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Heavy Metal Adsorption by CO_2- and CO_2 Steam-Activated Food Industry Waste Biochars

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International Energy and Environment Conference, Ostravice, September 7-9.09.2026

Why this study matters

Heavy metals persist in water systems, accumulate in ecosystems and require efficient removal routes.

The study connects two sustainability routes in a single material design question:

Food industry residues → **Gasification-derived biochars** → **Wastewater treatment**

Key challenge: high removal efficiency may be apparent when alkaline ash components trigger precipitation.

Research objective and novelty

Objective

Evaluate biochars from sunflower husks, buckwheat husks and cherry stones as low-cost adsorbents for Pb (II), Cu (II) and Ni (II) ions removal.

Novelty

- Link gasification atmosphere with ash chemistry and leaching behaviour,
- Separate true adsorption from precipitation-assisted removal,
- Use FTIR and SEM to verify post-sorption surface changes

Materials and conversion route

Feedstocks

SH
Sunflower husks

BH
Buckwheat husks

CS
Cherry stones

900 °C gasification

CO_2 atmosphere

Higher carbonisation
Lower oxygen content
Carbonation / stabilisation

CO_2–steam atmosphere

Stronger pore development
More alkaline species released
More reactive surfaces

Experimental design

Adsorption tests

0.2 g biochar + 100 mL metal solution
Pb^{2+} / Cu^{2+} / Ni^{2+} at 50, 100 and 150 $mg \cdot dm^{-3}$
60 min, 210 rpm, 22 °C

Characterisation

AAS: final metal concentration
N_2 adsorption: BET and porosity
FTIR: functional groups / minerals
SEM + Z-contrast: metal-rich phases

$$q_e = (C_0 - Ce) \cdot V / m$$

AIM: comparison of adsorption capacity with pH, leaching and surface evidence, not just with removal efficiency.

Leaching behaviour: alkalinity is driven by ash chemistry

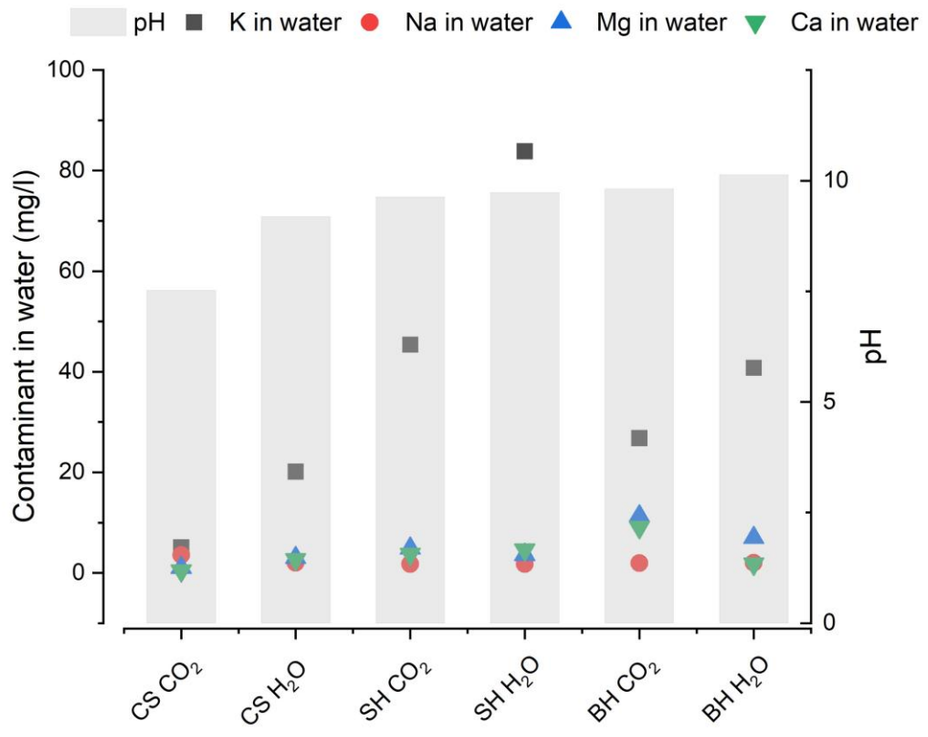

Figure 1. pH and ash-derived element leaching from biochars

83.8 mg/L

maximum K leaching ($SH\ H_2O$)

pH 9.73

highest pH ($SH\ H_2O$)

Steam gasification increases accessibility of mineral species and raises pH.

