

Upgrading of Biogas to Biomethane by using Biochars as CO₂ Sorbent in a Pressure Swing Adsorption Device

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This work investigates the use of biochar-based materials for the selective simultaneous capture of CO₂ and CH₄ by Pressure Swing Adsorption (PSA) in simulated feeds of biogas to biomethane. Two biochar batches were produced by pyro-gasification at Equivalence Ratios (ER) of 0.15 and 0.30, in a bench scale rotary kiln fed with vineyard pruning pellets. Samples of these two batches underwent activations treatments with KOH and HCl. Biochar-based materials were tested in a laboratory-scale packed-bed rig, performing PSA of a CO₂ (46.50 vol%) / CH₄ (53.50 vol%) synthetic mixture, 5-9 bar_a at ambient temperature. The highest CO₂ and CH₄ sorption capacities were obtained at all pressures by the material treated with both KOH and HCl, which had by far the highest surface area. The biochar produced with ER=0.30 showed higher the selectivity towards CO₂. Results are promising to develop selective sustainable materials for the PSA upgrading of biogas.

1. Introduction

Biochar is the solid product of the following biomass thermochemical treatments: torrefaction, slow pyrolysis, fast pyrolysis, gasification, and HydroThermal Carbonization (HTC). Each process produces biochar with different yields, carbon contents, and structural characteristics. Among these processes, slow pyrolysis is the most commonly used (G. Wang et al., 2020). Slow pyrolysis consists of feedstock heated up to 400-500 °C, with low heating rate, at atmospheric pressure, in a time range from minutes to days. During pyrolysis water evaporates, and volatile compounds are released. This causes an increase in the relative fixed carbon content of the solid biochar. Probably, polymerization of organic compounds in vapors and gases may generate secondary char formation and increase the solid yield (Yaashikaa et al., 2020). Byproducts of slow pyrolysis are pyrolysis oil (water, oxygenated and not organic compounds) and gas (H₂, CO, CO₂, CH₄ and C₂-C₃) (Park et al., 2012).

In last years, biochar is attracting the interest of scientific community as substitute of fossil carbon carriers in several applications to reduce greenhouse gas emissions and fight climate changes. (Weber & Quicker, 2018). In metallurgy field, biochar has attracted much attention as a potential substitute of conventional fossil fuels (coal or coke), due to its combustibility and reducing ability. It shows the potential to mitigate CO₂ emissions as its carbon content derives from photosynthesis (Barisano et al., 2021; Giuliano et al., 2020).

Gas cleaning with biochar occurs by adsorption process. Biochar is a low-cost sustainable sorbent with excellent adsorption properties that can be enhanced by further activation, modulation of surface characteristics (surface area, pore volume, and pore size distribution) (Zhang et al., 2019) and/or surface functionalization (Q. Wang et al., 2011). Biochar surface properties depends on the production conditions and feedstock, which determine the capacity to adsorb various contaminants from fluids (Rajapaksha et al., 2014). In the metal impregnation, alkaline earth metals (e.g., Ca and Mg) and transition metals (e.g., Fe and Cu) were mainly used in the previous studies (El-Molla et al., 2007; Zubbri et al., 2020). The impregnated metals acted as adsorption sites for H₂S, SO₂, Hg, and CO₂.

(Gallucci et al., 2020) investigated the application of hydrochar materials – obtained by HTC of silver fir sawdust – for CO₂ capture and the upgrading of biogas (mixture of CH₄ and CO₂, with minor traces of other components) to bio-methane, by Pressure Swing Adsorption. As an adsorbent material, biochar is interesting for that purpose too (Gallucci et al., 2020).

The PERCIVAL Project (Processi di EstRazione di bioprodotto da sCarti agroIndustriali e VALorizzazione in cascata, funded by PNR 2015-2020 Italian program), among its many objectives, aims to optimize the processes for the valorization of wastes/by-products of agro-industrial chains into biomaterials and bioenergy, falling into the production cycle according to a circular economy model. In this framework, biomethane represents a renewable energy carrier able to close the resource flow loops sustainably.

