

The Effect of Metal Impregnated Biochars in Carbon Dioxide Decrement

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The rapid increment in CO₂ levels in the atmosphere, mainly of anthropogenic origin, requires innovative solutions in the field of carbon dioxide capture and storage (CCS). Due to their improved physicochemical properties, metal-impregnated biochars should be promising materials for CO₂ reduction. The efficiency of CO₂ storage in case of biochar is significantly enhanced by the impregnation of metallic elements such as alkali, alkaline earth and transition metals, which provide additional active sites and change the electron structure of the surface. The mechanism of CO₂ capture in metal-impregnated biochars includes both physisorption and chemisorption. Metal ions on the biochar surface increase the electrostatic interactions with CO₂, which led to improving physisorption. Transition metals such as Fe, Cu, and Ni promote the chemisorption, in which CO₂ undergoes more stable binding or reduction effects to form new compounds. For example, impregnation with calcium and potassium improves the alkaline nature of biochar, resulting better adsorption through acid-base interactions with CO₂. The large surface area and porosity of biochar increase the availability of CO₂, while the metallic elements provide catalytic activity that accelerates the CO₂ adsorption and conversion processes. Metal-impregnated biochar, which is sustainably derived from biomass, is an energy-efficient and environmentally friendly solution for carbon dioxide capturing and storing. In this work, different metals were used for surface modification of sewage sludge derived biochar in order to obtain efficient waste-based adsorbent for CCS/CCU process.

Keywords: metal-impregnated biochar, CO₂ capture, carbon reduction, physisorption, chemisorption

1. Introduction

Global industrialization and economic development are accelerating the use of fossil fuels and thus the excessive emission of greenhouse gases, in particular carbon dioxide (CO₂), which poses a serious threat to the ecological environment. Increasing atmospheric carbon dioxide levels contribute to rising average temperatures, leading to global problems such as sea-level rise, extreme weather events, and ecological and economic damage. The UK's weather forecasting service said that carbon dioxide concentrations in 2024 will be around 420 ppm. This is dramatically higher than before the industrial revolution, when CO₂ levels were only about 280 ppm (Martina Igini, 2024). For this reason, CO₂ capture is seen as a potential strategy to reduce the amount of CO₂ emitted into the atmosphere. Solvent adsorption, membrane separation, cryogenic separation and adsorption with solids are commonly used to capture carbon dioxide after combustion (A.L. Yaumi et al., 2017). Adsorption is considered to be the best technique because of its low energy consumption, the wide temperature and pressure range where the technology can be applied, and the sorbent regeneration without generating unfavorable by-products. Thus, biochar can be a promising adsorbent for CO₂ reduction (M.S. Shafeeyan et al., 2010). Despite the fact, that biochar can be used directly for CO₂ capture, it generally shows limited adsorption performance. Therefore, the surface of biochar has to be modified (e.g. physicochemical properties, specific surface area, pore structure and surface functional groups, etc.). Different adsorbents have been extensively studied over the past decades. Solid adsorbents, such as amine-supported silica (Lee et al. 2018), carbonaceous materials (Kamran and Park, 2021), zeolites (Kumar et al. 2020), organo-metallic framework materials (Younas et al. 2020). Compared to the above mentioned solid adsorbents, biochar is a substance that is stable, highly aromatized and carbon-rich, therefore it is naturally able to adsorb carbon

dioxide. It has excellent potential due to its high porosity and its surface contains a large number of active sites. According to the International Biochar Initiative, biomass derived biochar, can be carbon neutral (Lee et al. 2018).

The economic feasibility of biochar production depends mostly on the cost of the feedstock, therefore biomass waste can be an advanced solution. Due to its relatively low cost, biochar can be produced using biomass and other waste such as crop residues, wood waste, animal manure, food waste, municipal solid waste and sewage sludge. In addition, the use of biochar from waste promotes sustainable waste management. According to Xue et al. (2022), carbon, hydrogen, oxygen and nitrogen are the primary components of biochar, with carbon content for more than 40% of all elements. Biochar produced from different raw materials generally exhibit different physicochemical properties (e.g. pore structure, specific surface area, surface oxygen-containing chemical groups and elemental composition, etc.) (Nguyen and Lee 2016; Mulabagal et al. 2015; Goldfarb et al. 2017; Lee et al. 2017) The carbon dioxide capacity can be further enhanced by various chemical treatments of biochar, such as surface oxidation or impregnation with metals (e.g. Ca, Mg, Zn, Ni, Cu). These impregnations facilitate reactions in the presence of alkali and alkaline earth metals, which enhance the adsorption process, for example by forming carbonate that binds carbon dioxide to the biochar surface (X. Xu et al., 2016).

