

Research article

Effects of pyrolysis parameters on biochar derived from sewage sludge including environmental risk assessment of heavy metals

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ABSTRACT

Pyrolysis is a promising thermochemical process for managing sewage sludge while simultaneously producing biochar, a valuable co-product. This study systematically investigated the effects of the pyrolysis parameters of temperature (200–800 °C), residence time (5–60 min), and inert gas flow rate (0.25–1.0 dm³/min) on the properties of biochars obtained from sewage sludge. Comprehensive characterization of the biochars was conducted, including composition analyses (ultimate, proximate, elemental, and molecular), acidity, specific surface area and pore size, and the assessment of eight heavy metals (As, Cd, Pb, Cr, Zn, Mn, Ni and Cu) in the biochars and sewage sludge. The results showed pyrolysis temperature and residence time were the most critical parameters affecting biochar quality, with negligible influence of inert gas flow rate. Higher pyrolysis temperatures (>500 °C) increased biochar pH to alkaline values (>10), ash content, and nutrient concentrations (Ca, K, Mg, P). Temperatures above 600 °C significantly increased biochar surface area, reduced pore size, and yielded H/C ratios below 0.57, improving suitability for soil remediation. Pyrolysis also facilitated volatilization of heavy metals, particularly As and Cd, which were reduced to safe levels, with Cd removal exceeding 90% at 700 °C. Metal analysis confirmed the immobilization of heavy metals in biochar, significantly reducing the environmental risk, from high (PERI=1158) in the sewage sludge feedstock to low (PERI<50) in biochar obtained at temperatures above 600 °C. Most heavy metals in biochar at these temperatures were concentrated in oxidizable and residual fractions. The results provide valuable new data to guide development of pyrolysis for the sustainable management of sewage sludge.

1. Introduction

Wastewater treatment plants generate significant quantities of sewage sludge that must be disposed of via incineration, landfill or other methods. In the European Union (EU) alone, approximately 10 million tons of sludge (dry weight) are produced each year (Valchev et al., 2024). As urban populations grow, the amount of sludge generated increases accordingly.

Sewage sludge management presents a significant economic challenge for wastewater treatment plants, accounting for only 1%–2% of the effluent volume, but 20%–60% of the total operating expenses (Khan et al., 2023). Current strategies for sludge management include incineration, landfill disposal, energy recovery, adsorbent preparation, and agricultural applications (Khan et al., 2023; Gao et al., 2020a).

However, the agricultural use of sewage sludge is declining due to the high levels of organic and inorganic pollutants found in sewage sludge. Under the EU Sludge Directive (EU Council, 2022), sludge must be analyzed for acidity/alkalinity and composition, including assessment of nitrogen, phosphorus, and heavy metal (HM) content. Heavy metals of particular interest include lead (Pb), chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), mercury (Hg), arsenic (As) and cadmium (Cd). The EU Sludge Directive specifies permissible metal concentrations and annual soil discharge limits. Prior work has reported increased Cu, Zn, Cr, Cd, and Mn in soil after sludge addition (Bourioug et al., 2015), with HMs accumulating in plants (Kominko et al., 2022) and fauna like snails (Bourioug et al., 2015), potentially transferring HMs into the food chain and posing environmental risks.

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Pyrolysis is increasingly used to manage sewage sludge, as pyrolysis significantly reduces unwanted components, making the material much safer to dispose of while also producing valuable renewable products, such as biochar that contribute to the economics of wastewater treatment facilities (Gao et al., 2020a; Huang et al., 2022). Biochar is particularly attractive as a product from sewage sludge due to the potential applications as a renewable energy source, an effective adsorbent with a large active surface area, and as a soil amendment to improve organic matter, nutrient content, water retention and aeration (Khan et al., 2023; Peng et al., 2011). Furthermore, gaseous and liquid products from pyrolysis have diverse potential applications, although the quality often requires further processing before use (Huang et al., 2022).

