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Is heteroatom doping of activated carbons always a good strategy for enhancing CO₂ adsorption?

R. Morales-Ospino^{1,⊥}, R. L. S. Canevesi^{1*,⊥}, S. Schaefer¹, A. Celzard^{1,2}, V. Fierro^{1,*}

¹ Université de Lorraine, Centre National de la Recherche Scientifique (CNRS), Institut Jean Lamour (IJL), F-88000, Épinal, France.

² Institut Universitaire de France (IUF), 75231 Paris, France

*Corresponding authors: rafael_canevesi@hotmail.com, vanessa.fierro@univ-lorraine.fr

[⊥]These two authors contributed equally to this work

24 **Abstract**

25 This study shows the substantial impact of textural properties, with greater weight than N-
26 doping, on CO₂ adsorption by carbon materials over a pressure range from 1 to 25 bar and a
27 temperature range from 273 to 323 K. It also highlights the importance of providing volumetric
28 CO₂ adsorption capacities when presenting newly developed materials. These results were
29 obtained by exploring the influence of O- and N-doping on CO₂ uptake on 14 activated carbons
30 (ACs) with distinct specific surface areas, from 1736 to 3200 m² g⁻¹, and micropore fractions
31 from 37 to 96%. Based on 3 commercial ACs, N content was maximized by hydrogen peroxide
32 oxidation and urea treatment, reaching around 11 at.%. O-N-doping mainly impacted the largest
33 pores, reducing material textural properties and thus CO₂ adsorption, although it improved
34 CO₂/N₂ selectivity, especially up to 5 bar and between 273 and 323 K. The contribution of
35 heteroatoms to CO₂ uptake was particularly significant at low pressures and high temperatures,
36 with threshold pressures increasing at higher temperatures. Breakthrough simulations were also
37 carried out and the results demonstrate that, despite a lower specific surface area, the O-doped
38 material exhibited longer breakthrough times than its commercial counterpart. This can be
39 attributed to a balance between CO₂ adsorption capacity, governed by the textural properties,
40 and tap density, i.e., adsorption capacity per unit volume.

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45 *Keywords: CO₂ capture, adsorption, nitrogen-doping, oxygen-doping, activated carbons.*

46

47 **1. Introduction**

48 The concentration of CO₂ in the atmosphere has been increasing rapidly since the industrial
49 revolution, and is predicted to reach 570 ppm by 2100, according to numerous studies^{1,2}. CO₂ is a major
50 contributor to the current climate change observed worldwide^{3,4}. As a result, the scientific community
51 and governments worldwide are making significant efforts to find solutions⁵. Two main approaches have
52 been adopted, namely, CO₂ emission reduction and CO₂ capture and storage (CCS)⁶⁻⁹. CCS is considered
53 a key method to reduce CO₂ emissions in the industrial sector¹⁰. Studies suggest that these technologies
54 have the potential to eliminate around 20% of CO₂ emissions by 2050¹⁰.

55 Various carbon capture technologies, including adsorption, absorption and membranes, are being
56 applied to the CCS processes^{11,12}. Adsorption, in particular, is receiving increasing attention due to its
57 relatively low energy consumption and lack of toxic by-products production. This makes it a more
58 environmentally-friendly option compared to traditional absorption-based capture systems¹³. A variety
59 of high-surface-area materials have been used as adsorbents for CO₂ capture, including zeolites^{14,15},
60 metal-organic frameworks (MOFs)^{15,16}, porous polymers¹⁷ and carbon materials^{18,19}.

61 Carbon materials are used as adsorbents in CCS due to their low cost, high chemical and mechanical
62 stability, and ease of manufacture. They can be derived from petrochemical sources such as coal²⁰⁻²³ or
63 produced by the pyrolysis of various C-containing materials, including bio-sourced precursors²⁴⁻²⁶, with
64 or without subsequent chemical or physical activation²⁰. Carbon materials comprising alkaline
65 functional groups, such as nitrogen and oxygen species, have emerged as promising candidates for CCS
66 technologies due to their enhanced CO₂ adsorption capacities²⁷⁻³⁰. Moreover, high-surface-area
67 activated carbons (ACs), having a considerable amount of ultramicropores (pores width $w < 0.7$ nm)
68 and supermicropores ($0.7 < w < 2$ nm), are of particular interest. Indeed, the micropore volume is closely
69 related to surface area and so therefore to CO₂ adsorption capacity³¹⁻³⁵.

70 Most studies into the development of materials for CO₂ adsorption are conducted using manometric
71 devices designed for textural characterization³⁶⁻⁴². These studies typically present adsorption data at 0
72 °C (or at best room temperature), using an ice bath to maintain this temperature, and report isotherms
73 up to 1 atm. Given that CCS processes typically operate at temperatures above ambient levels^{43,44}, it is

74 important to understand the thermal effects on CO₂ adsorption when using chemically modified
75 adsorbents featuring nitrogen- (N) and/or oxygen- (O) doping. Although the chemical and textural
76 properties of adsorbents are known to have an impact on CO₂ adsorption capacity, their implications for
77 practical processing conditions remain relatively unexplored. Furthermore, the specific conditions under
78 which heteroatom-doping can enhance CO₂ uptake are still unclear. The main objective of this study is
79 therefore to examine the impact of the presence of heteroatoms, in particular N and O at varying
80 percentages, on CO₂ adsorption under different temperature and pressure conditions. The study aims to
81 understand how the inclusion of these heteroatoms affects CO₂ adsorption capacity to explore optimal
82 conditions for enhanced CO₂ capture.

83 Another relevant aspect investigated in this study is the significance of volumetric capacities in the
84 context of gas adsorption, as they play a crucial role in determining the volume of the adsorption column.
85 Indeed, the tap density of the materials was systematically determined herein, and the material chosen
86 for breakthrough experiments was carefully selected with this crucial factor in mind, a point that is often
87 overlooked in favor of gravimetric capacities.

88 In this paper, three commercial ACs were used as precursors for N- and/or O-doped ACs, which
89 were prepared via chemical treatment with urea, with or without a preliminary oxidation step to increase
90 O content and reactivity. The textural properties and elemental compositions of the resulting materials
91 were characterized, and their CO₂ and N₂ adsorption isotherms were measured at temperatures of 273,
92 298, and 313 K up to 25 bar in order to consider a dry post-combustion carbon capture scenario. The
93 selectivity of CO₂ capture over N₂ was also evaluated to reveal the conditions under which heteroatom
94 doping can provide a better separation factor. Adsorption data were used to model breakthrough curves
95 under different temperature and pressure conditions. An analysis was performed to understand the effect
96 of N-doping on adsorption properties as a function of temperature and pressure.

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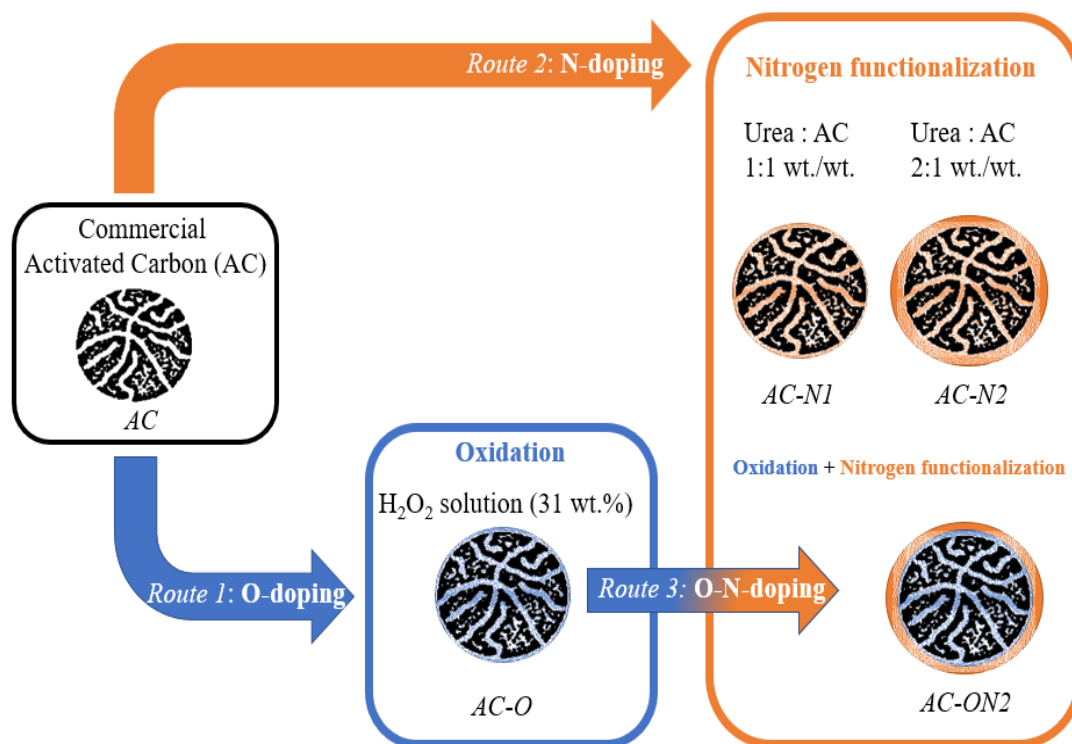
98 **2. Materials and methods**

99 **2.1. Activated carbons**

100 The precursors for the O- and/or N-doped adsorbents were three commercially available ACs,
101 namely MSP20X, MSC30, and CW30. The first two ACs were obtained from Kansai Coke &
102 Chemicals™ (Japan), while the third was supplied by Silcarbon & Aktivkohle (Germany). According
103 to the information furnished by the suppliers, the three ACs have well-developed textural properties,
104 with BET areas, A_{BET} , much higher than $1500 \text{ m}^2 \text{ g}^{-1}$.