CO_2 promotes carbonation and mineral stabilisation — especially in Ca–P-rich cherry-stone biochar.

Conclusions: atmosphere modifies mineral speciation; feedstock ash defines the final pH response.

FTIR: strongest spectral response for Pb (II) ions

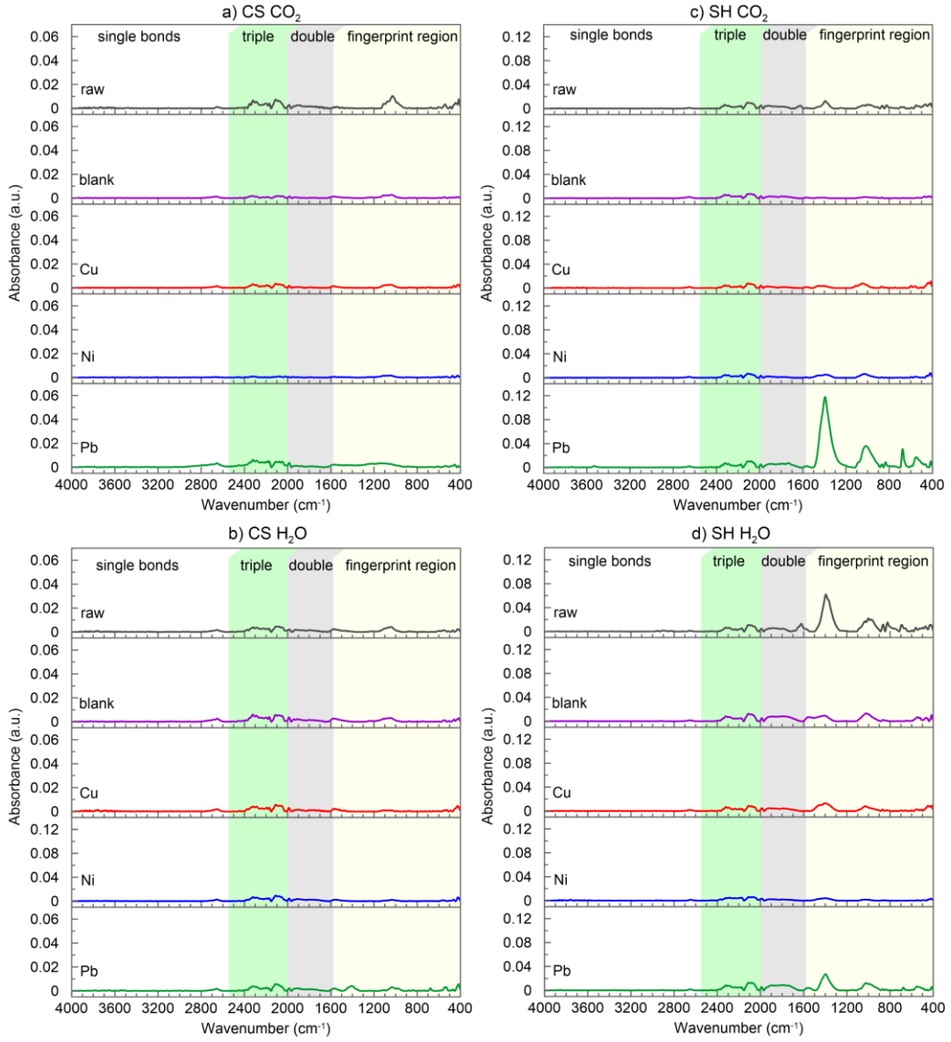

Figure 2. FTIR spectra before and after interaction with Cu^{2+}, Ni^{2+} and Pb^{2+}