The optimal temperatures for sludge pyrolysis, primarily aimed at producing solid products, range from 500 to 600 °C (Kistler et al., 1987). Ghodke et al. (2021) conducted sewage sludge pyrolysis in a fixed bed reactor at 250 to 700 °C, achieving yields at 500 °C: 58.7% biochar, 22.4% bio-oil, and 18.9% pyrolysis gas. Al-Mrayat et al. (2022) explored optimal biochar production conditions from sewage sludge, examining variables like temperature, heating rate (5 to 35 °C/min), and isothermal time (45 to 120 min) to ensure safe disposal and reuse. Developing an energy-efficient pyrolysis process requires identifying pyrolysis operating parameters such as temperature, reaction time, inert gas flow rate, and feedstock quantity for the specific feedstock (Gao et al., 2020a; Wang et al., 2012).

The heavy metals in sewage sludge pose significant challenges for use and disposal (Han et al., 2017). The toxic elements, primarily from industrial wastewater and surface effluent (Fijalkowski et al., 2017), are often bound to organic matter, sulfides, or oxides of Mn and Fe (He et al., 2010), and constitute 0.5 to 2% of sludge dry mass (Fijalkowski et al., 2017). The HMs content in pyrolysis products depends on the feedstock, with the highest concentrations found in the solid product due to the microporous structure of the solids (Kistler et al., 1987; Trinh et al., 2013; Song et al., 2014). Under pyrolysis conditions, metals like Cr and Pb are stabilized in oxidized or residual forms, reducing their mobility and leaching risk (Kistler et al., 1987; Trinh et al., 2013; Jin et al., 2016; Gao et al., 2020a). However, volatile metals like Cd, Hg, Se, and As can cause secondary pollution, as they are emitted in vapor or aerosol form at temperatures above 600 °C (Kistler et al., 1987; Trinh et al., 2013; Leng et al., 2014). Increasing pyrolysis temperature and duration generally improves HM release (Han et al., 2017; Kistler et al., 1987; Gao et al., 2020b).

Recent studies have shown the potential of sewage sludge-derived biochar as a sustainable soil amendment, particularly for contaminated soils. The biochar is pathogen-free, rich in carbon and nutrients, and improves soil fertility, fertilizer efficiency, and crop yields (Igalavithana et al., 2016; Al-Wabel et al., 2018; Sousa and Figueiredo, 2016; Faria et al., 2018). When combined with compost, biochar can effectively immobilize HMs, reduce soil toxicity, and facilitate the degradation of organic contaminants (Al-Wabel et al., 2018). Song et al. (2014) demonstrated that sewage sludge biochar produced at 450 °C significantly increased garlic yields. Although HM levels in biochar were higher than in local soils, they remained within acceptable limits for land application, and proper pyrolysis temperature minimized metal accumulation in crops (Song et al., 2014; Khanmohammadi et al., 2017).

Although the above-mentioned studies demonstrated the effect of some pyrolysis parameters on HM behavior, there are few studies that systematically consider the effects of pyrolysis operating conditions on biochar quality and HM form and content. Further, there is little known about the kinetics of the release of HMs from the sludge during pyrolysis, with the exception of Hg (Dziok et al., 2022). Improved understanding of HM behavior during pyrolysis is crucial for advancing sludge conversion methods (Han et al., 2017) and ensuring the quality and safety of biochar produced from pyrolysis of sewage sludge. Therefore, the objective of the current work is to provide the first

Table 1
Experimental pyrolysis reactor conditions studied.

Parameter	Range
Temperature ^a [°C]	200, 300, 400, 500, 600, 700, 800
Residence time ^b [min]	5, 15, 30, 60
Inert gas flow rate ^c [dm ³ /min]	0.25, 0.5, 0.75, 1

^a Temperature effects were evaluated using fixed residence time (30 min) and gas flow rate (0.5 dm³/min).

^b Residence time effects were evaluated using fixed temperature (300, 500, and 700 °C) and gas flow rate (0.5 dm³/min).

^c Flow rate effects were evaluated using fixed temperature (600 °C) and residence time (30 min).

comprehensive assessment of HM content of biochar as a function of pyrolysis operating conditions. Specifically, the concentration and chemical speciation distribution of heavy metals in sewage sludge and biochar produced by pyrolysis at varying key parameters are thoroughly examined in the current work. Additionally, the speciation data are used to perform an ecological risk assessment of the heavy metals. Since the environmental risks of heavy metals depend more on their chemical forms than their total content, the European Community Bureau of Reference (BCR method) three-step procedure provides a reliable method for assessing heavy metal mobility, availability, and environmental impact (Ure et al., 1993) and is used here. To fully assess biochar quality, the study of HM behavior during sludge pyrolysis is integrated with a comprehensive evaluation of the basic properties of biochar. Based on the findings related to heavy metal migration and transformation, as well as the ecological risk assessment, practical recommendations for sludge disposal are also offered in the current work.

