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1 **One-pot synthesis of digestate-derived biochar for carbon**
2 **dioxide capture**

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12 **Abstract**

13 Digestate from Anaerobic Digestion (AD) is a very common waste produced by
14 European biogas plants and its current method of reuse is as a fertilizer or as
15 soil amendment. This in turn however gives rise to some other environmental
16 concerns which include greenhouse gas emissions and volatilization of
17 ammonia causing ammonia pollution. Biochar is an environmentally friendly
18 and low-cost product for CO₂ capture and sequestration. Thus, we have
19 provided one simple method to convert AD digestate into biochar-based
20 sorbents of CO₂. In addition, the nitrogen-functionalised porous carbon has
21 been reported to be effective in improving the uptake of CO₂. However, most of
22 them were prepared using multiple steps. In this work, N-doped biochar was
23 prepared by a one-step method of modifying AD digestate by urea. The results
24 show that the addition of N can increase CO₂ uptake significantly. Thus, the
25 adsorbent modified by urea with a ratio of 1:1 results in the highest CO₂ uptake
26 capacity (1.22 mmol g⁻¹), indicating digestate's potential application for carbon
27 capture and storage.

28
29 *Key words:* AD digestate; Pyrolysis; Biochar; CO₂ capture

1. Introduction

The increase of CO₂ concentration in the atmosphere is responsible for climate change effects such as global warming and abnormal weather patterns. Therefore, various technologies including absorption, membrane separation, and cryogenic distillation, have been researched for capturing CO₂ [1-5]. Due to the strong stability, easy regeneration and good uptake, adsorption is considered as one of the most promising candidates for reducing CO₂ in the atmosphere [6-8]. Among the many adsorbent materials, porous carbons have been researched as a promising candidate for this purpose[9]. However, the expensive raw precursors, high pyrolysis temperatures (up to 950 °C) and/or chemical additions (e.g., ZnCl₂) in physical or chemical activation processes will result in significant economic and environmental burdens [10].

In addition, the introduction of nitrogen groups into porous materials could significantly improve the CO₂ capture capabilities because N-functionalities can strengthen and promote the interaction with CO₂ molecules. N-doped porous carbons are commonly prepared in two ways; post-synthesis with amine modification [11] or ammonia treatment [12], and carbonization of nitrogen-doped precursors [13, 14]. To reduce the cost and time requirements of multistep procedures such as extra activation steps, some one-step preparation methods of N-doped porous carbon have been adopted and reported [15-19].

For example, Mokaya et al.'s synthesized porous carbon by one-step activation of the KOH/biomass mixture is interesting with future potential for exploitation

[20]. However, apart from the pyrolysis activity, in most cases the preparation still includes an extra synthesis or activation step. Therefore, it is desirable and quicker to prepare the N-doped porous carbon materials directly and simply allowing for, good stability and low corrosivity of the amine reagents.

There is the possibility of the utilisation of another porous carbon framework material, biochar, which is much cheaper and more environmentally friendly than many other porous materials. It is also potentially an amended by-product from organic waste management so its reuse would contribute to a circular bioeconomy. Currently, biochar has been applied to a number of uses such as its addition to soil as an amendment [21-23], to remove contaminants in water [24, 25] and as a construction material [26, 27]. Biochar has also been researched as a CO₂ adsorbent because it can be produced from various waste biomass residues through one-step slow pyrolysis at relatively low temperature without sophisticated equipment [28-31]. Chen et al. adopted the ammonia treatment method under high temperature for biochar from cotton stalks for the uptake of CO₂ [32].

Anaerobic digestion (AD) of agricultural residues (animal manure, food waste, energy crops & other organic residues) has expanded in the EU for the production of electricity and heat as well as biomethane which is becoming a promising candidate for the current energy system via the natural gas grid in Europe [33, 34]. The residual product of AD is digestate, which is commercially used as a fertilizer and soil amendment due to its high organic matter and

74 nutrient content including nitrogen, phosphorous, potassium and carbon
75 compounds. However, digestate's relatively poor biological stability (N release)
76 and high moisture content give rise to environmental concerns including
77 greenhouse gas emissions, pollution via the volatilization of ammonia and
78 nutrient runoff which are starting to limit its current application.[35, 36]
79 Therefore, a more environmentally sound and effective way to manage and
80 utilise digestate is required.