Highly carbonised biochars show limited changes in most spectra

Fingerprint region reflects strong contribution of inorganic mineral phases

Pb (II) ions induces new/intensified bands, suggesting complexation and precipitation with minerals

Cu (II) and Ni (II) ions interactions are weaker or less visible in FTIR

Conclusions: removal is not only surface adsorption, a strong influence of mineral phase is observed.

Pb (II) and Cu (II) : high removal, but different levels of precipitation

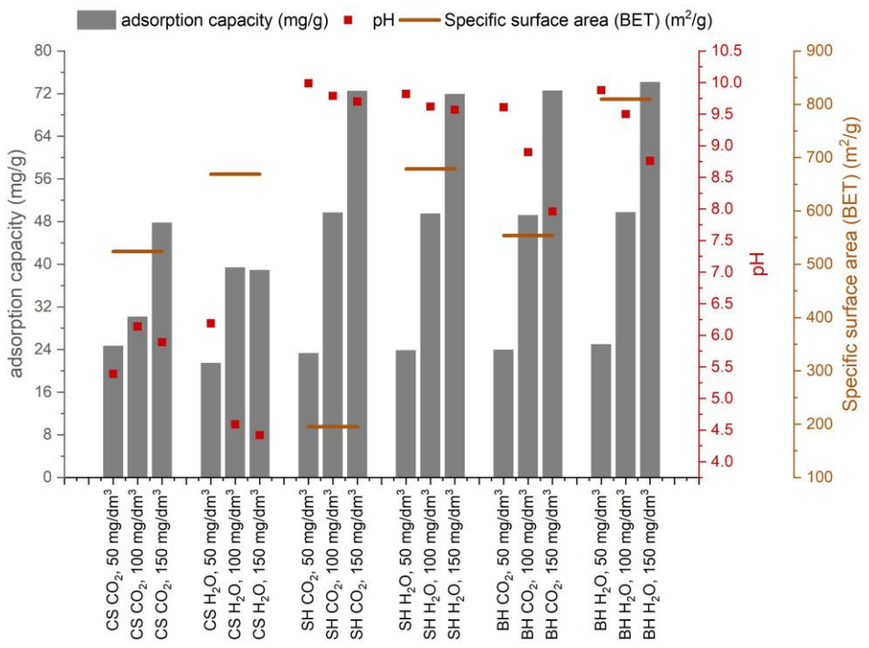

Figure 3. Pb (II) ion removal by biochars: relationship between BET surface area, pH, and gasification conditions