2. Materials and methods

Sewage sludge was sourced from a municipal wastewater treatment plant in an area with a large accumulation of urban sewage. The capacity of the treatment plant was 160,000 m³/day of wastewater. The sludge was subjected to a mechanical–biological treatment process with chemical support at the wastewater treatment facility. Specifically, the sludge underwent both aerobic and anaerobic treatment, followed by neutralization and mechanical dewatering using centrifuges before being sampled for the pyrolysis study. The processed sludge was collected and then air-dried at room temperature and homogenized for the pyrolysis tests. The sludge samples from the plant had a pH of 7.9 (as-collected). Sewage sludge samples were also preserved for future studies.

Pyrolysis studies were conducted using a tube furnace at the operating conditions shown in Table 1. A schematic and a photo of the pyrolysis reactor facility are provided in Fig. 1. Two repetitions were completed at each condition. The feedstock sludge and the resulting pyrolysis products were thoroughly characterized using the analytical methods listed in Fig. 1c. Sample preparation, analytical methods, and parameters for HMs determination by atomic absorption spectroscopy (AAS) along with the associated uncertainty are described in detail in the Supplemental Material.

The results of the biochar analysis were used to assess the heavy metal behavior, specifically using enrichment rates (ERs) and residual rates (RRs) in the biochar derived from the sewage sludge. The ER and RR were used to evaluate the degree of enrichment and immobilization of heavy metals due to pyrolysis, and were calculated using the following Eqs. (1) and (2).