81 Here, the AD digestate from a local AD plant is converted into biochar-based
82 CO₂ sorbent materials through pyrolysis at moderate to high temperature (400-
83 600 °C), which provides a new and potential application for this common waste
84 in European biogas plants. To further increase the capability of CO₂ capture,
85 urea is used to introduce N into the biochar because urea is cheap, and
86 environmentally friendly. Thus, it is described how the modification of urea can
87 produce N-doped biochar in order to enhance the capability of CO₂ capture.
88 This one-stage process illustrates a promising alternative use of solid AD
89 digestate as well as an easy way to produce N-doped biochar with urea
90 modification.

92 **2. Experimental Materials and methods**

93 **2.1. Materials**

94 The AD digestate solids were obtained from the Agri-Food and Biosciences
95 Institute (AFBI) from the anaerobic digestion of dairy cattle slurry and silage.

The digestate was dewatered using a FAN Press Screw Separator Urea was purchased from Sigma-Aldrich Company Ltd. (UK).

2.2 Sample Preparation.

The digestate solids were dried in an oven overnight at 90 °C. Dried digestate was ground into a fine powder in a ceramic mortar and sieved to less than 220µm size. The powder was then converted into biochar by slow pyrolysis in a horizontal quartz tubular reactor (20mm in out diameter and 250mm length) in the fix bed under the flow of nitrogen at a heating rate of 40 °C/min from room temperature to 400, 500, and 600°C, kept at that temperature for one hour and then allowed to cool. The samples are named as CAD 400, CAD 500 and CAD 600, respectively. The schematic diagram of the production of AD digestate-derived biochar is shown in Fig. 1.

Fig. 1. The schematic diagram for fabrication of AD digestate-derived biochar.

For the experiments requiring urea, it was physically mixed with the digestate with weight ratios of 1:1, 1:0.2, and 1:0.05 at 600°C. Thus, these biochars are named UCAD 1:1, UCAD 1:0.2, and UCAD 1:0.05, respectively.

2.3 Chemical Characterization

The resulting samples were characterized in terms of chemical composition and surface chemistry in order to detect and verify the existence of any surface functional groups. The ultimate analysis was carried out using a CHN Elemental Analyser (2400 Series II CHNS/O Analyser) in order to determine the chemical composition of the samples. Proximate analysis was carried out with the aid of Thermogravimetric analysis (TGA/DSC 1 STAR^e System) to determine the quantity of ash and volatile matter. The sample was heated in a nitrogen atmosphere to 110 °C at a heating rate of 25 °C min⁻¹ and held for 10 min corresponding to the determination of moisture in the sample. The sample was then heated to 925 °C in a nitrogen atmosphere, with weight loss recorded corresponding to the content of volatile matter. Finally, the fixed carbon content was determined by the introduction of air in order to combust the remaining fixed carbon in the sample, leaving only the ash in the alumina pan. Functional groups on the surface of the biochar samples were determined using Fourier-transform infrared spectroscopy (FTIR) equipped with ATR (The Agilent Cary 630 FTIR spectrometer) to obtain a spectrum in the range of 500-4000 cm⁻¹. The morphology and microstructure of materials were investigated using FE-

SEM (Quanta FEG 250). Textural properties were investigated using Bet Surface Area and Porosity Analyzer (JW-BK200B, China). All samples were vacuum degassed at 300 °C for 3 h to remove volatiles and subsequently used for characterization. Nitrogen adsorption isotherms were obtained at 77 K and a partial pressure range of (0.005–0.99) for estimation of BET surface area, pore volume, and pore size distribution using Non-Local Density Functional Theory (NLDFT). CO₂ adsorption and desorption isotherms were also investigated using Bet Surface Area and Porosity Analyzer (JW-BK200B) at 298 K, and the relative pressure was altered from 0.02 to 1.2 bar. Prior to the measurement, the samples were degassed at 300 °C for 3 h to remove the guest molecules from the pores. After cooling to room temperature, CO₂ was introduced into the system.

3. Results and discussion

3.1 Surface Properties

From the proximate analysis, the digestate contain 8.46% moisture, 72.36% of volatile, 9.98% fixed carbon and 9.10 % ash (the inorganic residue remaining after combustion of the sample). The elemental composition of the AD digestate is close to that reported in the literature, whereas both fixed carbon and ash contents were somewhat lower [37].