105 **2.2. Chemical modifications**

106 Oxygen- and/or nitrogen-doped activated carbons were prepared from the three aforementioned
107 commercial materials by chemical and/or thermal treatment using three different routes, as illustrated in
108 Figure 1.



109
110 Figure 1. Chemical modification routes of pristine carbon materials.

111 **Route 1: O-doped carbons** were obtained by oxidizing 3g of AC with a solution of hydrogen peroxide
112 (31 wt.%) at room temperature. To this end, the pristine materials were treated with 10 mL of H₂O₂

113 solution, adding it at one-hour intervals until a total of 30 mL was added with some stirring. ACs
114 obtained from this oxidation route were labeled *AC-O* (e.g., for MSP20X→MSP20X-O)

115 **Route 2: N-doped carbons** were prepared by mixing 1g of AC with urea powder (99.5 %, ACROS),
116 then subjecting the blend to heat treatment in a tubular furnace. Beforehand, the urea crystals were
117 ground using a PM 100 planetary ball mill (RETSCH) and then sieved to obtain particle sizes below
118 100 μm . The urea / carbon weight ratio was either 1 or 2, and the mixture was subjected to heat treatment
119 in an oven up to 623 K at a rate of 5 K min^{-1} . This heat treatment was carried out under a synthetic air
120 atmosphere with a flow rate of 50 $\text{cm}^3 \text{min}^{-1}$. The final temperature was maintained for 3 h, after which
121 the samples were cooled to room temperature under the same air flow. Finally, the materials were
122 washed with hot water until neutral pH and dried for 24 h in a ventilated oven at 378 K. N-doped carbons
123 following *route 2* were labeled *AC-N1* or *AC-N2* with the numbers 1 and 2 indicating the urea / carbon
124 ratio (e.g., for MSP20X→MSP20X-N1 or MSP20X-N2).

125 **Route 3: O-N-doped carbons** were obtained by mixing 1g of O-doped carbons from *route 1* with 2g of
126 urea powder, following the same synthesis protocol used in *route 2*. The resulting materials were labeled
127 *AC-ON2* (e.g., for MSP20X→MSP20X-ON2).

128 **2.3. Adsorbent Characterization**

129 N_2 and H_2 adsorption isotherms at 77 K were acquired using an ASAP 2020 automatic adsorption
130 device (MICROMERITICS). H_2 at 77 K was selected as probe molecule for characterizing the adsorbent
131 materials due to its rapid diffusion into ultramicropores, enabling the acquisition of a more
132 comprehensive pore size distribution (PSD). The reason lies in the supercritical state of H_2 under such
133 conditions and its smaller molecular size than N_2 . Furthermore, H_2 exhibits reduced susceptibility to
134 interactions with polar surface sites due to its smaller quadrupole moment, which distinguishes it from
135 other probe molecules like CO_2 at 273 K, which can also penetrate in ultramicropores⁴⁵.

136 The specific surface area was calculated from N_2 isotherms using the BET equation (A_{BET} , $\text{m}^2 \text{g}^{-1}$), or
137 from both N_2 and H_2 isotherms using the two-dimensional non-local density functional theory (2D-
138 NLDFT) to determine the specific surface area, S_{NLDFT} ($\text{m}^2 \text{g}^{-1}$). The total pore volume (V_T , $\text{cm}^3 \text{g}^{-1}$),

139 micropore volume ($V_{\mu\text{-NLDFT}}$, $\text{cm}^3 \text{g}^{-1}$), pore size distribution (PSD), and average micropore size (L_0 , nm)
140 were also calculated using the same 2D-NLDFT model. The mesopore volume (V_{MES} , $\text{cm}^3 \text{g}^{-1}$) was
141 estimated by subtracting $V_{\mu\text{-NLDFT}}$ from V_T .

142 Surface chemistry analyses were conducted by X-ray photoelectron spectroscopy (XPS) using an
143 ESCAPlus OMICROM system equipped with a hemispherical electron energy analyzer with an analysis
144 area measuring $1.75 \text{ mm} \times 2.75 \text{ mm}$. The spectrometer was operated at 10 kV and 15 mA and used a
145 non-monochromatized Mg X-ray source (1253.6 eV) under vacuum ($< 7 \times 10^{-9}$ mbar). Data processing
146 software (CASA) was employed for smoothing, Shirley-type background subtraction, peak fitting and
147 quantification. The carbon, hydrogen, nitrogen and oxygen contents (wt.%) of the samples were
148 determined using a Vario EL cube analyzer (Elementar), in which ~ 2 mg of each sample are burned at
149 $1700 \text{ }^\circ\text{C}$ in a mixed atmosphere of helium and oxygen. The gases generated are then selectively
150 separated with a chromatographic column and measured using a thermal conductivity detector (with a
151 sensitivity of approximately 40 ppm). This method enables the C, H, and N contents of the materials to
152 be calculated. In a second experiment, the O content is obtained by reducing the oxygen-containing
153 combustion gases to CO, and quantifying the latter.

154 Tap densities of the different carbonaceous materials were determined using an AUTOTAP device
155 (QUANTACHROME). The analysis was performed as follows: a graduated glass cylinder with a
156 diameter of 10 mm was filled with a known weight of sample. A tapping program with a frequency of
157 $260 \text{ taps min}^{-1}$ was run for 20 min. The final volume was obtained from the graduated cylinder, and the
158 tap density was calculated as the ratio between the weight and the final volume.

159 **2.4. High-pressure adsorption isotherms**

160 Adsorption isotherms of CO_2 and N_2 were carried out using the HPVA II high-pressure manometric
161 device (MICROMERITICS) at temperatures of 273, 298 and 323 K, up to 25 bar. Prior to measurements,
162 samples were degassed under vacuum at 383 K and 5×10^{-6} mbar for 12 hours. A sample cell with a
163 volume of 10 cm^3 was loaded with approximately 1g of carbon. After evacuation, the pressure was
164 increased incrementally to the target pressure level, up to 25 bar. To improve accuracy, the contribution
165 of the empty cell was systematically measured and subtracted from all data.

166 The single experimental equilibrium data were fitted to the Sips⁴⁶ adsorption model, as specified in
167 the supplementary information SI1. The binary equilibria for CO₂/N₂ gas mixture were predicted by the
168 Ideal Adsorbed Solution Theory (as detailed in SI1). The predicted multicomponent data allowed us to
169 calculate the selectivity of the materials, preferential adsorption of CO₂ over N₂ as described in SI1.

170 The isosteric heat of adsorption, Q_{st} (kJ mol⁻¹), was determined using the Clausius-Clapeyron
171 equation (1) along with the Sips model fit.

$$-\frac{Q_{st}}{R} = \frac{\partial \ln(P)}{\partial (1/T)} \quad (1)$$

172 where R is the universal gas constant (0.08314 L bar mol⁻¹ K⁻¹), P is the absolute pressure (bar) and T is
173 the temperature (K).

174 **2.5. Systematic study of the effect of the heteroatom content on CO₂ adsorption**

175 To better understand how textural properties and surface chemistry contribute to CO₂ adsorption, a
176 mathematical regression analysis was performed. Pore volumes V (cm³ g⁻¹) of the materials were split
177 into 3 different categories according to the average pore size L (nm), in line with the IUPAC
178 classification: $V_{<0.7}$ (ultramicropores), $V_{0.7 < w < 2}$ (supermicropores) and $V_{2 < w < 50}$ (mesopores). A
179 coefficient was then assigned to each range to represent its contribution to the adsorption process (a , b
180 and c). Additionally, the contribution of surface chemistry was determined by including the heteroatom
181 content (N+O content by XPS, C_{N+O}) with a coefficient called d . This allowed the adsorption capacity
182 $q_{CO_2}^{MODEL}$ to be expressed mathematically as in Equation (2):

$$q_{CO_2}^{MODEL} = a V_{w < 0.7} + b V_{0.7 < w < 2} + c V_{2 < w < 50} + d C_{N+O} \quad (2)$$

183 To determine the coefficients (a , b , c and d) of Eq. (2) at different pressures and temperatures,
184 multiple linear regression was performed on the experimental data. The coefficients were calculated for
185 a total of eight different pressures, spanning from 0.25 to 25 bar, at three distinct temperatures (273, 298
186 and 323 K).

187 **2.6. Modeling of breakthrough curves**

188 The mathematical modeling used in this study to simulate single CO₂ breakthrough curves at different
189 temperatures and pressures is based on validated models from previous works on adsorption⁴⁷⁻⁴⁹. The
190 mathematical model considered the following assumptions:

- 191 • Ideal gas behavior
- 192 • Heat, mass and momentum transport are only considered in the axial direction
- 193 • The Ergun equation can be used to describe momentum balance
- 194 • A bi-Linear Driving Force (bi-LDF) model to describe diffusion in both the macropore and
195 micropore region
- 196 • The void fraction, cross section and adsorbent properties are the same in all columns

197 The model incorporates mass, energy, and momentum balance equations, which are detailed in SI2.
198 The system of partial differential equations was solved with gPROMS software from Siemens (UK)
199 using a third-order orthogonal collocation method on a finite basis in the axial direction.