$$ER_i = \frac{C_{HM_i}^{\text{biochar}}}{C_{HM_i}^{\text{sludge}}} \quad (1)$$

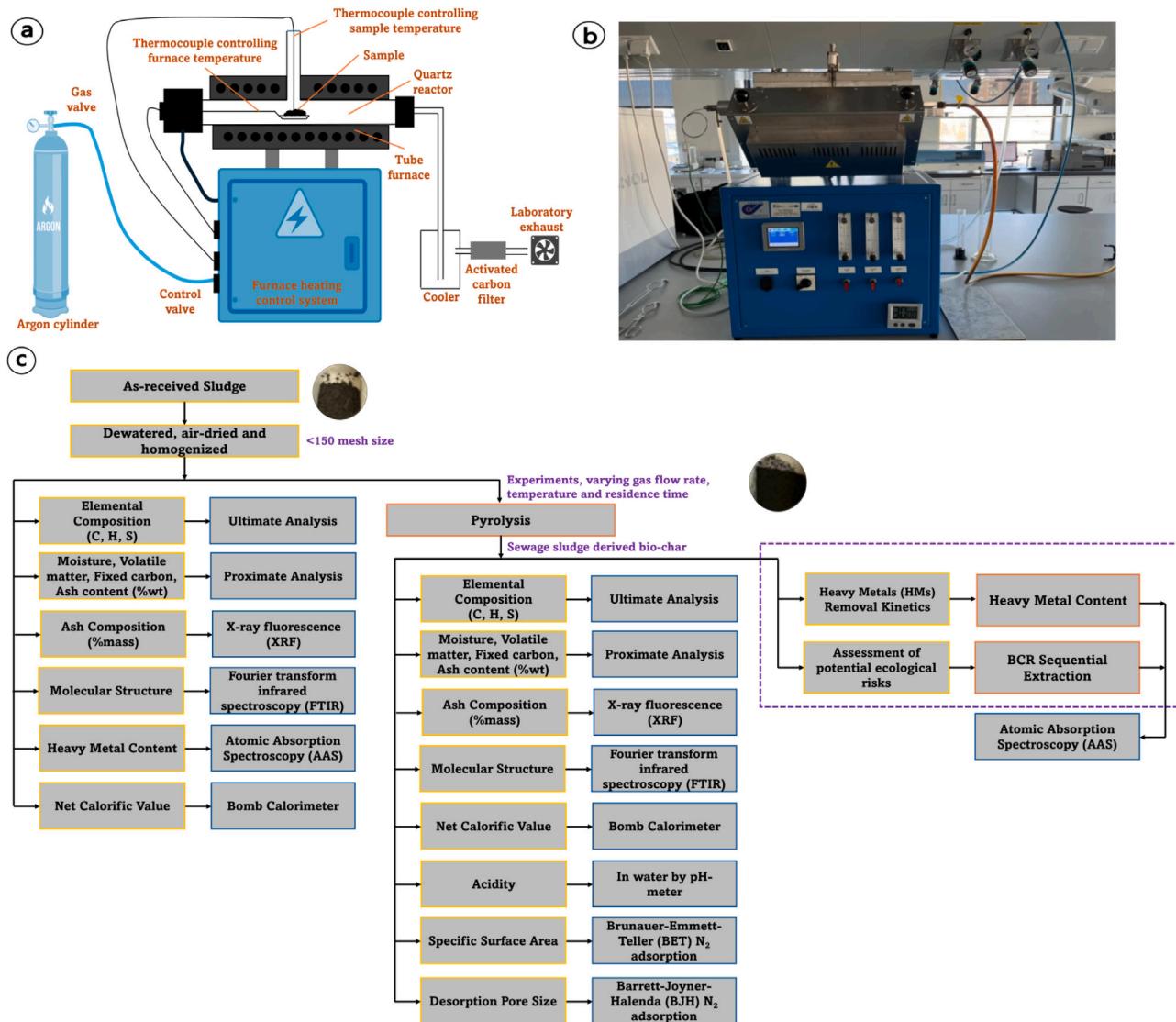


Fig. 1. (a) Schematic of the experimental setup — tube furnace with instrumentation; (b) Photograph of the experimental reactor; (c) Analytical methods used for characterizing sewage sludge feedstock and pyrolysis products.

where $C_{HM_i}^{\text{biochar}}$ is the concentration of each heavy metal in biochar (mg/kg); $C_{HM_i}^{\text{sludge}}$ is the concentration of each heavy metal in sewage sludge (mg/kg).

$$RR_i = ER_i \times Y_{\text{biochar}} \quad (2)$$

where Y_{biochar} is the yield of biochar (%), and was calculated by the ratio of the mass of biochar to the mass of pyrolysis feedstock.

The kinetics of the loss of heavy metals from the biochar were also assessed using the concentration of heavy metals in the biochar and sewage sludge. The activation energy and pre-exponential factors were derived for pyrolysis temperature (300, 500, and 700 °C) using the following, where X_{HM_i} is the metal removal percentage, which was evaluated across all experiments.

$$X_{HM_i} = 1 - ER_i \times Y_{\text{biochar}} \quad (3)$$

X_{HM_i} captures the extent of material loss during pyrolysis and is essential to evaluate the transformation of sewage sludge into char while considering metal retention or removal efficiency (Dziok et al., 2022; Sotiropoulou et al., 2019). The metal removal dynamics can be represented as a first-order decomposition process, with its asymptote

dependent on both time and temperature (see Eq. (4)).

$$\frac{dX_{HM_i}}{dt} = k(1 - X_{HM_i}) \Rightarrow X_{HM_i} = 1 - \exp(-kt) \quad (4)$$

Here, t is the time and k is the removal rate constant, which depends on temperature. The temperature dependence of k is described by the Arrhenius equation (see Eq. (5)), which was used to calculate the activation energy (E_m) and the pre-exponential factor (A_m).

$$k = A_m \exp\left(-\frac{E_m}{RT}\right) \Rightarrow \ln k = \ln A_m - \frac{E_m}{R} \frac{1}{T} \quad (5)$$

To determine the effect of pyrolysis on the immobilization of the considered HMs, their form in the biochars and sewage sludge was analyzed via sequential extraction. For this purpose, the Community Bureau of Reference Method (BCR) was applied (Mossop and Davidson, 2003; Ure et al., 1993). The sequential extraction procedure is widely recognized as a standard method to measure trace metals in samples. The procedure categorizes trace metals into four distinct fractions: F1 — the acid-soluble (ion-exchangeable) fraction; F2 — the reducible (connected to oxides) fraction; F3 — the oxidizable (organic and sulfides) fraction; F4 — the residual fraction (connected with minerals, mainly to silicate lattice or crystalline iron and manganese oxides).