As shown in Table 1, all the samples are rich in carbon (>33%). The AD digestate was rich in carbon (33.55%) and nitrogen (1.82%), which are related

to the organic matter of original biomass feedstock (e.g., carboxyl, hydroxyl, and amine) [10, 38, 39]. With the increase of pyrolysis temperature, the carbon and nitrogen contents increase to 50.68 wt% and 2.30 wt% at 600 °C. These results imply that temperature influences the degree of nitrogen fixation onto the carbon surface. Such high temperature is reported to significantly change the degree of carbonization and to reduce the number of acidic groups (decarboxylate above about 200 °C) [40, 41].

Table 1. Chemical analysis of the samples (wt.%, dry ash free basis).

Sample	C	H	N	O*
AD	33.55	4.20	1.82	60.43
CAD 400	42.96	2.35	1.88	52.81
CAD 500	48.27	1.66	1.91	48.16
CAD 600	50.68	1.55	2.30	45.47
UCAD 1:1	53.59	1.51	8.99	35.91
UCAD 1:0.2	52.66	1.78	3.61	41.95
UCAD 1:0.05	53.15	1.10	2.44	43.31

* Oxygen content was obtained by 100% subtract the total percentage of C, H and N.

We further mixed the urea with the biomass before pyrolysis at the ratios of 1:1, 1:0.2 and 1:0.05. According to the results of the ultimate analysis in Table 1, the N content increases with the increase in the quantity of urea, therefore UCAD 1:1 contains the highest N content.

To study the nature of the functional groups present on the surface of the samples, FTIR analysis was carried out (Fig. 2). The peak at about 1685 cm⁻¹ and 1500 cm⁻¹ can be assigned to the N-H in-plane deformation vibration and C-N stretching vibration, respectively, while the peaks around 850 cm⁻¹ can be assigned to the out-of-plane N-H deformation vibration [42, 43]. The peaks

between 2000 and 2400 cm^{-1} may be related to the nitrogenous groups [10]. It should also be noted that the FTIR spectra of all other nitrogen-doped carbons are similar, confirming that these biochar materials have been modified with N-containing groups.

Fig. 2. Representative FT-IR spectra of the AD digestate without urea modification, CAD 600 and samples modified by different amount of urea, UCAD 1:1, UCAD 1:0.2 and UCAD 1:0.05 (1:1, 1:0.2 and 1:0.05 are the weight ratios of AD digestate and urea).

3.2. Morphology

SEM was employed to investigate the structure of AD digestate, CAD 600 and UCAD 1:1. Notably, the pores distribution in the raw materials, AD digestate, is irregular and the pores are larger than them after pyrolysis (Fig.3). Clearly, CAD 600 derived from AD pyrolysis at 600°C exhibits more pores, which maybe

because of the evaporation of H_2O , CO_2 , and CO during pyrolysis (Fig. 3, c and d). Some particles can also be seen in the figures of CAD 600, which may be the residuals after decomposing. However, from SEM results, it is difficult to observe the difference of pore size for different biochar materials.

Fig. 3. SEM images of AD digestate (a and b), CAD 600 (c and d) and UCAD 1:1 (e and f).

3.3. Porous Texture

To probe the nature and similarity of porosity influenced by the urea, we measured the nitrogen sorption isotherms at 77 K (Fig. 4). All the samples exhibit the IUPAC Type III isotherm. This means that most of the pores are larger than 50nm. The temperature influenced the quantity of N_2 adsorption very insignificantly (Fig.4 a), however CAD 600 is a little higher than CAD 400 and CAD 500, because these three samples have very similar BET surface

areas and average pore diameters. In Fig. 4 (b), we can see that the N_2 adsorption of UCAD 1:0.2 is the highest while UCAD 1:1 shows the least, which is also confirmed by the BET surface areas (Table 1). The urea molecule in UCAD 1:1 might occupy some pores so that the UCAD 1:1 exhibits the lowest surface area and worst N_2 adsorption.

Fig. 4. N_2 sorption isotherms of the samples prepared at different temperatures (a) and mixed with different quantity of urea (b).

Table 2. N content, porous texture properties and CO_2 uptake capability of porous carbons derived from CAD under different conditions.