200 **3. Results and discussion**

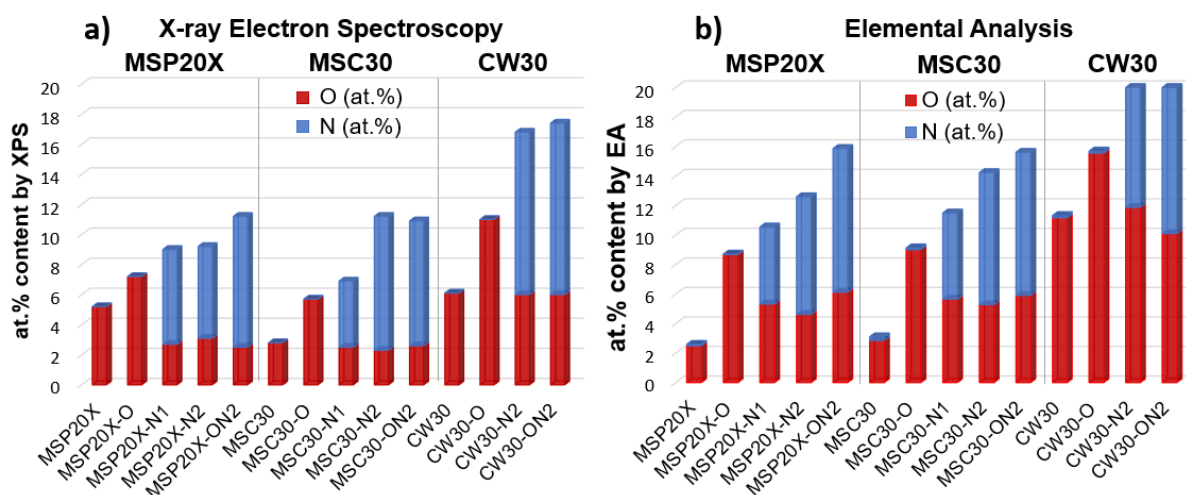
201 **3.1. Doping quantification**

202 Heteroatom doping leads to a loss of material that significantly affects the oxidation process, resulting
203 in an O-doped carbon yield of around 80%. Conversely, treatment with urea results in a significantly
204 higher yield of N-doped carbon, exceeding 95%. X-ray photoelectron spectroscopy (XPS) was
205 conducted on all materials, including the initial ACs, to quantify N and O contents and verify the
206 effective doping of the modified materials. Figure 2a illustrates that the untreated ACs had a negligible
207 presence of N on their surface (limit of quantification 1 at.%), while the three commercial ACs already
208 contained O with atomic percentages (at. %) ranging from 2.8 to 6.1. Figure 2a confirms the successful
209 N- and O-doping via *routes 1* and *2*, as evidenced by the noticeable increase in N and O contents. The
210 nitrogen content in the N-doped ACs using a urea / carbon weight ratio of 1 ranged from 4% to 6%,
211 whereas the N content varied from 6.1% to 11% in those with a ratio of 2. In contrast, when the amount
212 of urea was doubled in *route 2*, a corresponding proportional increase in the surface N percentage was

213 not observed, as is evident in the *AC-N2* carbon materials. The ACs modified through *route 3* had N
 214 contents ranging from 8.3% to 11.4%. However, the addition of heteroatoms did not consistently result
 215 in an overall increase in the combined N+O content compared with the *AC-N2* materials. The exception
 216 is sample MSC30-ON2, for which the initial O content appears to influence subsequent nitrogen
 217 incorporation; this might be attributed to the Hofmann rearrangement mechanism, as previously
 218 demonstrated by several authors^{50,51}.

219 The results of elemental analysis (EA), presented in Figure 2b in atomic percent (at. %), validate the
 220 incorporation of both O and N into the bulk composition of the carbons. While the trends observed by
 221 XPS and EA analysis align, O and N contents were higher in the bulk, as determined by EA, compared
 222 to surface measurements by XPS. This discrepancy becomes more pronounced with increasing
 223 heteroatom content, as shown in SI3 d. The complete elemental analysis data (both in weight and atomic
 224 percentages) are presented in the Supporting Information SI3, including the C content in addition to
 225 those for N, O and H.

226

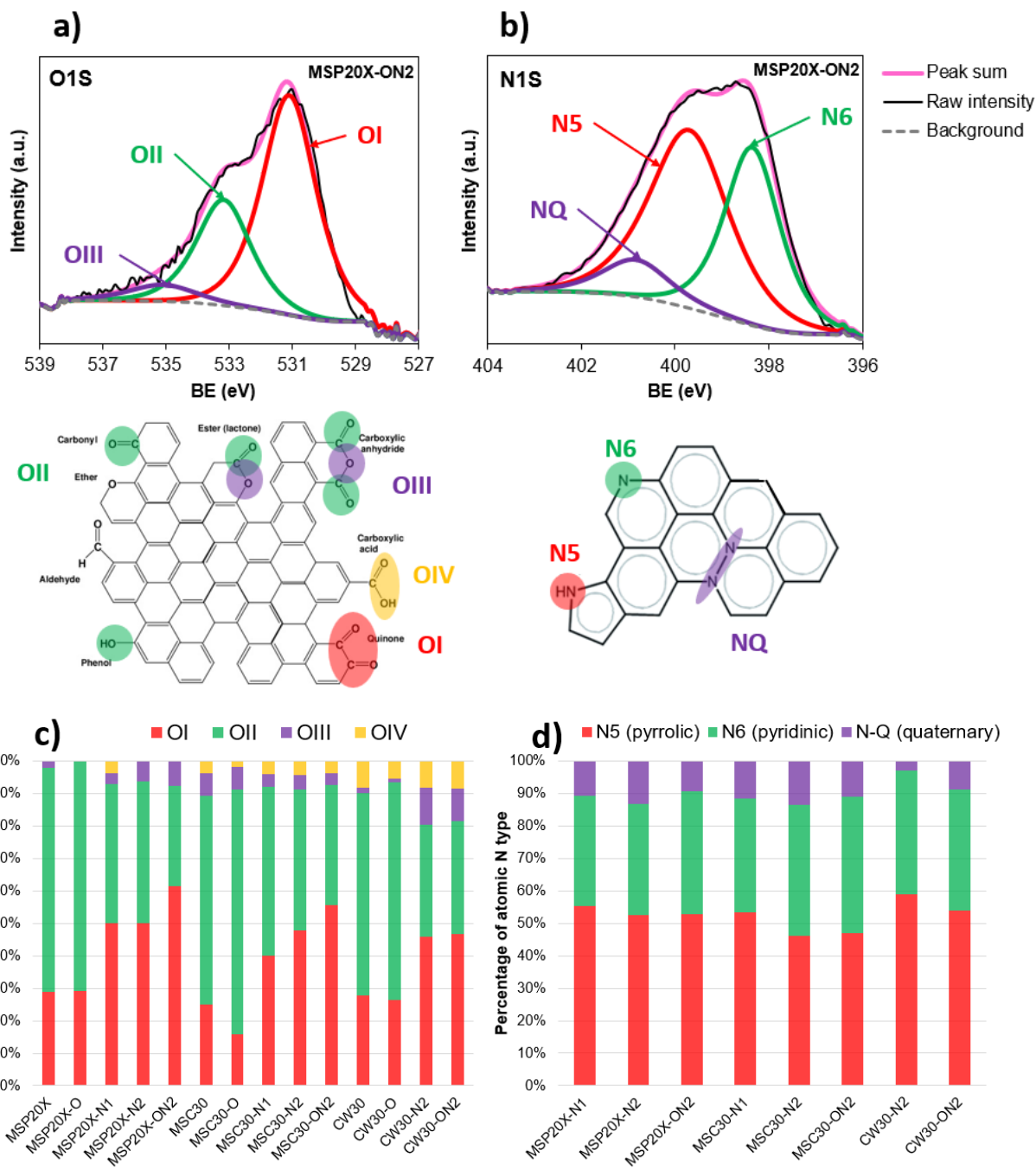


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228 Figure 2. (a) Atomic contents (at. %) of O and N obtained by X-ray Photoelectron Spectroscopy (XPS) and b)
 229 elemental analysis in atomic content (at. %) for O, N and H.

230

231 The deconvolution of the XPS analysis of sample MSP20X-ON2 is presented as an example and
 232 revealed the presence of specific types of O and N functional groups, which are illustrated in Figures 3a
 233 and 3b, respectively.



234

235

236 Figure 3. Example of deconvolution of the (a) O 1s and (b) N 1s regions of sample MSP20X-ON2. c) Atomic
 237 percentages of oxygen groups: OI (quinones), OII (carbonyl esters, acid anhydrides and hydroxyls),
 238 OIII (non-carbonyl esters and anhydrides) and OIV (carboxylic acids); d) atomic percentages of
 239 nitrogen groups: N5 (pyrrolic groups), N6 (pyridinic groups) and N-Q (quaternary groups).

240

241 Figure 3a shows typical O species, including OI (oxygen in quinones), OII (carbonyl oxygen in
 242 esters, acid anhydrides and hydroxyls), OIII (non-carbonyl oxygen in esters and anhydrides), and OIV
 243 (oxygen in carboxylic acids)²⁴. The deconvolution of sample MSP20X-ON2 proved the presence of OI,

244 OII and OIII species, but no OIV was identified. Similarly, N functional groups were identified as shown
245 in Figure 3b: pyrrolic (N5), pyridinic (N6), and quaternary (NQ) nitrogen groups^{52,53}.