The accuracy of the BCR testing was validated using certified reference material CRM 483 (sewage sludge amended soil) and comparison with reference data (Rauret et al., 2000). Recovery rates for each analyzed heavy metal are summarized in Table S7 of the Supplementary Material. All recovery values fall within the acceptable range for the applied analytical procedure.

The potential ecological risk of the heavy metals in the biochar samples was evaluated using the Potential Ecological Risk Index (PERI). PERI incorporates factors such as toxicity, environmental sensitivity, and heavy metal concentration to assess ecological risks in various research fields, including environmental chemistry and ecology. The index is particularly useful for providing a comprehensive evaluation of the ecological risks posed by heavy metals. The PERI is calculated using the following formulae:

$$C_f^i = \frac{C_B^i}{C_R^i} \quad (6)$$

$$E_r^i = T_r^i \times C_f^i \quad (7)$$

$$PERI = \sum_{i=1}^n E_r^i \quad (8)$$

where C_f^i is the contamination coefficient of the HM_i, C_B^i is the total concentration of HM_i distributed across the potentially mobile fractions (F1, F2, and F3), C_R^i is the concentration of HM_i within the stable fraction (F4), T_r^i is the potential ecological index of HM_i, E_r^i is the potential ecological risk index of HM_i, and PERI is the potential ecological risk induced by total contamination from 1 to n heavy metals. Based on Hakanson (1980), the potential ecological indices (T_r^i) for Zn, Cu, Ni, Mn, Cr, As, and Cd used in this study were 1, 5, 5, 1, 2, 10, and 30 mg/kg, respectively. The criteria for metal contamination and ecological risk levels are presented in the Supplementary Material.

3. Results and discussions

3.1. Sewage sludge characteristics

The sludge characteristics are summarized in Table 2. The variability of the parameters for the sludge from this wastewater treatment plant over time can be found in the database (Makowska, 2024). In pyrolysis studies (Fonte et al., 2012), sewage sludge typically contains 38.3–66.8% volatiles, 22.6–52.0% ash, 0.8–19.7% fixed carbon, 23.1–39.9% carbon, 3.8–5.9% hydrogen, and 0.8–1.0% sulfur. The results in Table 2 are consistent with these ranges of values, with ash on the high end of the range of observed values. With 51.4% ash content, the tested sewage sludge in this work is consistent with more lignocellulosic materials, requiring continuous ash removal in the facility reactors. The C/N ratio of the sludge sample subjected to pyrolysis was 5.77. The heating value of sewage sludge depends on the type of sewage sludge treatment, with higher values for samples with lower moisture and ash content and when organic matter is undigested. Digested and dry sludge has typical heating values from 8.5 to 17 MJ/kg, while undigested sludge can have heating values as high as 23 MJ/kg. Ash can contain elements like Fe, Ca, K, and Mg, which can catalyze pyrolysis reactions. For the sewage sludge tested in this study, the main oxides were SiO₂, Al₂O₃, P₂O₅, Fe₂O₃ and CaO, while Na₂O, MgO, MnO and others were present in smaller quantities. The sum of components in the ash composition analysis does not reach 100% due to the presence of additional minor constituents not listed in the composition, as well as the inherent uncertainty associated with the measurement of individual elements. Heavy metals such as Cr, Ni, Cu, Zn, Pb, Cd, and As were also found in the sludge.

Lead levels ranged from 27.4 to 58.6 mg/kg, zinc from 668 to 1701 mg/kg, and chromium from 36.0 to 237.5 mg/kg. Other metals, such as manganese, nickel, and copper, were observed in ranges of 200–338 mg/kg, 26.8–120.0 mg/kg, and 118–351 mg/kg, respectively.

Table 2

Characterization results for sewage sludge (subscript: ar — as received, db — dry basis).