In this work, new biochar-based materials were purposely synthesized, characterized and experimentally tested for the first time for PSA of a synthetic mixture containing CH₄ and CO₂ in the same proportion of a biogas from an actual anaerobic digester, at pressures between 5 and 9 bar_a. Those test conditions were tailored to build a preliminary study for future PSA application coupled with anaerobic digester. The biochar synthesis method along with the operative pressures both influenced sorption capacities and CH₄/CO₂ sorption selectivities. One of the tested materials emerged as a possible candidate for future applications in biogas upgrading.

2. Materials and methods

2.1 Biochar-based materials

Biochar was produced by a pyro-gasification process carried out in a bench scale rotary kiln fed with vineyard pruning pellets. In 2022, the Italian dry vineyard pruning theoretical potential availability was of 1662 ktons. A schematic diagram and details of the experimental rig used for the biochar production tests is showed by (Freda et al., 2018). The pyro-gasification of vineyard pruning pellets was carried out at 650 °C, at two equivalence ratios (0.15 and 0.30, named BC0.15 and BC0.30, respectively). Equivalence ratio is the ratio between the actual feed oxygen and the ones for stoichiometric complete combustion.

These biochar were treated for activation as described by (Gallucci et al., 2020): firstly, 1:2 mass ratio mixture of hydrochar and KOH was thermally treated under nitrogen gas flow and warmed (heating rate 3 °C/min from ambient temperature up to 600 °C, 1 h dwell at 600 °C); afterwards, the resulting solid was washed with 10 wt% HCl to remove any inorganic salts, then with distilled water until neutral pH, and finally dried at 105 °C for 24 h. BC0.15 and BC0.30 were both treated with KOH, obtaining solid samples named BC0.15KOH and BC0.30KOH. The acid treatment was performed only onto BC0.30KOH, obtaining the washed solid named BC0.30A.

2.2 Materials characterizations

The two starting biochars BC0.15 and BC0.30 were analyzed as concern, proximate and ultimate analysis, heating value. The biochars were prepared according to UNI EN 14778. Proximate analysis was carried out by a Perkin Elmer Thermogravimetric Analyzer TGA 7. Moisture, volatile matter, fixed carbon and ash content were determined, by weight loss measured with the following thermal scan: under nitrogen flux heating at 10 °C/min up to 105 °C isothermal at 105 °C for 20 min, heating up to 900 °C at 100 °C/min, isothermal at 900 °C for 7 min, cooling to 550 °C at 50 °C/min; under air flux isothermal at 550 °C for 40 min. The ultimate analysis of biochars was carried out by CHN Perkin Elmer Series II 2400, in order to quantify carbon, hydrogen, nitrogen according to ISO 16948. Oxygen was calculated by difference. The heating value was measured by an IKA Werke Bomb Calorimeter according to the UNI EN 14918.

All solid samples were sieved to obtain solid particles in the dimensional range 106-355 µm and characterized by:

- N₂ adsorption/desorption, to quantify surface specific area by Brunauer-Emmett-Teller (BET) method (pore size analyzer NOVA 1200e Alfates Quartachrome). Before each N₂ treatment, each sample was outgassed for 3 h at 100°C.
- by laser diffraction (Malvern Mastersizer 2000 analyzer) for particle size distribution and median particle diameter d(0.5).

2.3 Pressure Swing Adsorption (PSA) tests

PSA tests were carried out at ambient temperature and 5, 7 or 9 bar_a, on a bench-scale apparatus (Figure 1) constituted by BONKHORST inlet mass flow controllers, a packed-bed reactor and SIEMENS ULTRAMAT 23 analysers to measure outlet instantaneous CO₂ and CH₄ concentration. The reactor is fed with 184 Nml/min of a CO₂ (46.50 vol%) / CH₄ (53.50 vol%) synthetic mixture, representative of a biogas from an actual anaerobic digester. The sorbent (about 0.5-1 g, particles between 106-355 µm) is packed between two layers of inert glass beads (106-355 µm) in the reactor (ID ~1 cm). The complete test consists of two main steps: (i) adsorption under pressure, until evident complete breakthrough of the packed-bed; (ii) regeneration by pressure swing down to

atmospheric pressure and counter-current washing with N₂. CO₂ and CH₄ concentrations as functions of time during adsorption were recorded, and related molar flowrates as functions of time were calculated by an internal standard of N₂ fed to the analysers. Integrations were performed with respect to time to compile CO₂ and CH₄ mole balances. For each tested sorbent material, five PSA cycles were repeated.

