 ratio of char-to-KOH retained the maximum amounts of N or S functionalities. It is also important to note that these carbons have lower pore textural properties, and hence a tradeoff was established between nitrogen/sulfur functionalities and pore textural properties. XPS also successfully detected few mineral matters associated with Mg, Ca, Na, and K and most likely originating from the algae cell itself or the partial residue of the activation agents (K only). Both mineral matters and oxygen contents are found to be higher in chlorella-derived carbons. To compare with the literature, it should be mentioned that the nitrogen contents in spirulina and nanochloropsis-derived activated carbons retained about 1.09–4.65 and 0.84–4.53 at. % nitrogen, respectively, along with the nitrogen-fixing Maillard reaction. Hydrothermally synthesized carbon from spirulina demonstrated as high as 7.1–11.4 at. % nitrogen, but it did not undergo any activation result and therefore can be regarded as nonporous. None of the past results reported the sulfur content of the carbons. To the best of our knowledge, our work, for the first time, reports the nitrogen- and sulfur-doped carbons from algal biomass without any nitrogen-fixing Maillard reaction and can be considered as completely renewable carbon.

To investigate the external shape and morphology of these carbons under SEM imaging, two representative carbons from each type of algae (spirulina and chlorella), including S(1/2): (700/700), C(1/2): (700/700), S(1/3): (700/850), and C(1/3): (700/850), were selected. It is observed that the bulk size of carbon particles (Figure S2, Supporting Information) for chlorella-derived carbons is higher than that of spirulina-derived carbons. The size of chlorella-derived carbons (inset of Figure S2b, Supporting Information) is about 20–60 μm, whereas the size of spirulina-derived carbons (inset of Figure S2a, Supporting Information) is about 40–80 μm. High-resolution SEM images suggest that the surface of spirulina-derived carbons (Figure 3a,c) is very rough and consists of several cracks and crevices. These crevices are as large as 200 nm and hence contribute to the macropore nature of these carbons. On the contrary, the surface of chlorella-derived carbons is very smooth with much narrower cavities of 20–50 nm (Figure 3a,c).

2.3. Adsorption and Separation Results. CO2 and N2 adsorption isotherms at a pressure up to 760 Torr are shown in Figure 4a–d. The magnified plot of N2 adsorption at 298 K is provided in Figures S3 and S4 of the Supporting Information. CO2 and N2 adsorption isotherms at 298 K are shown in Figure 4a,b for spirulina- and chlorella-derived carbons, respectively. The spirulina- and chlorella-derived carbons adsorbed 3–4 and 2.75–4.3 mmol/g of CO2, respectively. For both carbons, N2 adsorption is 0.25–0.5 mmol/g, respectively. At 273 K, as expected, the amount of CO2 adsorbed increased to 6.2–6.7 mmol/g. The shapes of CO2 adsorption isotherms resemble type-I isotherms, whereas the N2 adsorption isotherms are linear (Henry’s law type) signifying a weaker interaction between N2 and the carbon surface at room temperature (298 K). CO2 adsorption at 313 K is shown in the Supporting Information (Figures S5 and S6). It should be emphasized that the carbons obtained from the char at 300 °C [C or S(1/1): (300/700)] demonstrated the highest CO2 uptake at all temperatures despite having the lowest BET SSA and micropore volume among all carbons. Such a result can be explained by the presence of abundant nitrogen (and sulfur) functionalities in these carbons. CO2 adsorbed amounts at 298 K and 760 Torr were 3.8–4.5 mmol/g in the previous publication on spirulina-derived and KOH-activated carbon, and the maximum CO2 adsorbed amount was marginally higher than that of our results. At 273 K, the CO2 adsorbed amount was 6.1–7.4 mmol/g in spirulina-derived carbon and 2–6 mmol/g in the carbons obtained from N. Salina. Despite CO2 uptakes being slightly lower than those of other nitrogen-doped carbons, like those obtained from polyacrylonitrile, based on these results, it can be concluded that the highest CO2 adsorption in our carbons are in a range similar to that of other carbons obtained from algae.