Sample	N content (wt%)	S_{BET}^a (m ² /g)	V_t^b (cm ³ /g)	PD ^c (nm)	CO_2 uptake (mmol g ⁻¹) ^d
CAD 400	1.88	15.32	0.043	11.24	0.69
CAD 500	1.91	11.32	0.044	15.42	0.91

CAD 600	2.30	13.18	0.047	14.15	1.02
UCAD 1:1	8.99	6.89	0.038	17.91	1.22
UCAD 1:0.2	3.61	15.17	0.062	16.26	1.02
UCAD 1:0.05	2.44	13.13	0.043	13.04	0.93

^a Surface area was calculated using the BET method at $P/P_0 = 0.2$. ^b Total pore volume at $P/P_0 = 0.99$. ^c Average pore diameter. ^d Measured at 298K, 1 bar.

Fig. 5. CO₂ sorption isotherms of the samples prepared at different temperatures (a) and mixed with different urea (b), measured at 298 K.

3.4. CO₂ Uptake Properties

CO₂ sorption on prepared biochar was investigated at 298K (Fig. 5). It was found that CO₂ uptake capacity of biochar CAD 500 performed best under low pressure (<0.5 bar), and CAD 600 performed best after 0.5 bar. In the low pressure from 0 to 0.5 bar, CAD 500 captured more CO₂ than that of CAD 400 and 600, which suggests that CAD 500 could be a better CO₂ adsorbent for

vacuum swing adsorption applications than the others. After the 0.5 bar, CAD 600 became the best CO₂ sorbent biochar of the three and this is likely because it has the highest N content. In contrast, CAD 400 had the lowest uptake among the three biochar under the different temperature studied because its N content is the lowest.

In summary, it is known that the temperature of pyrolysis has an influence on the performance of the sorbent materials. Under higher temperature, the interactions between biomass and urea might be enhanced. Thus, the high temperature of pyrolysis leads to more N, which will improve the CO₂ capture because N-containing groups, as basic and polar functional groups, can strengthen the interaction with CO₂ molecules. Hao et al. also proved that porous carbon under different pyrolysis temperatures ranging from 400 to 800 °C leads to different quantities of N and in turn the CO₂ capture capacity would be directly affected (e.g. an optimum 500 °C pyrolysis temperature was obtained in relation to the capacity of CO₂ capture using the derived biochar) [44].

Previous studies have also revealed that the presence of nitrogenous groups can improve the CO₂ capture capacity in porous carbon. For example, Zhang et al. introduced amino/nitro groups onto the surface of activated carbon formed from petroleum coke to improve its adsorption capacity of CO₂ [45]. In this work, we mixed the biomass with different quantities of urea before pyrolysis with the purpose of promoting CO₂ capture capacity. For all six samples, the UCAD 1:1,

which was modified by urea (with mixed ratio of 1:1), provides the best uptake capability of CO₂ (1.22 mmol g⁻¹ shown in table 2).

In addition, with the increase of urea (mixed ratio of 1:0.05, 1:0.2 and 1:1), the CO₂ capture capacity is also improved. Even though the surface area of CAD 600 is nearly twice that of UCAD 1:1. The better CO₂ uptake capacity of UCAD 1:1 proves that the urea improves the CO₂ uptake capacity significantly. This again confirms that the existence of N can strengthen the interaction with CO₂ molecules. In addition, the N contents of UCAD 1:0.05 and UCAD 1:0.2 are more than CAD 600 (3.61 wt% for CAD 1:0.05, 2.44 wt% for UCAD and 2.30 wt% for CAD 600), but neither show a better capability of CO₂ uptake than CAD 600 (1.02 mmol g⁻¹ for both CAD 600 and UCAD 1:0.2, 0.93 mmol g⁻¹ for UCAD 0.05). This may be due to the occupation of pores by urea, and the small quantities of N contributing little to the interaction with CO₂ molecules.

When the UCAD is compared with other sorbents functionalized with N, some improvements in CO₂ capture capacity are revealed (table 3). Dawson et. al reported amine-functionalized conjugated microporous polymer (CMP) networks which showed 0.98 mmol g⁻¹ uptake of CO₂ [46]. Jing et al. [47] and Yuan et al. [48] introduced amino group into porous aromatic frameworks to obtain the PAF-32-NH₂ with the 1.04 mmol g⁻¹ uptake of CO₂ [47] and PAF-33-NH₂ with the 0.75 mmol g⁻¹ uptake of CO₂ [48]. Huang et al. introduced highly crosslinked polymers (HCPs) with NH₂ for uptake of CO₂, among which HCP-A shows 0.96 mmol g⁻¹ at 298K [49]. Generally, both physical and chemical

sorption of CO₂ can occur in the biochar. Physical sorption was mainly related to the surface area and the pore volume, while the chemical sorption was closely associated with the chemical groups [50]. In this case, the chemical factors are more pertinent to CO₂ sorption because the biochar samples have very low surface areas and pore volumes.