246 The quantification in atomic percent (at. %) of O and N functional groups is shown in Figures 3c and
247 3d, respectively. OI and OII functional groups were found to be the most predominant, with OII type
248 accounting for 62-69%, while N5 and N6 accounted for over 80% of the N content. OI and OII groups
249 are common in the starting materials or precursor compounds used for the synthesis of activated carbons.
250 These O species may already be present in the initial carbonaceous material or introduced during the
251 carbonization or activation process. The pre-oxidation treatment (*route 1*) resulted in a clear increase in
252 O content, which is consistent with previous reports using H₂O₂ as an oxidizer^{54,55}. It is noteworthy that
253 the oxidation process primarily leads to an increase in the percentage of OII groups. The full XPS spectra
254 in the O1s and N1s regions for the three commercial ACs and their modification is shown in SI3.

255 Although not plotted, the high-resolution C1s spectra were deconvoluted into five peaks, which were
256 labeled from CI to CV. CI was assigned to Csp² in hydrocarbons, aromatics and aliphatics. CII was
257 assigned to Csp³ and C–O single bonds associated with ethers, phenols and anhydrides. CIII
258 corresponded to C=O double bonds in carbonyls and quinones. The CIV and CV peaks were assigned
259 to C–O single bonds in carboxylic groups and plasmon losses or shake-up π - π satellites,
260 respectively^{52,56,57}. The distribution of atomic carbon types, as well as the corresponding O- and N-
261 functional groups, are presented in Table SI4 in the supplementary information.

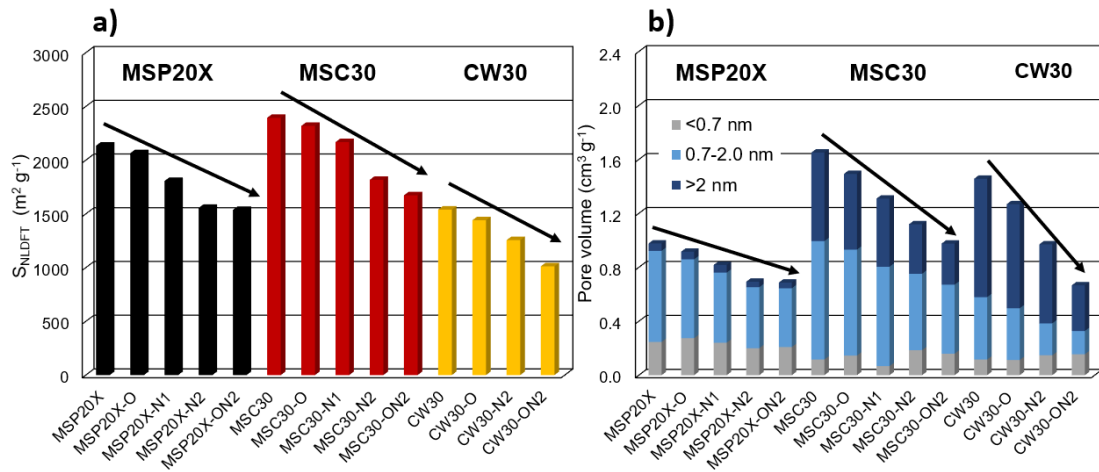
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263 **3.2. Textural properties**

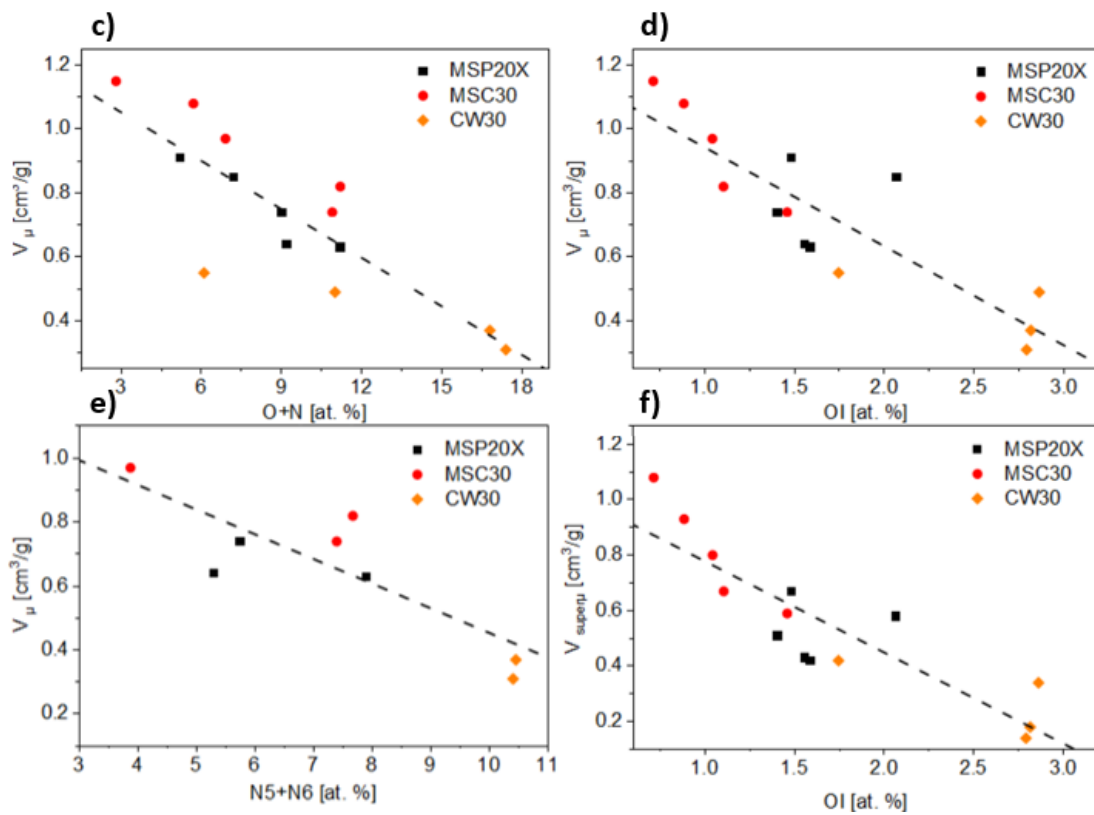
264 SI5 shows N₂ and H₂ adsorption-desorption isotherms and corresponding pore size distributions for
265 all samples. N₂ isotherms of pristine and doped MSP20X and MSC30 were characterized as Type I,
266 indicating microporous materials according to the IUPAC classification⁵⁸. Conversely, the isotherms for
267 pristine and derived CW30 ACs were identified as type IV and displayed a hysteresis loop at P/P₀ above
268 0.50, suggesting the existence of capillary condensation in the mesopores.

269 Using N₂ and H₂ adsorption isotherms, the textural properties were determined by applying the 2D-
270 NLDFIT method, and the results are shown in Figures 4a and b.

271



272



273 Figure 4. (a) S_{NLDFT} specific surface area; and (b) total pore volume (micro- and mesopores) and their distribution
 274 in the different pore width (w) ranges, namely $w < 0.7$ nm, $0.7 < w < 2.0$ nm, and > 2 nm $< w < 50$ nm.
 275 Evolution of micropore volume (V_{μ}) as a function of (c) O+N, (d) OI and (e) N5+N6 content; and (f)
 276 evolution of super micropore ($V_{super\mu}$) as a function of OI content. The textural parameters were
 277 calculated using the 2D non-local density functional theory (2D-NLDFT).

278 The specific surface areas and total pore volumes exhibit a continuous decrease in the following
 279 order: $AC > AC-O > AC-NI > AC-N2 > AC-ON2$. High values of S_{NLDFT} surface area, between 1030 and
 280 $2520 \text{ m}^2 \text{ g}^{-1}$, and total pore volume $V_{T,NLDFT}$ from 0.67 to $1.65 \text{ cm}^3 \text{ g}^{-1}$, respectively, were found. Previous
 281 research has linked this reduction in surface area after urea treatment to the attachment of nitrogen
 282 groups to the edges of the carbon layers, which can partially impede pore accessibility^{59,60}.

283 The MSP20X series is predominantly characterized by a microporous structure, while the MSC30
284 and CW30 series feature a combination of micro- and meso-porosity. The CW30 series has a larger
285 mesopore content, ranging from 30 to 40%. The calculated textural properties of all the materials studied
286 are gathered in Table SI6. Cumulative pore volume graphs for the three series of ACs are also shown in
287 the supplementary information, SI7.

288 Figures 4c, d, and e illustrate the changes in micropore volume as a function of total O+N content,
289 quinonic oxygen content (OI), and combined pyrrolic (N5) and pyridinic (N6) nitrogen content
290 (N5+N6). The reduction in micropore volume apparently correlates with O+N content, particularly in
291 the case of OI. These findings suggest that the introduction of O+N resulted in pore narrowing. Figure
292 4f shows the decrease in supermicropore volume with increasing OI content values, in contrast to the
293 ultra-microporous region (as seen in SI6). This behavior can be attributed to the limited ability of O and
294 N atoms to penetrate the narrowest pores.