To further correlate the CO2 adsorbed amounts with the pore textural properties and chemical functionalities, the CO2 adsorbed amounts at 298 K and 760 Torr were plotted with respect to BET SSA, micropore volume, and nitrogen functionalities (Figure 5a–d). Although C or S(1/1): (300/700) has 0.17–0.2 at. % sulfur that may have contributed to CO2 adsorption, we did not make an attempt to make similar plots with respect to sulfur functionalities, owing to very small sulfur contents in those carbons. From Figure 5a,b, it is clear that there is a decreasing trend of CO2 adsorbed with an increase in the BET SSA and micropore volume for both spirulina- and chlorella-derived carbons. This trend is unusual and inconsistent with the other results that we have reported for other biomass-derived carbons without any nitrogen or sulfur functionalities. On the contrary, it is observed that CO2 adsorption increases sharply with the increase in the nitrogen content and eventually flattens off at the highest nitrogen content (Figure 5c). Despite simple acid–base interactions between CO2 and different types of amine groups present on the carbon surface, several computational studies revealed the nature of interactions between CO2 and different other types of nitrogen functionalities. CO2 adsorption in nitrogen-doped carbons were studied by computational techniques, and the results confirmed that few specific types of nitrogen functionalities indeed influence CO2 adsorption. It has been theoretically established that acid–base interactions between the amine group and CO2 π–π interactions between pyridinic/pyrrolic groups, and CO2 hydrogen bonding between pyridine groups and CO2, and Lewis acid–base interactions between pyridinic groups and CO2 play key roles.
in the elevated adsorption of CO₂. It has also been demonstrated by density functional theory (DFT) calculations that the average binding energy between CO₂ and nitrogen-containing complexes is about 7.84 kJ/mol compared to 1.26 kJ/mol for pure carbons.²⁶ To further refine the dependence of CO₂ adsorption on amine, pyridinic, and pyrrolic nitrogen on carbon, we have narrowed down [see Figure 5d] the types of nitrogen functionalities to these functionalities only; however, the trend appears to be similar to that of Figure 5c for these types of carbons. In this context, it is also worth mentioning that other types of basicity that may be present on the carbon surface also contribute to the acid gas adsorption, such as CO₂. Computational studies suggested that few oxygen-containing groups, such as chromene, ketones, or pyrones, may act like basic sites²⁸,²⁹ and hence influence CO₂ adsorption. Furthermore, it was also suggested that the delocalized
electrons on the graphene plane of carbon also add to the overall basicity of the carbon, and hence facilitate CO₂ capture. We could not explicitly quantify the contribution of these functionalities in our system as there is no well-acceptable strategy to quantify them.

In this context, it should be mentioned that we did not make an explicit attempt to correlate the sulfur functionalities with CO₂ adsorption. The role of sulfur functionalities on CO₂ adsorption is not as explicitly defined as that of nitrogen functionalities. In the past computational research (DFT), it was claimed that CO₂ may react with mono- or dioxidized sulfur owing to the high negative charge of oxygen atom caused by the high positive charge on the sulfur atom. Grand canonical Monte Carlo simulation also claimed that the presence of sulfur may also increase CO₂ adsorption in graphene planes because of the electron overlap between CO₂ and sulfur functionalities. In our system, the sulfur content is extremely low (refer to Table 2a,b), less than 0.2 at. %, and that did not allow us to detect the individual functionalities. We believe that it is very difficult to establish the explicit role of sulfur functionalities based on such a low content, if there is any. Furthermore, the positive role of sulfur may also be masked by nitrogen functionalities, owing to its large content and a more pronounced effect toward CO₂ adsorption.

The kinetics of CO₂ adsorption at 298 K for all carbons are shown in Figure 6. Spirulina-derived carbons reached the saturation level of uptake within about 100 s. Although two of the chlorella-derived carbons [C(1/1):(300/700) and C(1/3): (300/850)] reached the saturation level within 50 s, the rest of those carbons took about 150 s to reach saturation. The kinetic profiles of these materials seem very similar, and the overall nature of saturation did not reveal any particular correlation with the pore textural properties or the nitrogen functionality. Because the key adsorption need for CO₂ lies with its separation from N₂ in a flue gas mixture mostly emitting from the coal-driven power plants, it is a common practice to report the selectivity of CO₂ with respect to N₂ in a binary mixture of CO₂ and N₂. Selectivity (S_{CO₂/N₂}) is defined as

\[
S_{CO₂/N₂} = \frac{x_{CO₂}/y_{CO₂}}{x_{N₂}/y_{N₂}}
\]

where \(x\) and \(y\) designate the adsorbed phase and the bulk mole fraction of CO₂ and N₂, respectively. The most common method of calculating selectivity from pure component adsorption data is the ideal adsorbed solution theory (IAST). In this theory, it is assumed that the adsorbed phase resembles an ideal solution, and the gas behaves like an ideal gas mixture. At thermodynamic equilibrium, the mole fractions of the species in the bulk are related to those in the adsorbed phase through equations resembling Raoult’s law in chemical thermodynamics. The selectivity values for all carbons at 298 K as a function of the total pressure are given in Figure 7a,b for spirulina- and chlorella-derived carbons, respectively. For the calculation, the mole fraction of CO₂ and N₂ in the bulk is chosen as 0.15 and 0.85, respectively, as it mimics the flue gas composition. For the carbons, the selectivity decreases with