Parameter	Unit	Value
Total moisture content M_{ar}	%wt	80.1
Ash content A_{db}	%wt	51.4
Volatile matter content VM_{db}	%wt	41.25
Net Calorific Value NCV	MJ/kg	9.4
Carbon content C_{db}	%wt	24.6
Hydrogen content H_{db}	%wt	4.57
Nitrogen content N_{db}	%wt	4.97
Sulfur content S_{db}	%wt	1.49
Chlorine content Cl_{db}	%wt	0.09
Ash Properties of Sewage Sludge		
Na ₂ O	%mass	0.533
MgO	%mass	2.09
Al ₂ O ₃	%mass	8.50
SiO ₂	%mass	40.6
P ₂ O ₅	%mass	11.49
K ₂ O	%mass	1.915
CaO	%mass	6.55
TiO ₂	%mass	0.937
MnO	%mass	0.117
Fe ₂ O ₃	%mass	12.60

Arsenic and cadmium concentrations were found to be 2.37–9.34 mg/kg and 0.47–1.57 mg/kg, respectively. The sludge samples used in the current work were characterized by high metal content with low variability in metal occurrence (see the Supplementary Material for details), which is consistent with sludge from other wastewater treatment plants.

3.2. Biochar characteristics

3.2.1. Effects of pyrolysis parameters on biochar yield, ash content, and pH

The results for biochar yield for the pyrolysis conditions studied are provided in Fig. 2 as a function of temperature, residence time and inert gas flow rate. For certain experiments conducted across a range of pyrolysis conditions, two biochar samples were evaluated to assess repeatability. As expected based on the pyrolysis literature, the biochar yield decreased as the pyrolysis temperature increased, which is attributed to the increased release of volatile matter at higher temperatures. The rate of decrease in biochar yield decreased as the temperature increased. For example, between 600 °C and 800 °C, the yield decreased by about 4.4% (from 61.4% to 57.0%). This suggests that at high temperatures most of the degradable organic material had already been volatilized, leaving a more thermally stable carbon structure. These findings are consistent with prior pyrolysis studies of biochar by Hossain et al. (2011) and Agrafioti et al. (2013). The effect of residence time on biochar yield (see Fig. 3) was also as expected. At higher temperatures, thermal degradation of the sludge biomass occurs more rapidly, reducing the influence of residence time on the biochar yield. As seen in Fig. 2, residence time has minimal effect on biochar yield for temperatures above 500 °C.

Fig. 3 shows the effects of pyrolysis temperature on biochar yield, ash content and pH. Residence time had little effect on the ash content in biochars produced at different temperatures. As the yield decreased with increased temperature, the ash content and pH increased. Specifically, the pH shifted from acidic values at lower pyrolysis temperatures to alkaline values at higher temperatures. The basic pH values are likely a result of the loss of acidic functional groups that decomposed at high temperatures. The shift in pH promotes the feasibility of using the pyrolysis product as an additive to acidic soils, and raising the pH of soil helps reduce the mobility of heavy metals (Brassard et al., 2019).