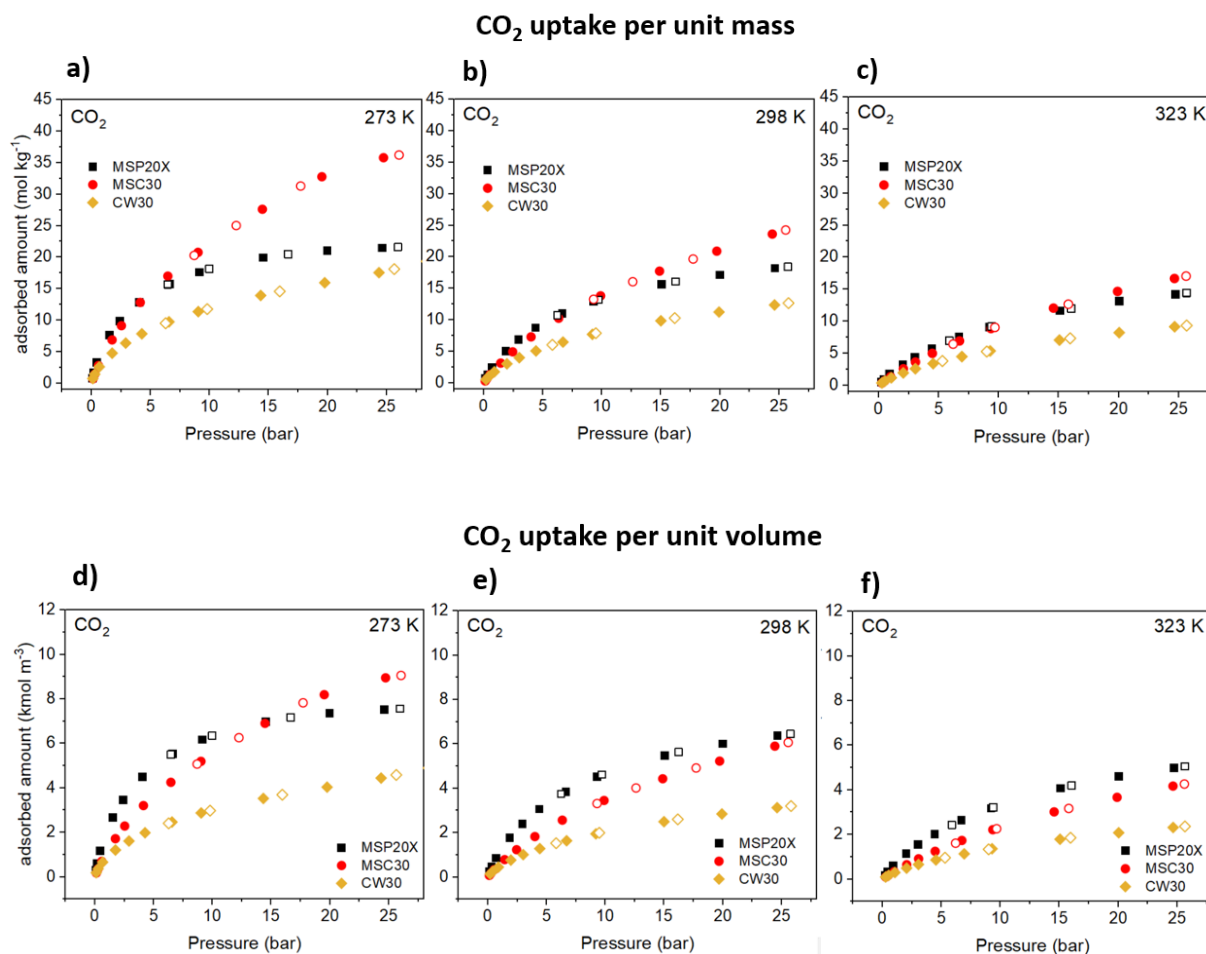
295 Chemical doping can lead to deformation of the carbon basal plane as well as direct steric hindrance.
296 Surface groups like amines, amides, carboxyls and hydroxyls can occupy pore volume, while functional
297 groups such as ethers, pyrroles and pyridines can distort the carbon structure based on simple
298 geometrical considerations. Mostazo-López et al.⁶¹ explained that such structures are frequently
299 observed in O- and N-doped carbons. Therefore, induced steric hindrance and local deformation of the
300 carbon structure led to pore narrowing and potential blocking³⁴.

301

302 **3.3. CO₂ and N₂ adsorption at different temperatures**

303 CO₂ adsorption isotherms, expressed in terms of mols per unit mass of adsorbent, were obtained for
304 the three commercial ACs at temperatures of 273, 298 and 323 K, as shown in Figures 5a, b, and c. As
305 expected for physisorption, there is a noticeable decrease in CO₂ uptake with increasing temperature.
306 Similar trends were observed for chemically modified materials (see SI8, SI9, and SI10). Among the
307 samples studied, MSC30 exhibited the highest CO₂ uptake at all three temperatures, up to 25 bar. This
308 can be attributed to its more developed textural properties compared with other commercial ACs.

309



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312

313 Figure 5. CO₂ isotherms per unit mass (mol kg⁻¹) for MSP20X, MSC30 and CW30 commercial ACs at (a) 273 K,
 314 (b) 298 K and (c) 323 K; and CO₂ isotherms (kmol m⁻³) for the same ACs per unit volume at (d) 273 K,
 315 (e) 298 K and (f) 323 K. Solid symbols represent adsorption and empty symbols represent desorption.

316

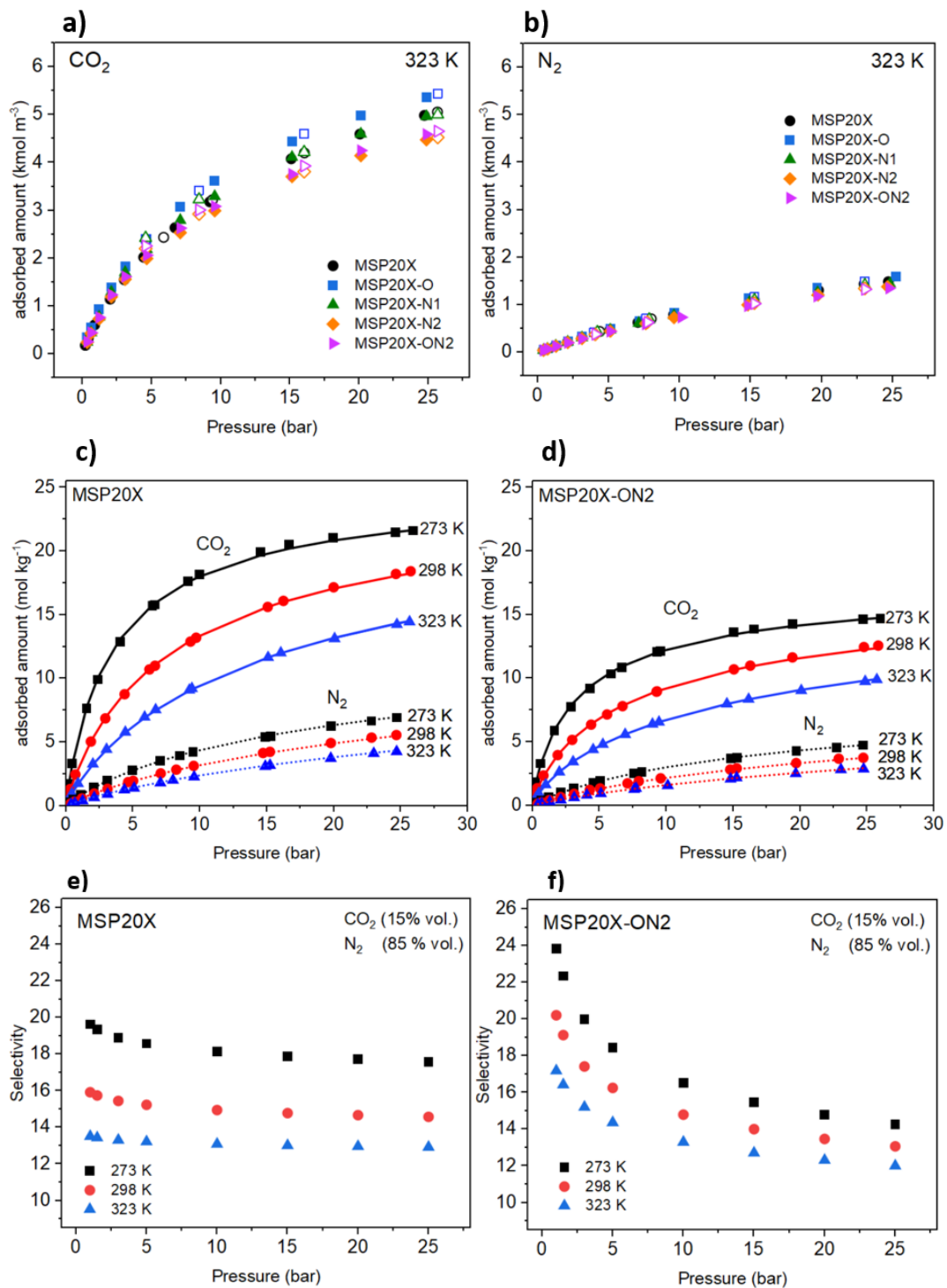
317 However, if the tap density of the commercial ACs is considered when plotting the isotherms per unit
 318 volume, the order of CO₂ uptake is altered, as observed in Figures 5d, e, and f. The tap densities of the
 319 three ACs are: 350 kg m⁻³ (MSP20X), 250 kg m⁻³ (MSC30) and 253 kg m⁻³ (CW30). Given the higher
 320 tap density of the MSP20X sample, the CO₂ uptake per unit volume exceeds that of the MSC30,
 321 particularly at temperatures of 298 K and 323 K. In the context of post-combustion CO₂ capture, where
 322 the use of fixed beds is common for CO₂ separation, the scenario involving 323 K and isotherms based
 323 on the volumetric capacities is considered more realistic for comparing adsorbents' capture
 324 performance. Consequently, based on this criterion, the MSP20X sample and its chemically modified
 325 counterparts have been selected for further analysis and discussion in this manuscript.