In this work, sewage sludge biochars were modified with different metals and the carbon dioxide capture was also investigated.

2. Materials and methods

2.1 Preparation and characterization of biochar

For biochar production animal sewage sludge was used. Raw material was dried and pyrolyzed in a batch steel reactor (inside volume $\sim 0.5 \text{ dm}^3$) under a nitrogen atmosphere at 400°C . The sewage sludge derived biochar was divided into different fractions by sieving: 3.15-2.50 mm (hereafter CM1) and 0.80-0.40 mm (hereafter CM2) (Figure 1).

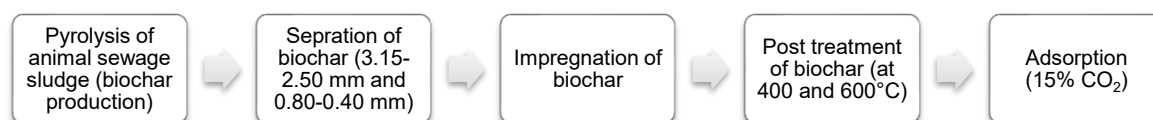


Figure 1: Production and application of metal impregnated biochar

The biochar fractions with different particle sizes were impregnated by wet impregnation. Five different metal salts were used: calcium-chloride (Sigma-Aldrich, 97-103%), magnesium-chloride-hexahydrate (VWR Chemicals, 99-101%), nickel-nitrate hexahydrate (thermo-scientific, 98%), zinc-nitrate hexahydrate (Molar Chemicals Kft.) and copper-sulphate pentahydrate (Molar Chemicals Kft.). The impregnation was carried out in a spherical flask with a recirculating cooler, which was placed in a temperature-controlled water bath to adjust the temperature of the impregnation. For the impregnation 60 g of the biochar was placed in the flask and 240 ml of 2 M metal-salt solution was added in a 1:4 ratio. The wet impregnation process was carried out at 80°C and 2°C for 2 hours using a magnetic stirrer (Faithful) with constant stirring. The samples were then filtered and dried in an oven (POL-EKO Aparatura) at 80°C to constant weight. Finally, after the impregnation, the materials were treated in a tubular reactor (Carbolite Gero). Samples were inertized in a nitrogen atmosphere for 20 minutes at room temperature before heat treatment. After the inertization, the metal impregnated biochars were heated at 400 and 600°C for 1 hour, with nitrogen flowrate of 2 l/h.

2.2 Adsorption

The CO_2 absorption properties of the biochar-based adsorbents were investigated at 25°C using 15 vol.% CO_2 - N_2 gas mixture. For the adsorption, 14 g of impregnated biochar was loaded into a U-tube, which was placed in thermostat (Julabo) to ensure a constant temperature (30°C). The gas flow rate was set to 4.1 l/. The CO_2 concentration was measured by a Draeger X-am 7000 multi-gas detector. The acquired CO_2 breakthrough curves were used to determine the breakthrough time (t_{br}) of the CO_2 , which was used to determine the adsorption capacity (q) in $\text{mg CO}_2/\text{g sorbent unit}$.

3. Results and discussion

3.1 Adsorption isotherms

The CO₂ adsorption breakthrough curves of the biochar-based sorbents obtained are shown in Figure 2. Based on the results, it can be concluded that for the reference samples, the breakthrough occurs slightly earlier (~25 seconds) for the 0.80-0.40 mm particle size fraction than for the 3.15-2.50 mm particle size fraction. Accordingly, the reference samples CM1 and CM2 have a capacity of 2.9 mg CO₂/g sorbent and 3.5 mg CO₂/g sorbent respectively. This is probably because the CM1 sample may have a larger particle size but higher porosity than the CM2 sample, so their specific surface areas may be nearly the same.