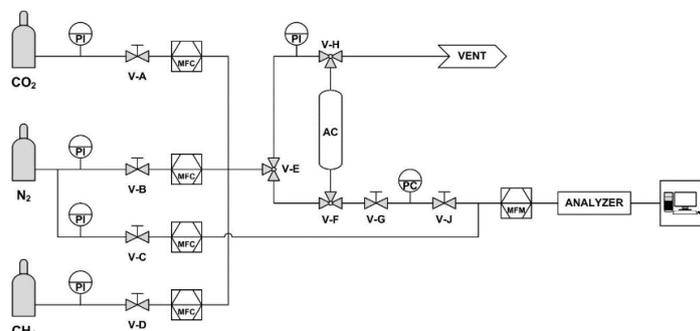


Figure 1: Flowsheet of the experimental lab-scale PSA test rig (Gallucci et al., 2020)

Sorbent materials were tested at the chosen pressures. A blank test was performed for each investigated pressure, with inert solid material (glass beads of 106-355 μm) substituting the sorbent samples.

A first order with dead time model for gas mixing is applied to evaluate the CO₂ and CH₄ response curves of all tests: the data from the blank tests represent the CO₂ and CH₄ holdups of the system without any capture, at a given pressure, only because of its volume; the difference between the blank test and results with a sorbent material at the same pressure quantifies the actually captured CO₂ and CH₄ (Di Felice et al., 2011).

3. Results

The chemical physical analyses of the two biochars BC0.15 and BC0.30 are reported in Table 1 on dry basis. The differences highlighted by the proximate analysis of the biochars can be justified by the different experimental condition adopted for their production. More in detail, different equivalence ratios were adopted in the two tests. As expected, the biochar produced at higher equivalence ratio was richer in ash because of the major advancement of gasification and combustion reactions. The lower ash content of BC0.15 together with its higher fixed carbon determines its major heating value compared to BC0.30.

Table 1: Chemical-physical analysis of biochars

Proximate analysis	BC0.15	BC0.30
Volatiles, wt %	9.75	15.38
Fixed carbon, wt %	80.66	48.32
Ash, wt%	9.59	36.30
Ultimate analysis	BC015	BC0.30
C, wt%	82	59
H, wt%	1.6	2.0
N, wt%	0.8	0.9
O, wt%	6	1.8
HHV (MJ/kg)	30.63	19.67

Table 2: Specific surface areas by BET method

Material	BC0.15	BC0.30	BC0.15KOH	BC0.30KOH	BC0.30A
S _{BET} [m ² g ⁻¹]	1.336	0.007	0.158	0.365	756.413

Figure 2(a) shows the particle size distribution of the five samples, Figure 2(b) the related median particle diameters. No substantial differences in these quantifications emerged among samples. A minor fraction of fines (even after the preparatory manual sieving between 106-355 μm) was detected in Figure 2(a), indicating an

intrinsic fragility. Figure 2(a) also confirms the correctness of the choice of the glass beads as an inert material to substitute sorbents in blank tests, having similar diameters ranges.

Table 2 shows the specific surface areas (S_{BET}) of materials: BC0.15 and BC0.30 have negligible S_{BET} , as the corresponding version treated with KOH; an important surface area was developed (BC0.30A) because of the HCl treatment, in agreement with Gallucci et al. (Gallucci et al., 2020).

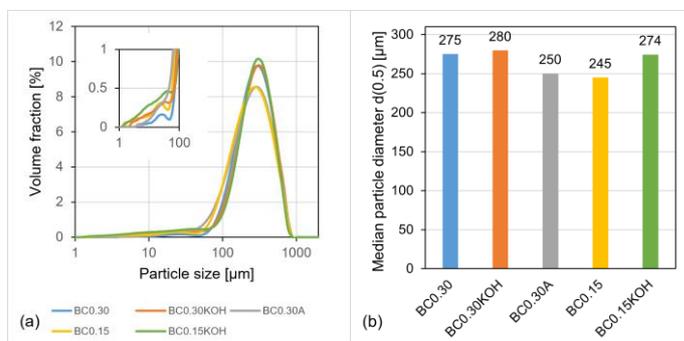


Figure 2: Particle size distributions (a) and median particle diameters (b)