326 Figures 6a and b show CO₂ and N₂ adsorption-desorption isotherms at 323 K for the MSP20X series.
 327 The general trend is that CO₂ and N₂ uptakes decrease as the textural properties of the adsorbents are
 328 reduced, confirming that physisorption is the predominant adsorption mechanism. Comparison of

329 Figures 6a and b clearly shows that CO₂ is better adsorbed than N₂. This can be attributed to the higher
330 quadrupole moment and polarizability of the CO₂ molecule, resulting in stronger interactions with the
331 adsorbent surface during physisorption⁶²⁻⁶⁴. It is important to note that the results of this study are
332 applicable in the context of doping ACs with heteroatoms. Previous studies⁶⁵⁻⁶⁷ have suggested that ACs
333 doped with heteroatoms, where doping takes place prior to activation, may exhibit higher CO₂ uptake
334 per unit mass compared to the starting material. However, it remains difficult to distinguish the effect
335 of textural properties from that of surface chemistry. To further investigate the relationship between
336 textural properties, surface chemistry and their impact on CO₂ adsorption, a mathematical regression
337 analysis was carried out in section 3.4.

338 The Sips adsorption model was used to analyze experimental CO₂ and N₂ adsorption data of
339 commercial and chemically modified ACs. Figures 6c and d show the Sips model fits (represented by
340 lines) for both the commercial AC MSP20X and the pre-oxidized, N-doped material MSP20X-ON2,
341 allowing a direct comparison between a non-doped and a highly-doped material. Figures illustrating
342 experimental isotherms and corresponding Sips model fits for the three series of materials can be found
343 in SI8, SI9 and SI10. The values for the fitted parameters, together with the determination coefficients,
344 are reported in SI11 for all samples. The determination coefficients obtained ranged from 0.99 to 1.0,
345 indicating very good fits. This suggests that the parameters obtained can be used to calculate the isosteric
346 heat of adsorption with the Clausius-Clapeyron approach.

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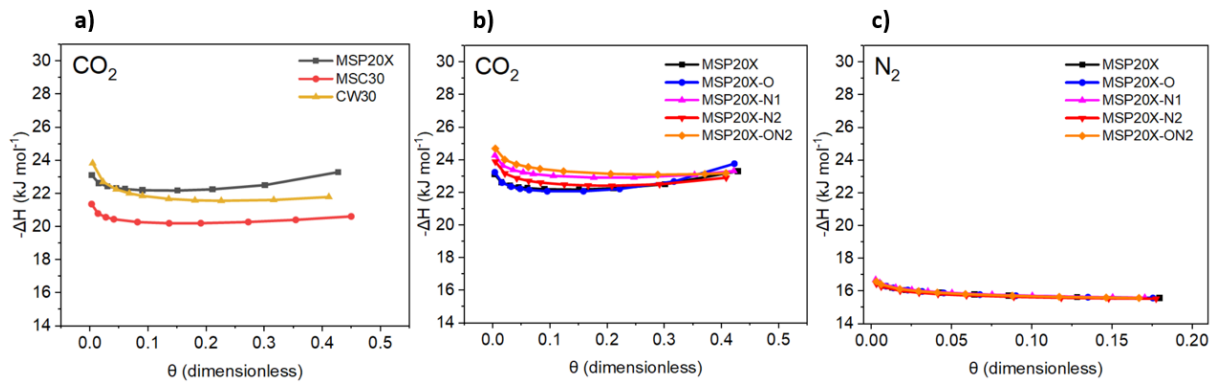
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Figure 6. Experimental isotherms (kmol m⁻³) of (a) CO₂ and (b) N₂ at 323 K for the AC series MSP20X. Solid symbols represent adsorption and empty symbols represent desorption. Experimental and fitted isotherms of CO₂ and N₂ of samples (c) MSP20X and (d) MSP20X-ON2 at 273, 298 and 323 K. Solid symbols represent experimental data and lines (straight and dotted) represent Sips model fits. CO₂/N₂ selectivity (15% vol. CO₂/85% vol. N₂) values for samples (e) MSP20X and (f) MSP20X-ON2 at 273, 298 and 323 K.

360 The selectivity of CO₂ capture over N₂ for the aforementioned samples was estimated using the
 361 well-known Ideal Adsorption Solution Theory (IAST) model as explained in SI1. Figures 6e and f show
 362 the selectivity of samples MSP20X and MSP20X-ON2 at different temperatures, specifically
 363 considering a dry post-combustion scenario with a binary mixture of CO₂ and N₂ in the flue gas, in
 364 which CO₂ accounts for 15% by volume. The results indicate that doping the material improves
 365 selectivity, particularly at lower pressures (below 5 bar). This suggests that the effect of heteroatoms is
 366 more advantageous at these pressure levels, where the energetic interaction between the material surface
 367 and heteroatoms is more pronounced. This observation is in line with the results in Figure 7a, where
 368 doped materials from the MSP20X series exhibit a higher isosteric heat of adsorption at low coverage.
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370

371 Figure 7. Isosteric heats of CO₂ adsorption on: (a) raw commercial ACs and (b) MSP20X series as a function of
 372 CO₂ fractional coverage (θ); and (c) Isosteric heats of N₂ adsorption on the MSP20X series as a function
 373 of N₂ fractional coverage.

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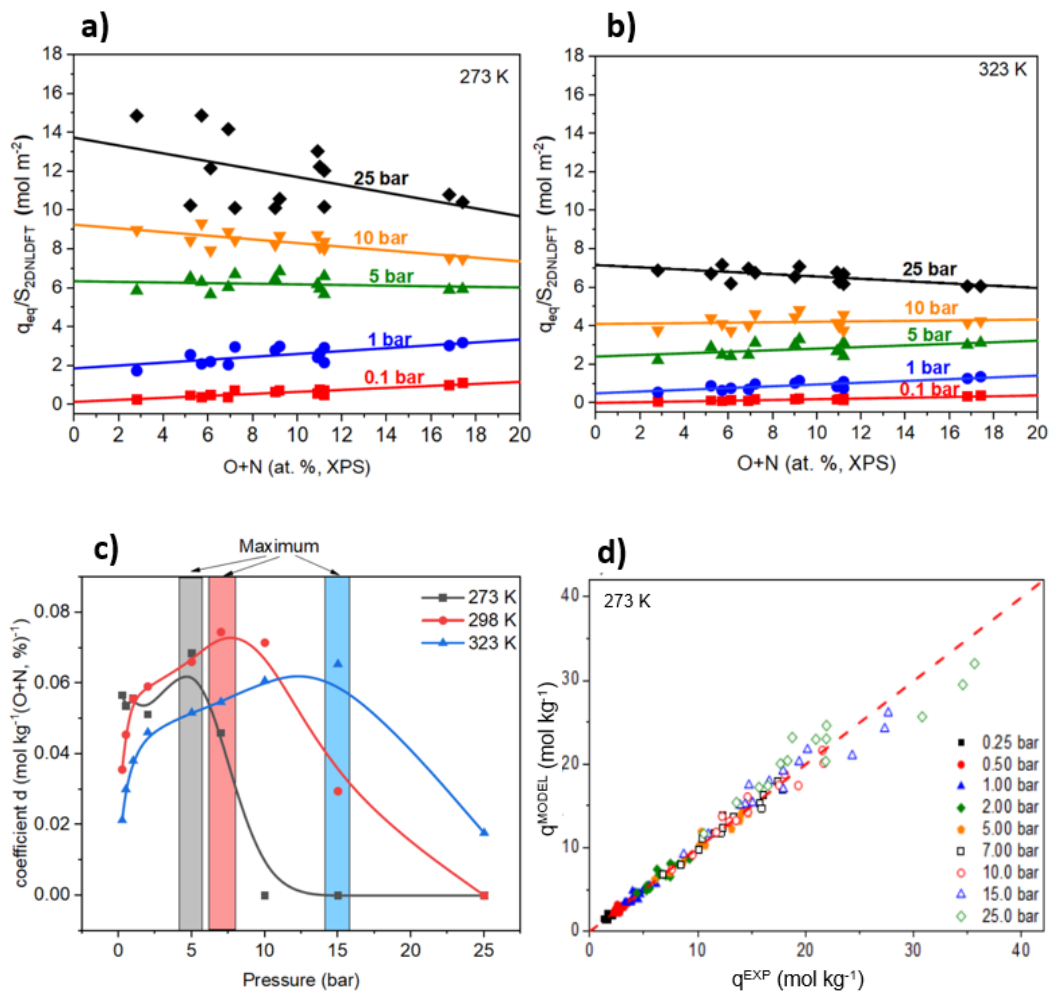
375 Heat release during adsorption plays an essential role in a gas capture process, as it can influence
 376 adsorbent temperature, generate hot spots and impact adsorption kinetics¹⁴. The isosteric heats of
 377 adsorption were obtained from the fitted isotherms with Sips model at 273, 298, and 323 K in
 378 conjunction with the Clausius-Clapeyron equation (Equation 1) and they are plotted in Figure 7. Figure
 379 7a shows a subtle increase in the isosteric heat of CO₂ adsorption for MSP20X with fractional CO₂
 380 coverage ($\theta > 0.2$), in contrast to the decreasing trend shown by MSC30 and CW30. This behavior can
 381 be attributed to a predominance of intermolecular interactions between CO₂ molecules rather than
 382 surface-molecule interactions upon micropore filling completion^{68,69}. Similar features in the isosteric
 383 heat of adsorption have been demonstrated for CO₂^{70,71} as well as for other gases⁷²⁻⁷⁴ and validated by