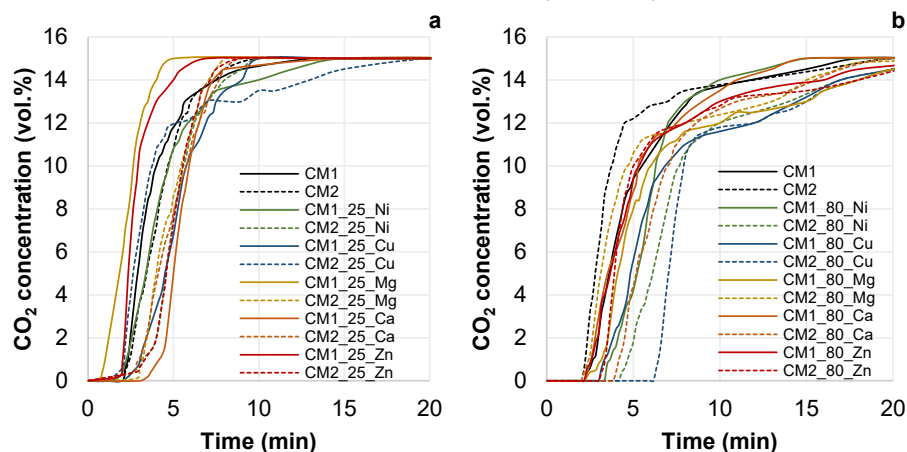


Figure 2: CO₂ breakthrough curves of adsorbents: a. impregnated at 25°C and b. impregnated at 80°C

As function of particle size, the results show that the CO₂ breakthrough of the impregnated sorbents occurred at least at the same time as for the reference sample ($2,1 \text{ min} < t_{br} < 4,0 \text{ min}$), so the capacity of sorbents increased or remained almost the same as a result of impregnation. The change in the capacity was independent of the temperature to be used during the impregnation process. For most of the samples, the 0.80-0.40 mm particle size had higher capacity, than that of 3.15-2.50 mm. The capacity increased by an average of 1.9 mg CO₂/g sorbent compared to the reference, an overall increase of 89% on average. The highest capacity was found for CM2_{80_Cu}, which was 4.1 mg CO₂/g sorbent. However, the results show that the capacity for some samples impregnated at 25°C was worse than that of samples impregnated at 80°C. As it is known, the adsorption is favored by the low temperature, therefore at room temperature more metals are likely to have been impregnated onto the surface of the biochar, blocking the pores of the sorbent and reducing its capacity.

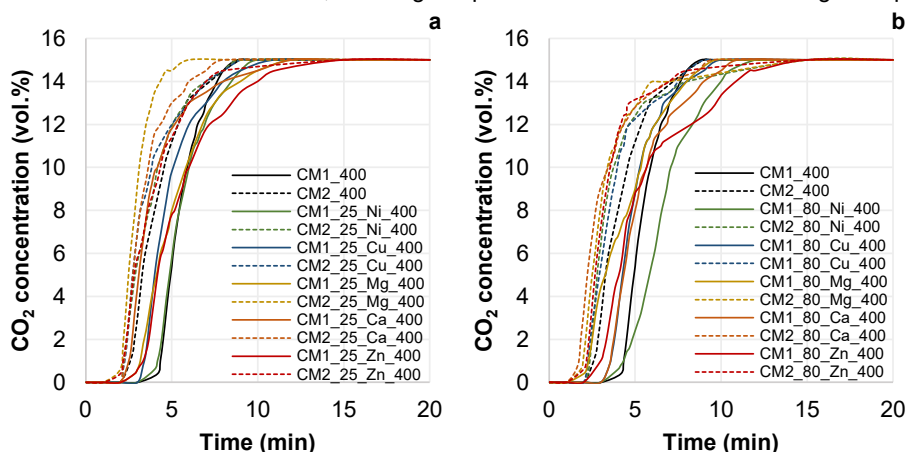


Figure 3: CO₂ breakthrough curves of adsorbents: a. impregnated at 25°C and heat treated at 400°C and b. impregnated at 80°C and heat treated at 400°C

Regarding the heat treatment, the results show that the heat treatment after impregnation had a positive effect on the CO₂ capture of the impregnated sorbents (Figure 3 and Figure 4). Similarly to the reference samples,

due to the heat treatment, most of the impregnated CM1 sorbents showed a longer breakthrough time, resulting sorbents with higher specific capacities than the impregnated CM2 sorbents. This observation is true for samples with both particle size ranges treated at 400°C and 600°C. The increase in the breakthrough times at 400°C and 600°C was at least 6.5% and 17.5% respectively.