![Figure 6. CO₂ adsorption kinetics at 298 K for (a) spirulina-derived carbons and (b) chlorella-derived carbons.](image)

![Figure 7. IAST-based selectivity for CO₂/N₂ in (a) spirulina- and (b) chlorella-derived carbons at 298 K. For all cases, the mole fraction of CO₂ and N₂ in the bulk are set to 0.15 and 0.85, respectively.](image)
increasing pressure. For spirulina-derived carbons, the maximum selectivity is demonstrated by S(1/4):(700/700) followed by S(1/1):(300/700). For chlorella-derived carbons, the maximum selectivity is exhibited by C(1/1):(300/700). It should be mentioned that the maximum CO2 adsorption was shown by S(1/1):(300/700) and C(1/1):(300/700) (i.e., carbons obtained from low-temperature char with the highest nitrogen and sulfur functionalities), and these materials also demonstrated the relatively higher selectivity. Furthermore, the carbons that demonstrated the maximum surface area and pore volume [i.e., S(1/3):(700/850) or S(1/3):(700/850)] exhibited the lowest CO2 selectivity and adsorption capacity as shown in Figure 4a,b.

The IAST method was also applied to calculate the binary or mixed adsorption isotherms for CO2 and N2 in the gas mixtures. The equilibrium adsorption amounts, qCO2 and qN2 (mmol/g), can be calculated from the relation of $q_{CO2} = x_{CO2}q^*$ and $q_{N2} = x_{N2}q^*$, where the symbols bear their usual meaning. According to the IAST method, the total adsorbed amount, q, can be calculated from the following ideal solution formula

$$\frac{1}{q} = \frac{x_{CO2}}{q^*_{CO2}} + \frac{x_{N2}}{q^*_{N2}}$$  \tag{2}$$

where $q^*_1$ and $q^*_2$ indicate the adsorbed amounts of pure species at the same temperature and spreading pressure (surface potential) as the binary mixture and are obtained from experimental pure component adsorption isotherms, as shown in Figure 4. For computational purposes, the pure component adsorption isotherms were fitted to the Sips equation. The binary adsorption isotherms for S(1/1):(300/700) and C(1/1):(300/700) are shown in Figure 8a–d as a function of the total pressure (at a constant mole fraction of CO2 of 0.15) and the mole fraction of CO2 (at the constant total pressure of 760 Torr). Similar results for the rest of the carbons are provided in the Supporting Information (Figures S7–S10) section.

The enthalpy or heat of adsorption is calculated by the Van’t Hoff equation

$$\frac{\Delta H}{RT^2} = -\left(\frac{\partial \ln P}{\partial T}\right)_a$$  \tag{3}$$

where $\Delta H$ is the enthalpy or heat of adsorption, $P$ is the pressure, $T$ is the temperature, and $a$ is the adsorption amount. Integration of Van’t Hoff equation translates to

$$\frac{\Delta H}{RT} = \ln P + C$$  \tag{4}$$

where C is a constant of integration. The slope of the ln P versus 1/T plot at a fixed adsorbed amount provides the heat of adsorption. The heat of adsorption of CO2 in the adsorbents synthesized is shown in Figure 9a in terms of the adsorbed amount. Except C(1/4):(700/700), the heat of adsorption of CO2 decreases with the adsorbed amount, designating a traditional energetically heterogeneous carbon surface. The heat of adsorption at higher adsorbed amounts is higher for samples generated with low-temperature char and contained higher nitrogen content [S(1/1):(300/700) and C(1/1):(300/700)]. This trend is similar to the adsorption capacity and selectivity. As observed in the literature, the heat of CO2 adsorption in the nitrogen-doped carbons synthesized from N. Salina was in the range of 30−26 kJ/mol. This is within the CO2 adsorbed amounts of 0−2.4 mmol/g,18 whereas the heat of adsorption is within 22−30 kJ/mol at the adsorbed amount of 0.7 mmol/g for spirulina-derived carbons.19 From the plot, it is observed that several of our carbons have demonstrated higher heat of adsorption at the same CO2 adsorbed amount.