384 grand-canonical Monte Carlo modelling⁷⁵. Figure 7b shows a decrease in isosteric heat of CO₂
385 adsorption as the amount adsorbed increases, particularly at low coverage for most of the doped ACs in
386 the MSP20X family. This suggests stronger interactions between CO₂ and the surface at low pressure,
387 indicating that the strongest adsorption sites are occupied first. Furthermore, the isosteric heat of CO₂
388 adsorption was slightly higher in the doped samples than in the untreated ACs, suggesting that
389 heteroatom doping may increase energetic interactions at low surface coverage. A similar pattern was
390 observed in the other two series of ACs (see SI12). The average heat of CO₂ adsorption, calculated for
391 all materials (see SI13) considering coverage up to 0.5, was found to be well below 50 kJ mol⁻¹,
392 confirming that the primary adsorption mechanism is based on physical interactions. Previous studies
393 on ACs that have undergone chemical treatment have also reported similar average heats of adsorption
394 (ranging from 20 to 30 kJ mol⁻¹)^{14,77,78} to those presented in this study, ranging from 20 to 26 kJ mol⁻¹.
395 These average heats of CO₂ adsorption fall within the range of the enthalpy of sublimation and
396 vaporization of CO₂, which are 26.1 kJ mol⁻¹ and 16.7 kJ mol⁻¹,⁷⁹ respectively. This suggests that within
397 the nanopores of ACs, the strong interaction forces present can cause CO₂ to exhibit a solid- or liquid-
398 like behavior, depending on pore size and adsorption conditions. On the other hand, the isosteric heat
399 for N₂ adsorption in the MSP20X series, as depicted in Figure 7c, remained almost constant, around 16
400 kJ mol⁻¹, across the coverage range evaluated, indicating the potential absence of intermolecular
401 interactions and binding site heterogeneity⁷⁶. Notably, isosteric heat values for adsorbed N₂ were
402 observed to be lower than those for CO₂, aligning with the expected trend.

403 **3.4. Effect of surface chemistry and textural properties on CO₂ uptake**

404 Bearing in mind that the primary adsorption mechanism is based on physical interactions, and to
405 evaluate the real effect of surface chemistry on CO₂ adsorption capacity, we normalized CO₂ uptakes
406 with respect to S_{NLDFT} specific surface area. Figures 8a and b illustrate CO₂ uptake per unit area as a
407 function of O+N content for all ACs, pristine and doped, at different pressures of 0.25, 1.0, 7.0 and 25
408 bar at 273 and 323 K. Figure 8a shows a linear trend line with a positive slope up to 1 bar, meaning that
409 higher O+N content results in improved CO₂ uptake per specific surface area at his pressure. However,
410 the same figure shows that O+N content has no significant impact on CO₂ uptake at 5 bar. At higher

411 pressures, the slope of the linear trend line becomes negative, indicating that the presence of heteroatoms
 412 no longer offers any advantage for overall CO₂ uptake. Figure 8b shows the same data as Figure 8a when
 413 the adsorption temperature is raised to 323 K. At higher temperatures, the maximum pressure at which
 414 O+N content positively influences CO₂ uptake is higher, somewhere between 10 and 25 bar.
 415 Consequently, AC doping becomes more relevant at higher temperatures, demonstrating its efficacy
 416 over a wider pressure range.



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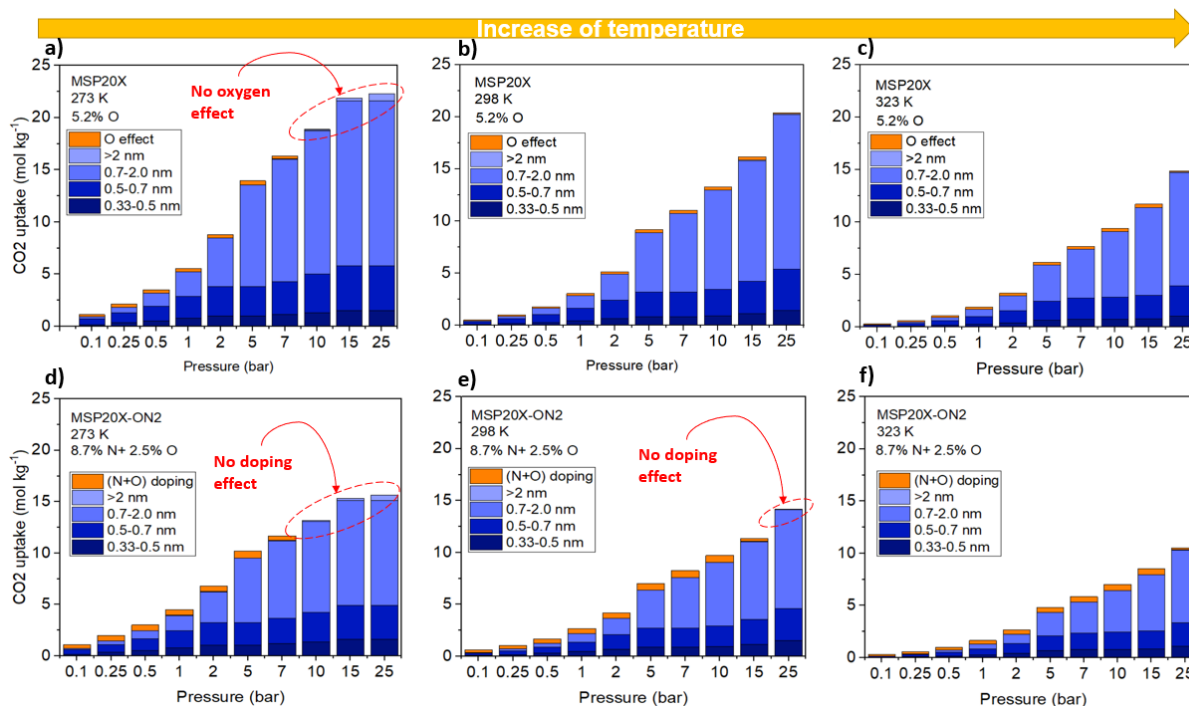
419 Figure 8. Relationship between O+N surface content and the CO₂ uptake per unit specific surface area $S_{2DNLDFT}$ at
 420 (a) 273 and (b) 323 K at different pressure levels for the ACs studied in this work. Solid lines
 421 represent the linear trend line for each selected pressure level: 0.1, 1, 5, 10 and 25 bar. (c) Coefficient
 422 d in Equation (2) versus pressure at different temperatures, and (d) comparison of experimental CO₂
 423 uptake (q^{EXP}) versus predicted CO₂ uptake (q^{MODEL}) with Equation (2) at 273 K.

424

425 The mathematical regression analysis performed to better understand how textural properties and
 426 surface chemistry contribute to CO₂ adsorption was carried out as follows. Using the data given in the
 427 supplementary information, SI14, the adsorption capacity q_{CO_2} was fitted by Equation (2) and the

428 coefficient values for each temperature and pressure can be found in the Supplementary Information,
429 SI15. Figure 8c illustrates the variation of coefficient d in Equation (2) as a function of pressure. A
430 consistent upward trend is observed up to a certain threshold, beyond which a noticeable decrease in
431 coefficient d becomes evident. Additionally, the maximum value of parameter d shifts towards higher
432 pressures as the isotherm temperature increases. This indicates that surface chemistry exerts a more
433 prolonged influence over a broader pressure range at higher temperatures. Notably, at 323 K, the d
434 coefficient does not approach a nearly negligible value as observed at the other two lower temperatures.
435 In contrast, Figure 8d presents a comparison between experimental (q^{EXP}) and calculated (q^{MODEL}) CO₂
436 uptakes for different pressure levels and 273 K. The results indicate that the data predicted using
437 Equation (2) are more accurate at lower pressures. Nonetheless, this mathematical approach proves to
438 be a reliable method for estimating overall CO₂ uptake.

439 To highlight the impact of porosity and heteroatom content, we selected two samples, namely
440 MSP20X and MSP20X-ON2. Sample MSP20X was chosen because it had not been chemically
441 modified, yet had a surface heteroatom content of 5.2 at. % oxygen. On the other hand, sample MSP20X-
442 ON2 underwent pre-oxidation and subsequent nitrogen-doping to further enhance its heteroatom content
443 (11.2 at. % N+O). Based on the results presented in Figure 9, it can be observed that the influence of
444 heteroatoms on CO₂ uptake becomes more prominent at higher pressure levels with increasing
445 temperature. At the lowest temperature considered (298 K), neither sample exhibits a significant effect
446 of heteroatoms in the 10-25 bar range. However, as temperature rises, the heteroatom effect becomes
447 gradually evident at higher pressures, which is agreement with the results presented in Figure 8c.
448 Additionally, it is worth noting that the doping effect is more pronounced in MSP20X-ON2 than in
449 MSP20X, indicating that a higher overall heteroatom content may reinforce the significance of surface
450 chemistry in CO₂ uptake. Nevertheless, Figure 9 shows that textural properties play a more important
451 role in CO₂ adsorption, since higher uptakes were obtained with the pristine AC.