Table 3. Summary of CO₂ uptake at 298 K, 1 bar in nitrogen-doped amine functionalized porous materials (mmol g⁻¹).

Sample	CO ₂ uptake/T=298K	Reference
Biochar	1.22	This work
CMP-1-NH ₂	0.98	[46]
PAF-32-NH ₂	1.04	[47]
PAF-33-NH ₂	0.75	[48]
HCP-A	0.96	[49]

4. Conclusion

AD digestate derived biochar is used to be the candidate for sorbents of CO₂. The temperature of pyrolysis contributes to the content of N, thus it has a big influence on the capture capabilities of CO₂. Furthermore, one-step method of preparing N-doped biochar from the modification of urea is investigated. As expected, the N content can increase the CO₂ uptake ability to some extent. Although all the samples show a relatively low BET surface area and pore volumes, the material still captures a moderate quantity of CO₂ better than some reported samples with N functionalities. The highest uptake capacity (1.22 mmol g⁻¹) was reached when the sorbent was obtained from the ratio of 1:1 of AD digestate and urea. This simple but cost-effective method to prepare

CO₂ sorbents from a very common waste as well as the introduction of N into the biochar to obtain N-doped biochar is potential for further research and application.

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References

- [1] D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: prospects for new materials. *Angew Chem Int Ed Engl* 2010;49(35):6058-82.
- [2] Lackner KS, Brennan S, Matter JM, Park A-HA, Wright A, Van Der Zwaan B. The urgency of the development of CO₂ capture from ambient air. *Proceedings of the National Academy of Sciences* 2012;109(33):13156-62.
- [3] Liang Z, Fu K, Idem R, Tontiwachwuthikul P. Review on current advances, future challenges and consideration issues for post-combustion CO₂ capture using amine-based absorbents. *Chinese Journal of Chemical Engineering* 2016;24(2):278-88.
- [4] Meisen A, Shuai X. Research and development issues in CO₂ capture. *Energy Conversion and Management* 1997;38:S37-S42.
- [5] Samanta A, Zhao A, Shimizu GK, Sarkar P, Gupta R. Post-combustion CO₂ capture using solid sorbents: a review. *Industrial & Engineering Chemistry Research* 2011;51(4):1438-63.
- [6] Gargiulo N, Pepe F, Caputo D. CO₂ adsorption by functionalized nanoporous materials: a review. *Journal of nanoscience and nanotechnology* 2014;14(2):1811-22.
- [7] Yu C-H, Huang C-H, Tan C-S. A review of CO₂ capture by absorption and adsorption. *Aerosol Air Qual Res* 2012;12(5):745-69.