Figure 8. IAST-based simulated binary adsorption isotherms for CO2 and N2 as a function of pressure (for bulk mole fraction of CO2: 0.15) for (a) S(1/1):(300/700) and (b) C(1/1):(300/700); IAST-based simulated adsorptions as a function of the mole fraction of CO2 (for a constant pressure of 760 Torr) for (c) S(1/1):(300/700) and (d) C(1/1):(300/700). Similar plots for the rest of the carbons are given in Figures S7–S10 in the Supporting Information.
than those previously reported for nitrogen-doped carbons synthesized from algal biomass. To correlate the heat of adsorption with the nitrogen content, we plotted the values of heat of adsorption with respect to the total nitrogen content at a fixed adsorbed amount of 2 mmol/g (the "maximum" adsorbed amount available for all samples, as observed in Figure 9a), and the results are shown in Figure 9b. As observed in this figure, the heat of adsorption increases with nitrogen content, which may indicate an influence of nitrogen functionality on CO₂ adsorption.

The working capacity can be calculated as the difference between the adsorption capacity at 1 bar and the desorption capacity at 0.1 bar at a constant temperature of 298 K. In this study, two carbons from spirulina and chlorella, [S(1/1):(300/700) and C(1/1):(300/700)], were chosen as they demonstrated both higher adsorption capacity and selectivity. The adsorption and desorption capacities were measured under continuous cycles of nine adsorption and desorption branches, and the results are shown in Figure 10. It is observed that both the carbons demonstrated excellent stability without significant deterioration after nine cycles.

The dynamic column experiment was performed to study the breakthrough behavior of CO₂ and N₂ in the carbons that may simulate a real-world separation. The breakthrough results are shown in Figure 10. The difference in the breakthrough time between N₂ and CO₂ is 1.625 and 4.4 min for S(1/2):(700/700) and C(1/2):(700/700), respectively. The large difference in the breakthrough time for CO₂ in chlorella-derived carbons can be attributed to its larger mass compared to spirulina-derived carbons in the dynamic column. It is also obvious that altering the mass of the carbon in the dynamic column study will change the breakthrough time of CO₂. The delay in the breakthrough time between N₂ and CO₂ suggests a possible separation of those gases. The sharpness of the outlet concentration profiles is indicative of the importance of axial diffusion effects that may affect the quality of a large-scale industrial separation (Figure 11).

3. CONCLUSIONS

In this work, nitrogen and sulfur dual-doped carbons were synthesized from two types of algae, *S. platensis* and *C. vulgaris*, with a BET specific surface and pore volume as high as 2685 m²/g and 1.4 cm³/g, respectively. The nitrogen and sulfur functionalities were in the range of 0.9−5.69 and 0.05−0.2 at %, respectively. Harsh synthesis conditions, including higher temperature or larger KOH mass, enhanced the pore textural properties but decreased the nitrogen and sulfur functionalities. CO₂ adsorption was measured at 273, 298, and 313 K and at a pressure up to 760 Torr, and the results suggested that the
CO₂ adsorbed amount decreased with the BET SSA and micropore volume but increased with nitrogen functionality. The IAST-based selectivity for CO₂ and N₂ adsorption at 298 K also suggests that the porous carbons with higher nitrogen functionality possess better selectivity. The calculated heats of adsorption revealed that carbons with higher nitrogen content exhibit higher heat of CO₂ adsorption that further confirmed the influence of N₂ functionality in CO₂ adsorption. The breakthrough behavior of a mixture of CO₂ and N₂ was studied through dynamic column experiments. The overall results suggest that algae-derived carbons can serve as potential adsorbents for CO₂ separation from N₂.