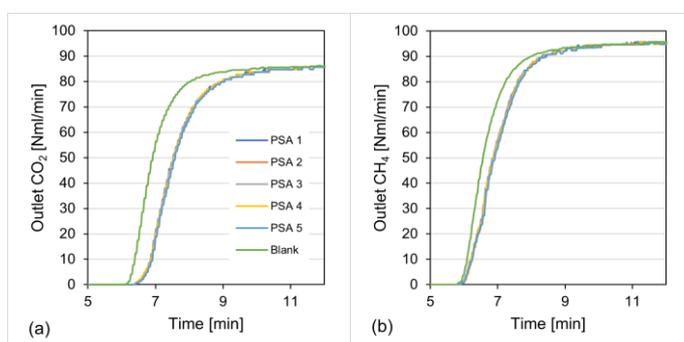


Figure 3: Example of CO₂ (a) and CH₄ (b) response curves BC0.30 at 5 bar_a (legend in (a) is also valid for (b))

Figure 3 shows an example of response curves of CH₄ (Figure 3 (a)) and CO₂ (Figure 3 (b)) in the rig, as functions of time. As exemplified in Figure 3, in all cases the complete breakthrough was realized, and PSA was always completely repeatable. According to the method described in Section 2.3, the difference between integrals of blank and PSA curves (e.g., Figure 3) is proportional to the sorption capacity of tested materials.

Figure 4 and Table 4 show the sorption capacities of CO₂ (Figure 4(a)) and CH₄ (Figure 4(b)), measured for the tested materials as functions of pressure: values are in line (even higher) with those of literature (Bahrun et al., 2022). The first two tests were carried out on BC0.15 and BC0.30: BC0.30 behaved better than BC0.15 (Figure 4, Table 4), as these two materials showed very close sorption capacities of CO₂ (Figure 4(a)), while that of CH₄ was appreciably smaller for BC0.30 (Figure 4(b)). As results, further tests were done on materials from BC0.30. Specific surface areas (Table 2) influenced sorption capacities (Figure 4 and Table 4): BC0.30A is the material with by far the highest surface area and expressed the highest sorption capacities of both CO₂ and CH₄ at all pressure. The different performances between BC0.30KOH and BC0.30 (Figure 4 and Table 4) cannot be related to specific surface areas, which are equally low for both materials (Table 2). A possible explanation follows: BC0.30KOH contained a lower mass of carbon than BC0.30 because of residues of KOH; considering the affinity of CO₂ for basic sites in chemisorption, this result suggests that the observed phenomena are due to physisorption (plausible at the low investigated temperature). The sorption capacities generally increase along with pressure (Figure 4 and Table 4): as to CO₂, this effect is always significant, except for BC0.15 and BC0.30 between 7 and 9 bar; as to CH₄, this effect was evident for BC0.30A.

Table 4 presents the ratios of sorption capacities, an index of selectivity of CO₂ vs. CH₄: BC0.30 and BC0.30A show the highest sorption capacity ratios. BC0.30A has lower sorption capacity ratios than BC0.30 at the same pressure (Table 4), but quite higher absolute sorption capacities; this indicates that the activation treatment leads to an increase in the sorption capacity of the biochar (Table 4 and Figure 4), at the expenses of CO₂ capture selectivity (Table 4). For all tested materials (except BC0.30KOH), a decrease in the sorption capacity

ratios occurred as the pressure increased; this effect was also observed by (Rocha et al., 2017) for biogas upgrading with a Carbon Molecular Sieve (CMS) and put in relation with CO_2 and CH_4 pores diffusion. Overall, BC0.30A at 5 bar_a had the most convenient performance for biogas upgrading to biomethane by PSA (Table 4 and Figure 4): 5 bar_a is a convenient choice, since anaerobic digestion occurs at near-ambient pressures; at 5 bar_a, BC0.30A had one of the highest selectivity indexes (Table 4), with sorption capacities more than twofold the second best material (BC0.30, Table 4 and Figure 4). PSA tests with BC0.30A at 5 bar_a showed that a consistent time window existed, during which combustible gas with > 95 vol% of CH_4 can be produced (Figure 5); this is interesting, considering the purity threshold of 95 vol% of CH_4 are representative for the use in the Italian natural gas distribution network.