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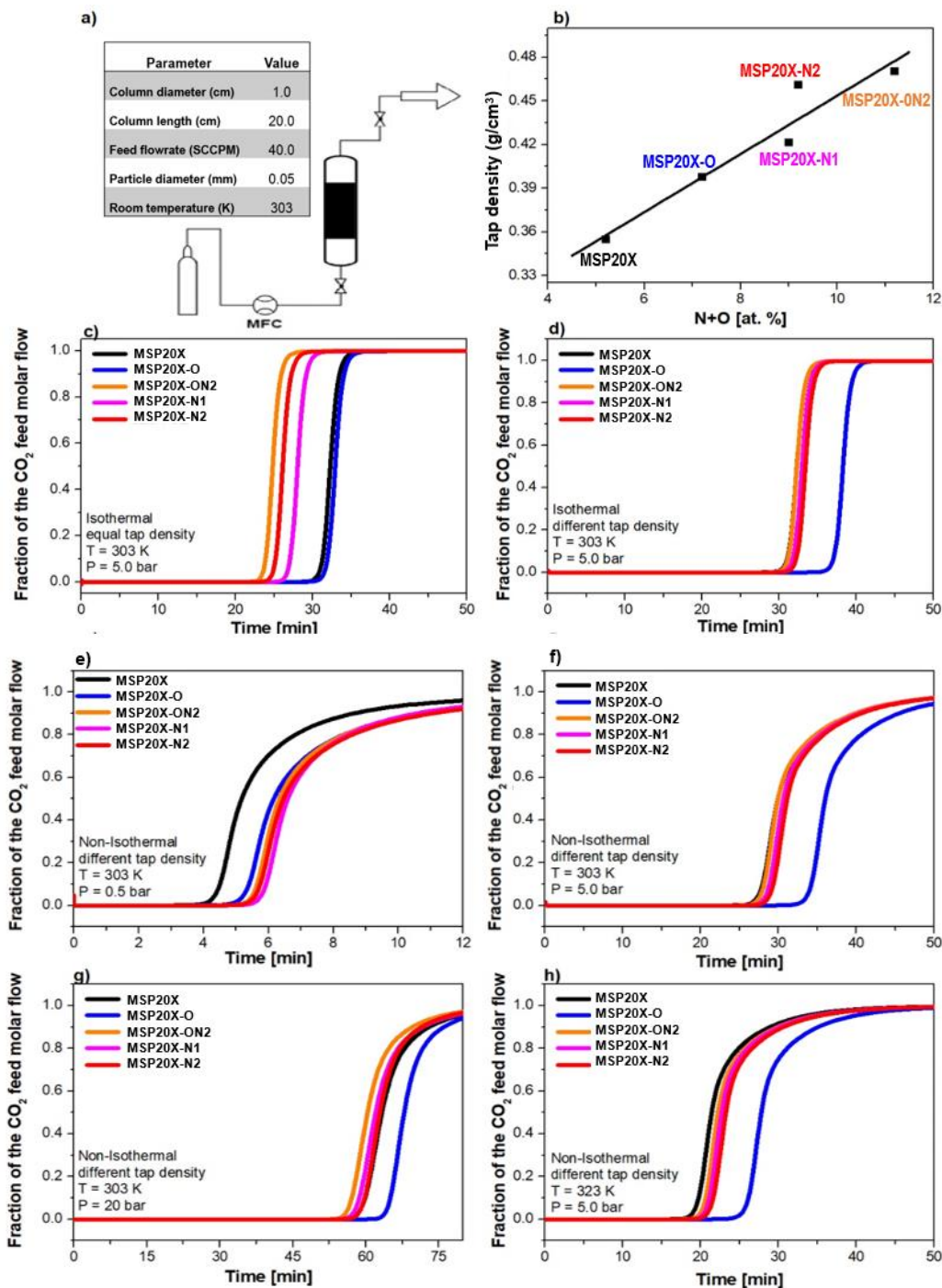
453 Figure 9. Influence of pore size distribution and surface heteroatoms on CO₂ uptake for samples MSP20X at (a)
 454 273 K, (b) 298 K and (c) 323 K, and for MSP20X-ON2 at (d) 273 K, (e) 298 K and (f) 323 K.
 455

456 3.5. Adsorbent tap density and breakthrough curve simulation

457 Adsorbent doping density plays a crucial role in the design of an adsorption process, more specifically for
 458 the cases where fixed-beds are used. Assuming constant adsorption capacity per unit mass, a material
 459 with a higher packing density will result in more effective adsorption per unit volume. Consequently,
 460 the denser material will result in lower vessel costs and occupy less space in an industrial facility. Figure
 461 10b provides a visual representation of the relationship between tap density and variation in N+O content
 462 in the MSP20X series.

463 To better understand the impact of the adsorption parameters analyzed, a simulation of the
 464 adsorption breakthrough curves was carried out for the MSP20X series under different conditions,
 465 according to the scheme described in Figure 10a. Figure 10a also presents the selected parameters used
 466 to solve the model, as described in the experimental section. Figure 10c shows the breakthrough
 467 simulation at 5 bar in an ideal scenario, where all materials have an isosteric heat of adsorption of zero
 468 and have the same bulk density. However, when the simulation was run with the actual tap density, the
 469 dynamics changed as shown in Fig. 10d. Increasing the tap density led to a prolonged breakthrough time

470 for MSP20X-O. The performance of the other N- and O-N-doped materials improved only slightly, with
 471 breakthrough times very close to those of MSP20X.



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474 Figure 10. (a) Schematic of simulated fixed-bed system. For the MSP20X series: (b) tap density as a function of
 475 O+N content; (c) isothermal breakthrough simulation at 303 K and 5 bar, considering all tap densities
 476 equal to that of the raw AC; (d) isothermal breakthrough simulation at 303 K and 5 bar considering the
 477 tap density of the ACs; (e) non-isothermal, adiabatic breakthrough simulation at 303 K and 0.5 bar; (f)
 478 non-isothermal, adiabatic breakthrough simulation at 303 K and 5 bar; (g) non-isothermal, adiabatic
 479 breakthrough simulation at 303 K and 20 bar; (h) non-isothermal, adiabatic breakthrough simulation at
 480 323 K and 5 bar.

481 Three simulations were carried out to analyze a non-isothermal adsorption process under the
482 following conditions: process temperature of 303 K and pressures of 0.5 bar (Figure 10e), 5 bar (Figure
483 10f), and 20 bar (Figure 10g). At a pressure of 0.5 bar, the doped materials exhibited a higher affinity
484 for CO₂, as evidenced by the shorter breakthrough time for the raw MSP20X compared with its doped
485 counterparts. At 5 bar and 303 K, MSP20X-O emerged as the best performing sample in terms of CO₂
486 uptake. Even when the temperature was increased to 323 K, as shown in Figure 10h, the trend in results
487 remained the same as at 303 K. The superior performance of MSP20X-O can be attributed to a balance
488 between CO₂ adsorption capacity, essentially governed by textural properties, and tap density. This
489 undoubtedly underlines the crucial importance of volumetric adsorption capacity, and the need to present
490 it alongside specific adsorption capacities in reports on the performance of newly developed materials.

491 Comparing the breakthrough at temperatures of 303 K (Figure 10g) and 323 K (Figure 10h), it is
492 evident that an increase in temperature reduces the performance of MSP20X compared with doped
493 materials, confirming the greater influence of surface chemistry at higher temperatures. Overall, the
494 results suggest that a particular degree of doping plays a more important role in improving adsorption
495 performance, especially when the pressure is below 5 bar, and preferably at elevated temperatures such
496 as 323 K. Conversely, under conditions of higher pressures and lower temperatures than those mentioned
497 above, the impact of surface chemistry is relatively low.

498

499 **4. Conclusion**

500 This study unequivocally demonstrates that up to pressures of 25 bar and in the temperature range
501 273-323 K, textural properties take precedence in determining CO₂ uptake by carbon materials. N-O-
502 doping primarily affects larger pores, resulting in reduced textural properties and subsequent adsorption.
503 Nonetheless, it improved CO₂/N₂ selectivity, particularly up to 5 bar and in the temperature range 273-
504 323 K. Therefore, we can conclude that heteroatom doping is not always the best strategy for enhancing
505 CO₂ adsorption, which was corroborated mathematically by considering the pore size distribution and
506 the presence of N+O heteroatoms. Doping increased the isosteric heat of adsorption for fractional
507 coverage below 0.2, but the average isosteric heat of adsorption remained below 50 kJ mol⁻¹, consistent

508 with physical adsorption processes. Furthermore, this study underlines the importance of a crucial
509 parameter that should be systematically taken into account for practical applications: the tap density of
510 the adsorbent. This parameter has a significant influence on breakthrough performance in fixed-bed
511 columns, but is not systematically reported in studies focusing on the development of new adsorbents.

512

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