4. EXPERIMENTAL SECTION

4.1. Sample Preparation. Spirulina (spray dried, food grade, protein content: 70%, total ash: 8.33%, moisture: 4.7%) and chlorella (spray dried, food grade, protein content: 65.1%, total ash: 6.0%, moisture: 4.9%) were obtained from commercial sources (buylgae.com) and used without any further modification. In the course of synthesis, the reaction parameters that were varied are the types of algae (Spirulina or Chlorella), char-forming temperature, ratio of char to potassium hydroxide, and activation temperature. All char-forming and activation operations were performed in an inert atmosphere with N₂ (flow rate 40 cm³/min). Typically, algae was placed in a porcelain boat and the boat was inserted in a Lindberg/Blue tube furnace. Two different char-forming temperatures were used, 300 and 700 °C. To obtain a char-forming temperature of 300 °C, the temperature of the furnace was ramped at a rate of 5 °C/min, whereas for 700 °C, it was ramped at a rate of 10 °C/min. The materials were dried at the final temperature for 2 min and then cooled to room temperature. The char was activated by mixing 3 g with potassium hydroxide at a ratio of 1:2, 1:3, and 1:4. During activation, the char and KOH mixture was placed in an alunina boat and inserted in the tube furnace. The temperature was ramped to 700 °C or 850 °C at a rate of 10 °C/min and then immediately cooled to room temperature. To activate using CO₂, 1 g of char (formed at 700 °C) was placed in a porcelain boat and inserted in the tube furnace. The temperature of the furnace was ramped to 850 °C at a rate of 10 °C/min in N₂ flow. Then, the gas was switched to CO₂ (50 cm³/min) and held to the final temperature for 100 min. The gas was finally switched back to N₂, and the furnace was cooled to room temperature. All activated samples were washed several times with copious amounts of deionized water till the pH of the wash water was close to 7. The samples that were activated by KOH are labeled as S(x/y):(T1/T2) or C(x/y):(T1/T2), where C or S stands for chlorella or spirulina, (x/y) is the ratio of char to KOH, T1 is the char-forming temperature, and T2 is the activation temperature. The samples that were activated with CO₂ are termed as S(CO₂):(700/850) or C(CO₂):(700/850), where S or C has their usual meaning.

4.2. Sample Characterization. The pore textural properties for all samples were characterized by the BET specific surface area and pore size distribution. The BET surface area was calculated from the N₂ adsorption–desorption plot at 77 K measured by a Quantachrome Autosorb-iQ-Any Gas instrument. The NLDFT-based pore size distribution was obtained by analyzing N₂ adsorption at 77 K and CO₂ adsorption at 273 K in the same instrument. Samples were selected based upon pore textural properties for further characterization by XPS for surface functionality and SEM for particle size and shape. XPS data was obtained in a Thermo Fisher K-Alpha instrument with an Al Kα X-ray anode. The energy of the X-ray was 1486.6 eV and that of the solution was 0.5 eV. The sample was mounted on a carbon tape, and the charge neutralization was performed by 2 eV Ar⁺ ions. SEM images were obtained in a Carl Zeiss Merlin SEM microscope operating at 1 kV.

4.3. Gas Adsorption Studies. Gas adsorption studies were performed in the same Quantachrome’s Autosorb-iQ-Any Gas instrument. All samples that underwent the extended sample characterization were analyzed with CO₂ adsorption at 272, 298, and 313 K and N₂ adsorption at 298 K and up to 1 bar pressure. Each sample was outgassed to 300 °C before the adsorption experiment. All gases were of ultrahigh purity grade. The temperature was maintained by a Julabo external chiller with a 1:1 mixture of water and propylene glycol as the chilling fluid. The working capacity of two of the adsorbents from spirulina and chlorella were measured under nine continuous cycles of adsorption and desorption at 298 K in the same instrument under the “hysteresis” mode.

The dynamic column experiments were performed in a custom-made dynamic column with a packed bed volume of 0.655 cm³. In all studies, the volume ratio of CO₂ and N₂ in the mixed gas streams was maintained as 15:85 by two mass flow controllers (FMA5520A, Omega Engineering Inc.). The experiment was conducted with two different carbons, 0.222 and 0.295 g of S(1/1):(700/700) and C(1/1):(700/700). Both the carbons were outgassed prior to analysis as mentioned in the adsorption section. The gas composition at the outlet of the bed was monitored by a Hewlett Packard 5898B mass spectrophotometer. The response of the mass spectrophotometer was calibrated against a known set of gas concentrations prior to the dynamic column experiment.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02892.

TGA of raw spirulina and chlorella, SEM images in low magnification, N₂ adsorption isotherms in 298 K, CO₂ adsorption isotherms at 313 K, and IAST-based simulated binary adsorption isotherms at a constant pressure and mole fraction of CO₂ (PDF)

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Notes
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