Table 4: Sorption capacities of CO_2 and CH_4 and their ratios ($\text{CO}_2 / \text{CH}_4$)

	Pressure [bar _a]	BC0.15	BC0.30	BC0.30KOH	BC0.30A
CO_2 [mmol/g]	5	2.07 ± 0.07	2.46 ± 0.10	0.16 ± 0.11	5.25 ± 0.57
	7	2.96 ± 0.01	3.07 ± 0.06	0.48 ± 0.01	6.46 ± 0.05
	9	3.18 ± 0.26	3.14 ± 0.16	0.77 ± 0.11	6.88 ± 0.23
CH_4 [mmol/g]	5	1.06 ± 0.12	0.83 ± 0.13	0.30 ± 0.13	2.15 ± 0.41
	7	1.84 ± 0.06	1.23 ± 0.12	0.69 ± 0.12	3.38 ± 0.27
	9	2.51 ± 0.69	1.51 ± 0.22	0.72 ± 0.22	4.04 ± 0.23
CO_2/CH_4 [mol CO_2 /mol CH_4]	5	1.95	2.95	0.54	2.44
	7	1.60	2.49	0.70	1.91
	9	1.27	2.08	1.08	1.27

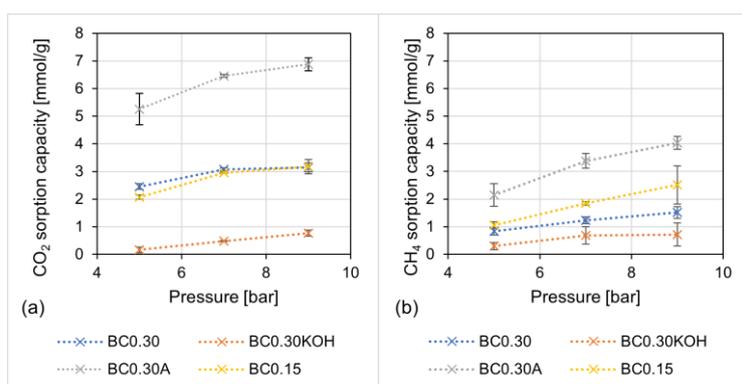


Figure 4: CO_2 (a) and CH_4 (b) sorption capacities as functions of pressure; error bars = 95% confidence intervals

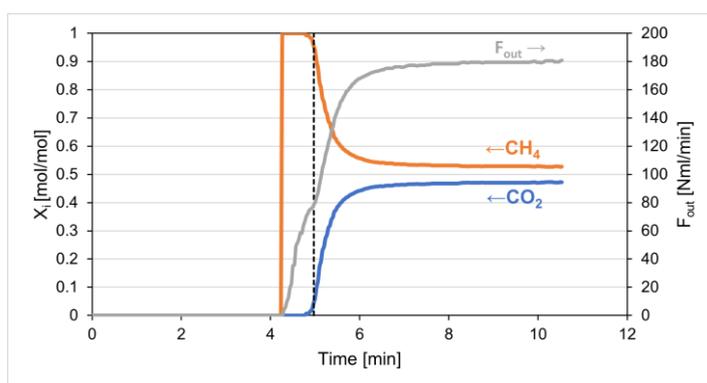


Figure 5: Outlet overall flow rate (F_{out}) and molar fractions of CO_2 and CH_4 (X_i , $i = \text{CO}_2, \text{CH}_4$) as functions of time, (5 bar_a, BC0.30A). Black dashed line represents the threshold of 95 mol% of CH_4

4. Conclusions

The biochar obtained by a pyro-gasification of vineyard pruning pellets was tested as received and after activation with KOH and HCl, in a PSA process to simulate the upgrading of biogas to biomethane at 5, 7, 9 bar_a. Results show that the material activated by KOH and HCl treatment (BC0.30A) had the highest surface area by-far compared to the virgin biochars; this led BC0.30A to have the highest sorption capacities of CO₂ and CH₄ at all tested pressures, with values comparable or even higher to analogue materials in the literature. As the pressure was increased: (i) sorption capacities generally increased; (ii) there was a reduction in the overall CO₂ selectivity (except for BC0.30KOH). BC0.30A was the material with the highest sorption capacities of CO₂ and CH₄ and a favourable selectivity at the lowest exerted pressure (5 bar_a), so emerging as a good candidate for future developments and scale-up studies about the upgrading of biogas to biomethane. Future work may include an extension of investigated materials and related characterizations, as well as modelling studies on the PSA responses.