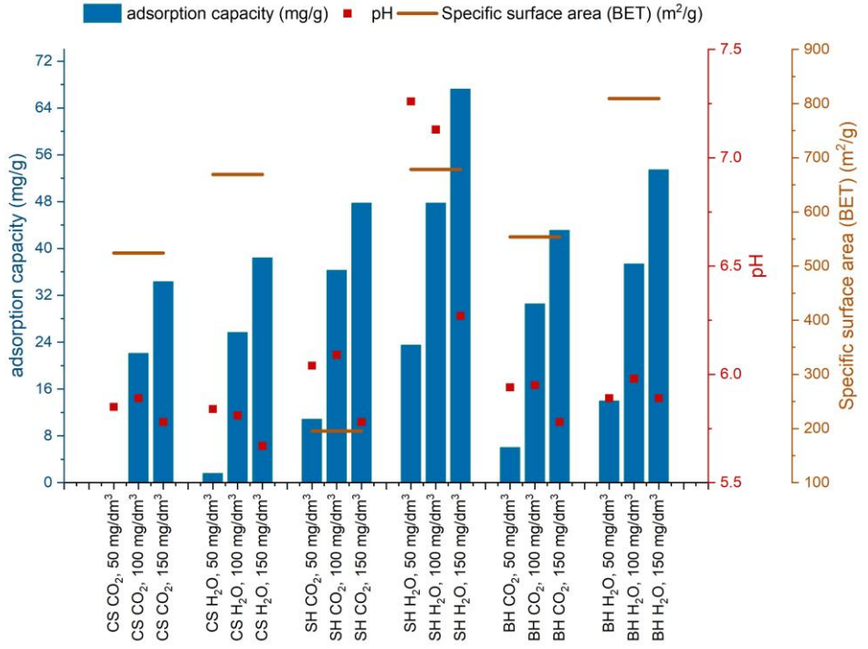

Figure 4. Cu (II) ion removal by biochars: relationship between BET surface area, pH, and gasification conditions

Pb (II): nearly complete removal for SH and BH; precipitation is dominant under alkaline conditions.

Cu (II): mixed adsorption–precipitation; visible blue precipitate confirms mineral/hydroxide contribution.

Ni (II): the clearest indicator of intrinsic adsorption performance

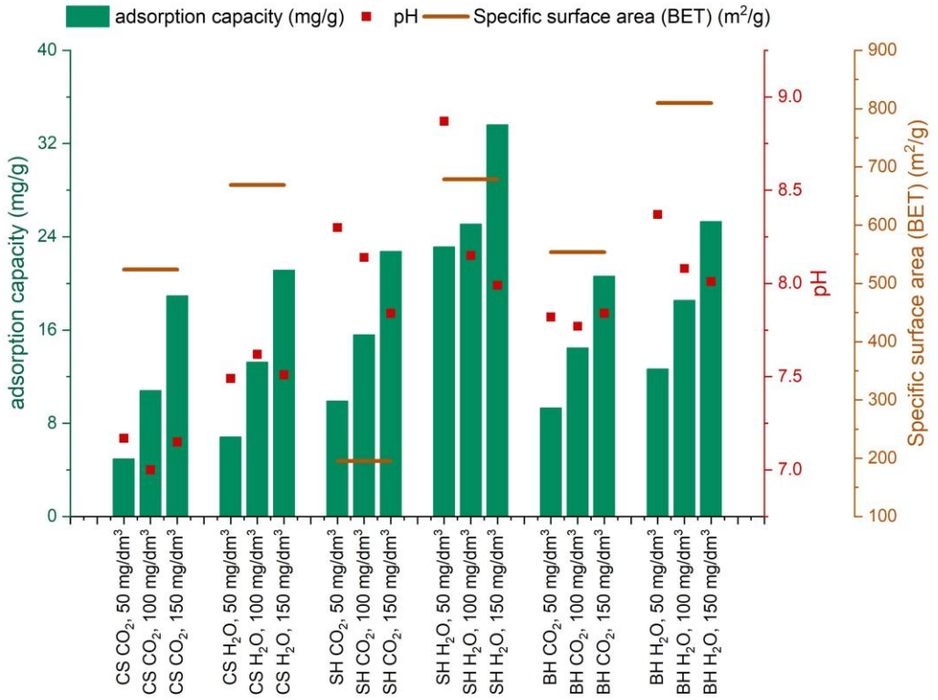

Figure 5. Ni (II) ion removal by biochars: relationship between BET surface area, pH, and gasification conditions

up to 800 m^2/g

BET surface area
for steam-activated biochars

30–33 mg/g

Ni (II) ions uptake
for steam-activated biochars

Ni (II) ions removal follows porosity and accessible surface area more clearly than Pb (II) or Cu (II) ions.

Freundlich fitting supports heterogeneous adsorption behaviour, while precipitation becomes relevant only near pH 9.