The results show that in case of 400°C heat treatment, the capacity of the CM2 sample did not change significantly (0.7 mg CO₂/g sorbent increase in capacity), whereas the capacity of the reference sample increased by 2.5 times using CM1 biochar. At higher temperatures (600°C), the heat treatment can increase the capacity of the reference samples (CM1 and CM2) by at least 1.5 times. However, the capacity of the CM1_600 particle size fraction decreased compared to the samples heated at 400°C. The capacity of the CM1_600 sample (3.6 mg CO₂/g sorbent) was 25% lower than that of the CM1_400 sample (4.9 mg CO₂/g sorbent). However, the capacity of the other particle fraction (CM2) increased by 34% after heat treatment at 600°C.

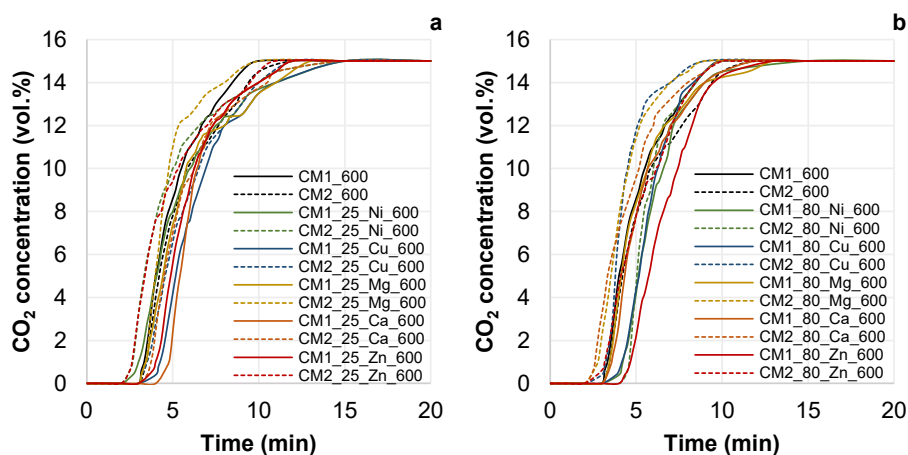


Figure 4: CO₂ breakthrough curves of adsorbents: a. impregnated at 25°C and heat treated at 600°C and b. impregnated at 80°C and heat treated at 600°C

3.2 CO₂ capacity of the sorbents

The specific capacity for the different adsorbents is shown in Figure 5 and 6. For both the CM1_80_400 and CM1_80_600 impregnated samples, it can be concluded that the sorbent capacity increased or remained almost unchanged after heat treatment. But the opposite trend was observed for CM2_80_400 and CM2_80_600, where the capacity was reduced by the heat treatment. On average, the capacity decrease was 45%. A similar conclusion was found for samples impregnated at 25°C.

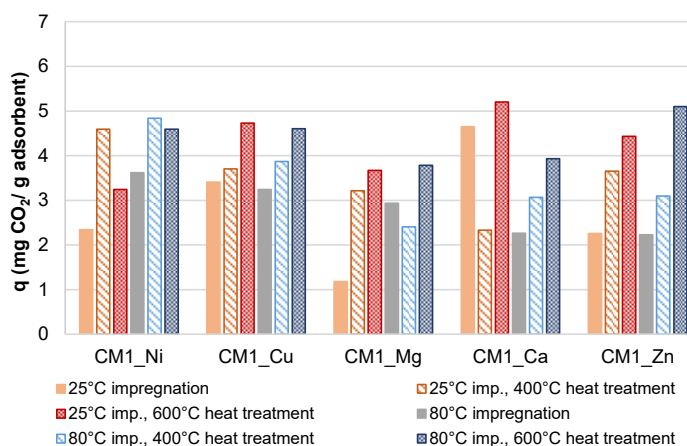


Figure 5: Specific CO₂ capacity of the adsorbents 3.15-2.50 mm

It was found that the capacity of the adsorbents increased or remained almost unchanged after heat treatment for both CM1_25_400 and CM1_25_600 samples. The average increase of the capacity was 12%. The best performance was achieved with Ni, Cu and Zn impregnated sorbents, and the highest capacity was obtained