- 324 [8] Younas M, Sohail M, Leong L, Bashir MJ, Sumathi S. Feasibility of CO
325 2 adsorption by solid adsorbents: a review on low-temperature systems.
326 International journal of environmental science and technology
327 2016;13(7):1839-60.
- 328 [9] Olivares-Marín M, Maroto-Valer MM. Development of adsorbents for
329 CO₂ capture from waste materials: a review. Greenhouse Gases:
330 Science and Technology 2012;2(1):20-35.
- 331 [10] Creamer AE, Gao B, Zhang M. Carbon dioxide capture using biochar
332 produced from sugarcane bagasse and hickory wood. Chemical
333 Engineering Journal 2014;249:174-9.
- 334 [11] Zhao L, Bacsik Z, Hedin N, Wei W, Sun Y, Antonietti M, et al. Carbon
335 dioxide capture on Amine-Rich carbonaceous materials derived from
336 glucose. ChemSusChem 2010;3(7):840-5.
- 337 [12] Wang X, Lee JS, Zhu Q, Liu J, Wang Y, Dai S. Ammonia-treated ordered
338 mesoporous carbons as catalytic materials for oxygen reduction reaction.
339 Chemistry of Materials 2010;22(7):2178-80.
- 340 [13] Kou J, Sun L-B. Fabrication of nitrogen-doped porous carbons for highly
341 efficient CO₂ capture: rational choice of a polymer precursor. Journal of
342 Materials Chemistry A 2016;4(44):17299-307.
- 343 [14] Geng JC, Xue DM, Liu XQ, Shi YQ, Sun LB. N-doped porous carbons
344 for CO₂ capture: Rational choice of N-containing polymer with high
345 phenyl density as precursor. AIChE Journal 2017;63(5):1648-58.
- 346 [15] Yu J, Guo M, Muhammad F, Wang A, Zhang F, Li Q, et al. One-pot
347 synthesis of highly ordered nitrogen-containing mesoporous carbon with
348 resorcinol–urea–formaldehyde resin for CO₂ capture. Carbon
349 2014;69:502-14.
- 350 [16] Liu F, Huang K, Ding S, Dai S. One-step synthesis of nitrogen-doped
351 graphene-like meso-macroporous carbons as highly efficient and
352 selective adsorbents for CO₂ capture. Journal of Materials Chemistry A
353 2016;4(38):14567-71.
- 354 [17] Yang Z, Zhang G, Xu Y, Zhao P. One step N-doping and activation of
355 biomass carbon at low temperature through NaNH₂: An effective
356 approach to CO₂ adsorbents. Journal of CO₂ Utilization 2019;33:320-9.
- 357 [18] Rao L, Liu S, Wang L, Ma C, Wu J, An L, et al. N-doped porous carbons
358 from low-temperature and single-step sodium amide activation of
359 carbonized water chestnut shell with excellent CO₂ capture performance.
360 Chemical Engineering Journal 2019;359:428-35.
- 361 [19] Rao L, Liu S, Chen J, Wang L, An L, Yang P, et al. Single-Step Synthesis
362 of Nitrogen-Doped Porous Carbons for CO₂ Capture by Low-
363 Temperature Sodium Amide Activation of Petroleum Coke. Energy &
364 fuels 2018;32(12):12787-94.
- 365 [20] Balahmar N, Al-Jumaily AS, Mokaya R. Biomass to porous carbon in one
366 step: directly activated biomass for high performance CO₂ storage.
367 Journal of Materials Chemistry A 2017;5(24):12330-9.

- [21] Chan KY, Van Zwieten L, Meszaros I, Downie A, Joseph S. Agronomic values of greenwaste biochar as a soil amendment. *Soil Research* 2008;45(8):629-34.
- [22] Chan K, Van Zwieten L, Meszaros I, Downie A, Joseph S. Using poultry litter biochars as soil amendments. *Soil Research* 2008;46(5):437-44.
- [23] Singh B, Singh BP, Cowie AL. Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Research* 2010;48(7):516-25.
- [24] Inyang M, Dickenson E. The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: a review. *Chemosphere* 2015;134:232-40.
- [25] Mohan D, Sarswat A, Ok YS, Pittman Jr CU. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent—a critical review. *Bioresource technology* 2014;160:191-202.
- [26] Gupta S, Kua HW. Factors determining the potential of biochar as a carbon capturing and sequestering construction material: critical review. *Journal of Materials in Civil Engineering* 2017;29(9):04017086.
- [27] Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, et al. Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere* 2014;99:19-33.
- [28] Plaza M, González A, Pis J, Rubiera F, Pevida C. Production of microporous biochars by single-step oxidation: Effect of activation conditions on CO₂ capture. *Applied energy* 2014;114:551-62.
- [29] Huang Y-F, Chiueh P-T, Shih C-H, Lo S-L, Sun L, Zhong Y, et al. Microwave pyrolysis of rice straw to produce biochar as an adsorbent for CO₂ capture. *Energy* 2015;84:75-82.
- [30] Li Y, Ruan G, Jalilov AS, Tarkunde YR, Fei H, Tour JM. Biochar as a renewable source for high-performance CO₂ sorbent. *Carbon* 2016;107:344-51.
- [31] Mohd A, Ab Karim Ghani WW, Resitanim NZ, Sanyang L. A review: carbon dioxide capture: biomass-derived-biochar and its applications. *Journal of dispersion science and technology* 2013;34(7):974-84.
- [32] Zhang X, Zhang S, Yang H, Feng Y, Chen Y, Wang X, et al. Nitrogen enriched biochar modified by high temperature CO₂-ammonia treatment: Characterization and adsorption of CO₂. *Chemical Engineering Journal* 2014;257:20-7.
- [33] Garlapalli RK, Wirth B, Reza MT. Pyrolysis of hydrochar from digestate: Effect of hydrothermal carbonization and pyrolysis temperatures on pyrochar formation. *Bioresource technology* 2016;220:168-74.
- [34] Holm-Nielsen JB, Al Seadi T, Oleskowicz-Popiel P. The future of anaerobic digestion and biogas utilization. *Bioresource technology* 2009;100(22):5478-84.
- [35] Bustamante M, Albuquerque J, Restrepo A, De la Fuente C, Paredes C,