SEM evidence: metal-rich surface phases after adsorption

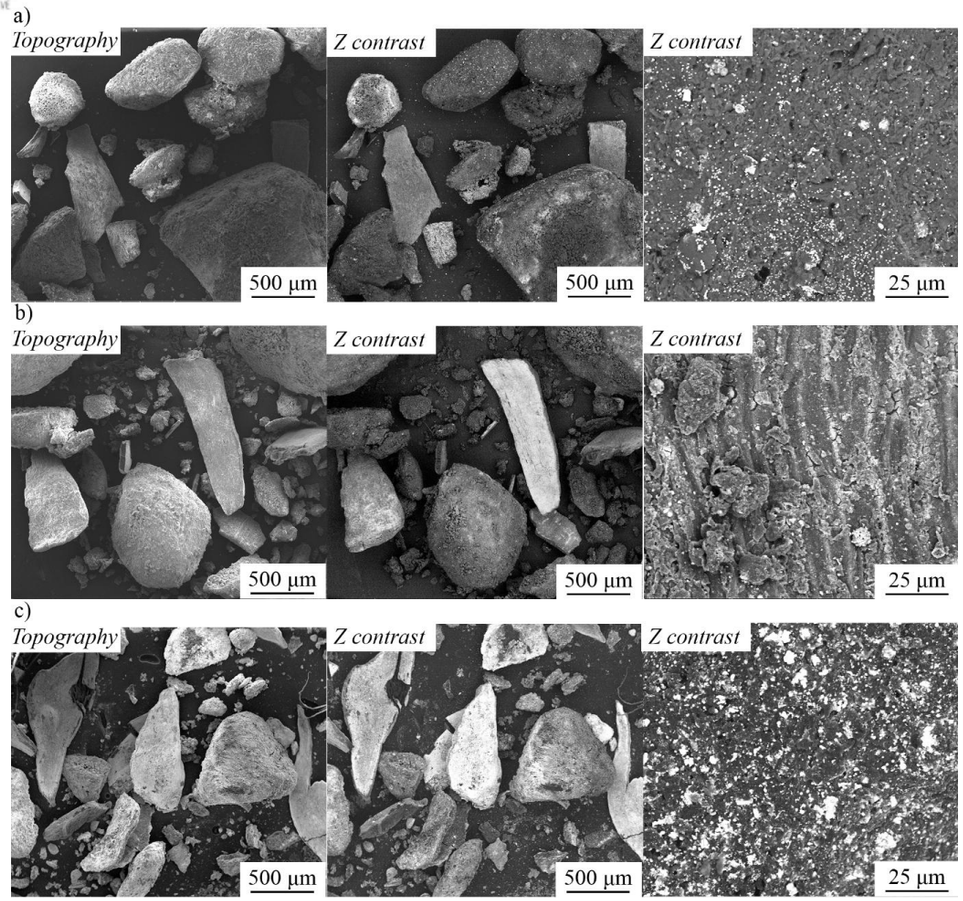

Figure 6. CS H_2O after a - Cu (II), b - Ni (II) and c -Pb (II) adsorption

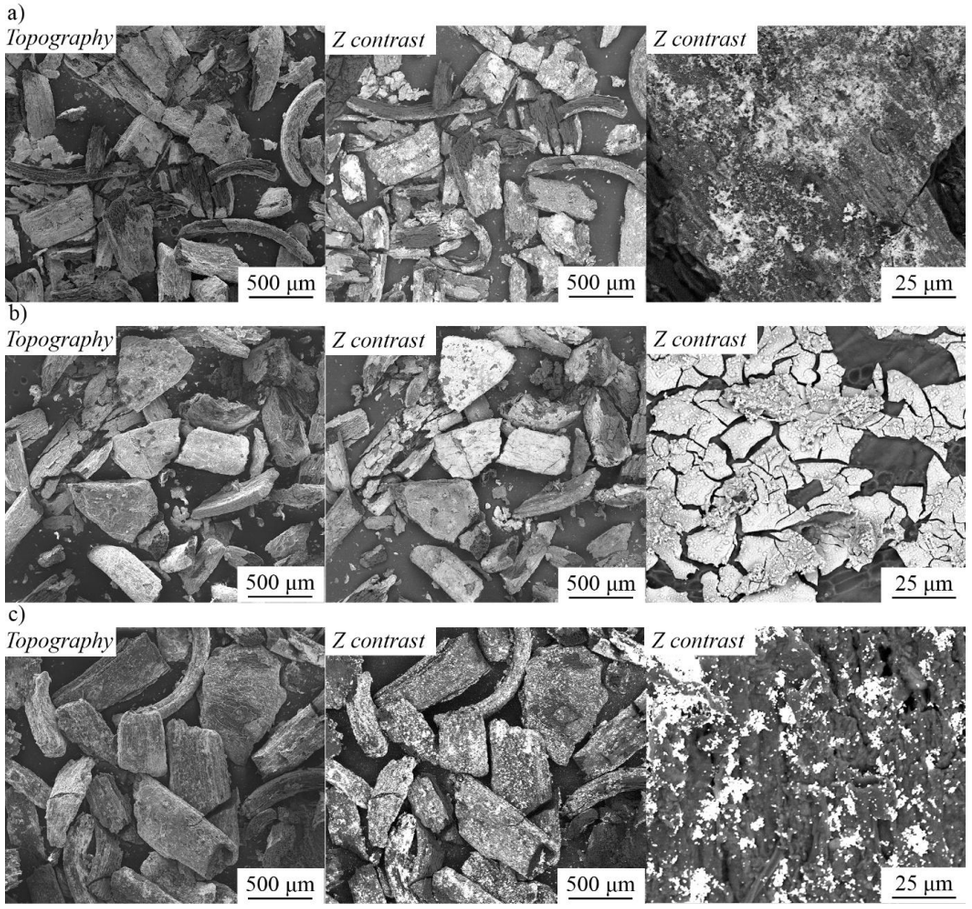

Figure 7. H_2O-activated biochar after a - Cu (II), b -Ni (II) and c -Pb (II) adsorption

Z-contrast images show dense bright Pb-rich deposits, confirming stronger Pb retention and precipitation/surface binding.

Mechanism of removal: adsorption vs apparent removal

Pb^{2+}	Dominated by precipitation and formation of Pb-rich phases; very high removal is not pure adsorption.
Cu^{2+}	Mixed behaviour: surface adsorption plus hydroxide/carbonate precipitation under alkaline conditions.
Ni^{2+}	Mostly surface-controlled; best proxy for intrinsic adsorption, especially when precipitation is minimised.

Interpretation rule: high qe values in alkaline systems should be reported as apparent removal unless precipitation is excluded.

Conclusions and implications

- CO_2–steam activation improves porosity and increases alkaline mineral release.
- CO_2 activation promotes mineral stabilisation via carbonation, especially in Ca–P-rich CS biochars.
- Ash-derived components modulate pH and drive precipitation pathways.
- Pb^{2+} and Cu^{2+} removal should be interpreted cautiously because precipitation contributes strongly.
- Ni^{2+} provides the most reliable comparison of adsorption performance across biochars.

SUMMARY

Design of waste-derived biochar adsorbents must couple carbon porosity with mineral chemistry and leachate pH.

Acknowledgements

This work was supported by the National Science Centre, Poland (Grant No. 2023/51/B/ST8/01531). Additional funding was provided by the Ministry of Science and Higher Education, Poland (AGH grants No. 16.16.210.476/501.00-210000-10000 and 16.16.110.663/501.00-110000-10000). Textural property analyses were carried out using research infrastructure purchased under the “Excellence Initiative – Research University” programme at AGH University of Krakow. It was co-funded also by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 101182827, project name “PARADISE - Development of next generation pathways leading to just energy transition and industrial deep decarbonization”.

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Journal of Environmental Chemical Engineering 13 (2025) 119279

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Applied Thermal Engineering 260 (2025) 124968

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