with CM1_Ni, CM1_Cu and CM1_Zn adsorbents. The average capacity was higher than 4.0 mg CO₂/g sorbent. Overall, it can be concluded that the thermal treatment after impregnation has a positive effect on the CO₂ adsorption properties of sorbents. To the fact that, after impregnation, the metals are present on the sorbent surface in the form of chlorite, nitrate and sulphate salts, which thermally decompose and form oxides at the heat treatment temperature. As confirmed by earlier measurements, metal oxides are more efficient for CO₂ absorption.

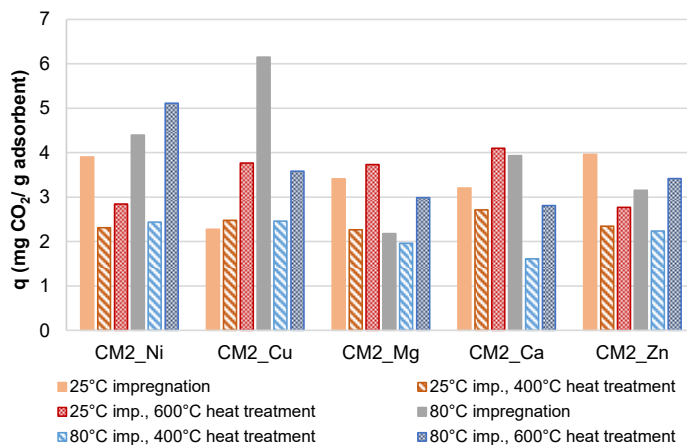


Figure 6: Specific CO₂ capacity of the adsorbents 0.80-0.40 mm particle size fraction

3.3 Elemental composition of char

The elemental composition of the used adsorbents was analysed by a Shimadzu EDX-8100 Energy Dispersive X-ray Fluorescence spectroscopy. The results showed that both the impregnation temperature and the particle size had an effect on the amount of metals impregnated on the char surface. The results show that in the case of biochar impregnated at 80°C, less metal was impregnated on CM1 particles than on CM2 particles. Considering the amount of metal components impregnated on the sorbent surface, the more metal impregnated on the sorbent surface, the higher the sorbent capacity. For sorbents impregnated at 80°C the results show that although the nickel fraction was the smallest in the sorbent after impregnation, it was the second largest capacity measured. In the presence of nickel, the sorbent capacity increased by 2-3 times. Regarding the effect of metals, zinc and magnesium had the least effect on the capacity.

4. Conclusion

The CO₂ adsorption capacity of metal-impregnated and heat-treated biochar-based sorbents was investigated. The effects of impregnation temperature and post-treatment temperature on biochar with different particle sizes were investigated. Fractions of 3.15-2.50 mm and 0.80-0.40 mm biochar were used for the investigation. The investigated biochar-based sorbents were prepared by a wet impregnation method using 5 different metal compounds (Ni, Cu, Zn, Mg and Ca) at 2 different temperatures (25°C and 80°C). The sorbents prepared by impregnation were heat treated at 400°C and 600°C. It was found that adsorbents with 3.15-2.50 mm particle size have better CO₂ adsorption capacity, than adsorbents with 0.80-0.40 mm particle size. The difference in capacity was 14%. As a function of particle size, the results show that the capacity of sorbents increased or remained almost the same as a result of impregnation. The highest capacity increase was achieved when biochars were impregnated with Ni and Cu salts (average capacity of 3.4 mg CO₂/g adsorbent). Furthermore, it can be concluded that the heat treatment after impregnation has a positive effect on the CO₂ adsorption. It was found that the capacity of the adsorbents increased or remained almost unchanged after heat treatment, both at 400° and 600°C. The capacity increase is mostly favored by the 600°C heat treatment. The average increase of capacity after the 600°C heat treatment was 12%.

Acknowledgments

Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

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