- 412 Moral R, et al. Co-composting of the solid fraction of anaerobic
413 digestates, to obtain added-value materials for use in agriculture.
414 Biomass and bioenergy 2012;43:26-35.
- 415 [36] Nkoa R. Agricultural benefits and environmental risks of soil fertilization
416 with anaerobic digestates: a review. Agronomy for Sustainable
417 Development 2014;34(2):473-92.
- 418 [37] Shen Y, Linville JL, Ignacio-de Leon PAA, Schoene RP, Urgun-Demirtas
419 M. Towards a sustainable paradigm of waste-to-energy process:
420 Enhanced anaerobic digestion of sludge with woody biochar. Journal of
421 Cleaner Production 2016;135:1054-64.
- 422 [38] Uchimiya M, Chang S, Klasson KT. Screening biochars for heavy metal
423 retention in soil: role of oxygen functional groups. Journal of Hazardous
424 Materials 2011;190(1-3):432-41.
- 425 [39] Inyang M, Gao B, Ding W, Pullammanappallil P, Zimmerman AR, Cao X.
426 Enhanced lead sorption by biochar derived from anaerobically digested
427 sugarcane bagasse. Separation Science and Technology
428 2011;46(12):1950-6.
- 429 [40] Adib F, Bagreev A, Bandosz TJ. Adsorption/oxidation of hydrogen sulfide
430 on nitrogen-containing activated carbons. Langmuir 2000;16(4):1980-6.
- 431 [41] Papirer E, Dentzer J, Li S, Donnet J. Surface groups on nitric acid
432 oxidized carbon black samples determined by chemical and
433 thermodesorption analyses. Carbon 1991;29(1):69-72.
- 434 [42] Babaie M, Davari P, PouyanTalebizadeh, Zare F, Rahimzadeh H,
435 Ristovski Z, et al. Performance evaluation of non-thermal plasma on
436 particulate matter, ozone, and CO₂ coleration for diesel exhaust emission
437 reduction. Chem Eng Journal 2015;276 240-8.
- 438 [43] Wang S, Li W-C, Zhang L, Jin Z-Y, Lu A-H. Polybenzoxazine-based
439 monodisperse carbon spheres with low-thermal shrinkage and their CO₂
440 adsorption properties. Journal of Materials Chemistry A
441 2014;2(12):4406-12.
- 442 [44] Hao GP, Li WC, Qian D, Lu AH. Rapid synthesis of nitrogen-doped
443 porous carbon monolith for CO₂ capture. Advanced materials
444 2010;22(7):853-7.
- 445 [45] Zhang C, Song W, Sun G, Xie L, Wang J, Li K, et al. CO₂ capture with
446 activated carbon grafted by nitrogenous functional groups. Energy &
447 fuels 2013;27(8):4818-23.
- 448 [46] Dawson R, Adams DJ, Cooper Al. Chemical tuning of CO₂ sorption in
449 robust nanoporous organic polymers. Chemical Science
450 2011;2(6):1173-7.
- 451 [47] Jing X, Zou D, Cui P, Ren H, Zhu G. Facile synthesis of cost-effective
452 porous aromatic materials with enhanced carbon dioxide uptake. Journal
453 of Materials Chemistry A 2013;1(44):13926-31.
- 454 [48] Yuan R, Ren H, Yan Z, Wang A, Zhu G. Robust tri (4-ethynylphenyl)
455 amine-based porous aromatic frameworks for carbon dioxide capture.

- 456 Polymer Chemistry 2014;5(7):2266-72.
- 457 [49] Huang J, Zhu J, Snyder SA, Morris AJ, Turner SR. Nanoporous highly
458 crosslinked polymer networks with covalently bonded amines for CO₂
459 capture. Polymer 2018;154:55-61.
- 460 [50] Xu X, Kan Y, Zhao L, Cao X. Chemical transformation of CO₂ during its
461 capture by waste biomass derived biochars. Environmental Pollution
462 2016;213:533-40.

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