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References

- Bahrn, M. H. V., Bono, A., Othman, N., & Zaini, M. A. A. (2022). Carbon dioxide removal from biogas through pressure swing adsorption – A review. In *Chemical Engineering Research and Design* (Vol. 183, pp. 285–306). Institution of Chemical Engineers.
- Barisano, D., Canneto, G., Nanna, F., Villone, A., Fanelli, E., Freda, C., Grieco, M., Cornacchia, G., Braccio, G., Marcantonio, V., Bocci, E., Foscolo, P. U., & Heidenreich, S. (2021). Investigation of an Intensified Thermo-Chemical Experimental Set-Up for Hydrogen Production from Biomass: Gasification Process Performance—Part I. *Processes*, 9(7), 1104.
- Di Felice, L., Foscolo, P. U., & Gibilaro, L. (2011). CO₂ Capture by Calcined Dolomite in a Fluidized Bed: Experimental Data and Numerical Simulations. *International Journal of Chemical Reactor Engineering*, 9(1).
- El-Molla, S. A., El-Shobaky, G. A., & Sayed Ahmed, S. A. (2007). Catalytic Promotion of Activated carbon by Treatment with Some Transition Metal Cations. *Chinese Journal of Catalysis*, 28(7), 611–616.
- Freda, C., Cornacchia, G., Romanelli, A., Valerio, V., & Grieco, M. (2018). Sewage sludge gasification in a bench scale rotary kiln. *Fuel*, 212, 88–94.
- Gallucci, K., Taglieri, L., Papa, A. A., Di Lauro, F., Ahmad, Z., & Gallifuoco, A. (2020). Non-energy valorization of residual biomasses via HTC: CO₂ capture onto activated hydrochars. *Applied Sciences* (Switzerland), 10(5).
- Giuliano, A., Freda, C., & Catizzone, E. (2020). Techno-Economic Assessment of Bio-Syngas Production for Methanol Synthesis: A Focus on the Water–Gas Shift and Carbon Capture Sections. *Bioengineering*, 7(3), 70.
- Park, S.-W., Jang, C.-H., Baek, K.-R., & Yang, J.-K. (2012). Torrefaction and low-temperature carbonization of woody biomass: Evaluation of fuel characteristics of the products. *Energy*, 45(1), 676–685.
- Rajapaksha, A. U., Vithanage, M., Zhang, M., Ahmad, M., Mohan, D., Chang, S. X., & Ok, Y. S. (2014). Pyrolysis condition affected sulfamethazine sorption by tea waste biochars. *Bioresource Technology*, 166, 303–308.
- Rocha, L. A. M., Andreassen, K. A., & Grande, C. A. (2017). Separation of CO₂/CH₄ using carbon molecular sieve (CMS) at low and high pressure. *Chemical Engineering Science*, 164, 148–157.
- Wang, G., Dai, Y., Yang, H., Xiong, Q., Wang, K., Zhou, J., Li, Y., & Wang, S. (2020). A Review of Recent Advances in Biomass Pyrolysis. *Energy & Fuels*, 34(12), 15557–15578.
- Wang, Q., Luo, J., Zhong, Z., & Borgna, A. (2011). CO₂ capture by solid adsorbents and their applications: current status and new trends. *Energy Environ. Sci.*, 4(1), 42–55.
- Weber, K., & Quicker, P. (2018). Properties of biochar. *Fuel*, 217, 240–261.
- Yaashikaa, P. R., Kumar, P. S., Varjani, S., & Saravanan, A. (2020). A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. *Biotechnology Reports*, 28, e00570.
- Zhang, J., Shao, J., Jin, Q., Li, Z., Zhang, X., Chen, Y., Zhang, S., & Chen, H. (2019). Sludge-based biochar activation to enhance Pb(II) adsorption. *Fuel*, 252, 101–108.
- Zubbri, N. A., Mohamed, A. R., Kamiuchi, N., & Mohammadi, M. (2020). Enhancement of CO₂ adsorption on biochar sorbent modified by metal incorporation. *Environmental Science and Pollution Research*, 27(11), 11809–11829.