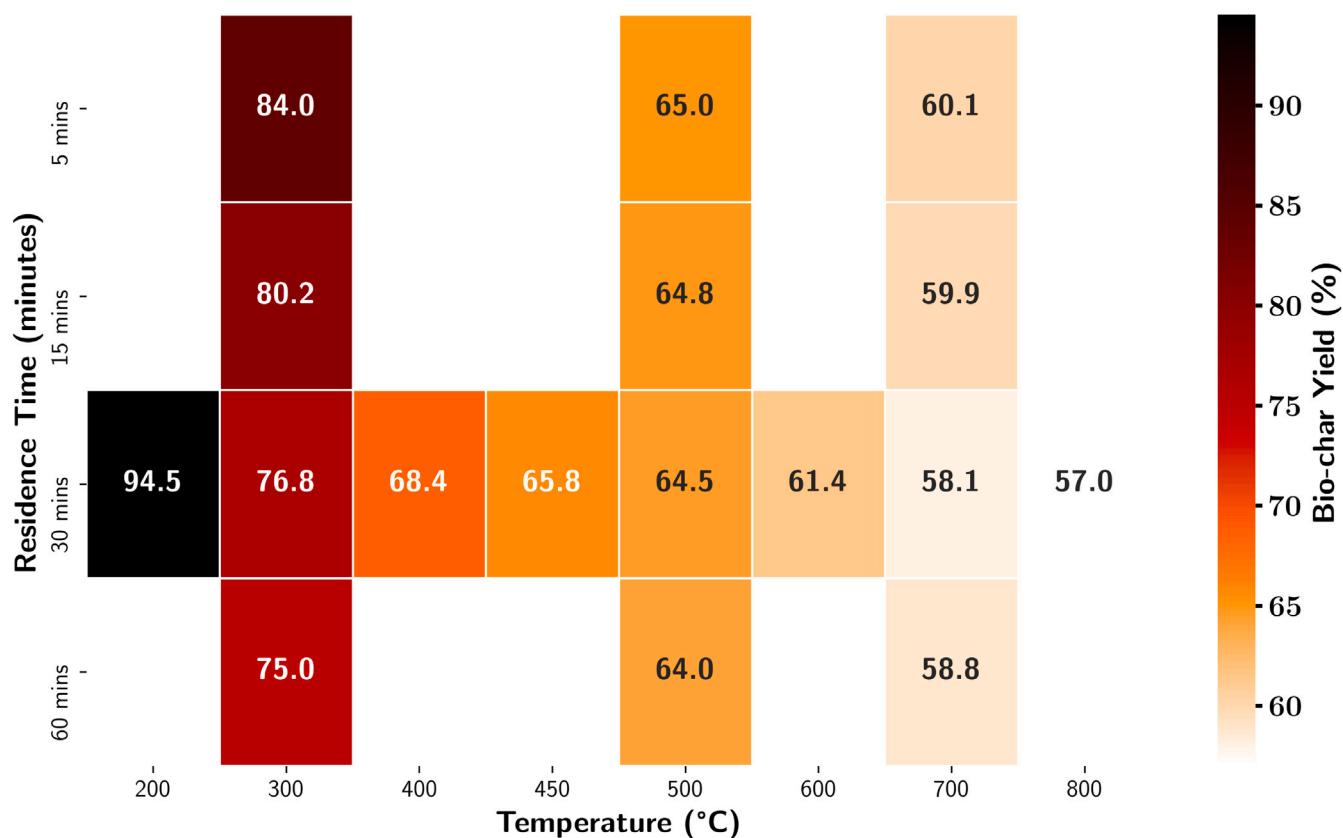


Fig. 2. Heatmap results for the effects of temperature and residence time on biochar yield for fixed inert gas flow rate at 0.5 dm³/min.

3.2.2. Effects of pyrolysis parameters on biochar physicochemical characteristics

Biochar composition was analyzed using ultimate analysis (Fig. 4) and FTIR spectroscopy (Fig. 5). Interpreting FTIR spectra for carbon materials is challenging due to overlapping functional group bands, especially for sludge-derived biochar with unique compositions and no standard reference spectra. Thus, FTIR analysis was combined with elemental analysis. Fig. 4a presents the elemental composition as a function of pyrolysis temperature. Changes in carbon (C) and hydrogen (H) content were consistent with sludge mass loss during pyrolysis. As pyrolysis temperature and residence time increased, C and H content in the char decreased, while the C share in the combustible part increased, and the H share decreased. The sulfur (S) content decreased steadily with temperature up to 500 °C, but increased slightly at 800 °C, suggesting S was bound in the noncombustible fraction. On a dry and ash-free basis, the C and S shares increased, while the H decreased as expected.

The H/C molar ratio data presented in Fig. 4b indicates biochar organic aromaticity. A ratio of ≤ 0.3 suggests condensed aromatic ring structures, while ≥ 0.7 indicates lower aromaticity (Jin et al., 2017). In this study, the H/C ratio decreased with higher temperature and residence time, confirming dehydrogenation and the formation of condensed aromatic structures. At 200 °C, the H/C ratio was 1.396, showing limited aromaticity, but at 800 °C, it decreased to 0.103, indicating a highly aromatic and stable biochar matrix. Longer residence times further reduced the H/C ratio. Biochars with H/C ratios ≤ 0.57 exhibit higher aromaticity, improving their resistance to oxidation, making them attractive for environmental applications like soil remediation (Brassard et al., 2019).

The effects of pyrolysis temperature on the biochar FTIR spectra are shown in Fig. 5. The spectra show clear shifts in key wavelength regions. As pyrolysis temperature increased, moisture content decreased (OH , wide band, 3700–3200 cm⁻¹). At 700 °C, this band is completely

absent, indicating no moisture remained. Aliphatic group content also decreased (stretching vibrations, C–H, two sharp bands of low intensity in the 3000–2800 cm⁻¹ range) with increasing temperature. Combined with the decreasing C and H content in the chars, the changes indicate decomposition and evaporation of hydrocarbon chains in the form of volatile components. Stretching C–O bonds increased significantly (wide, high-intensity band at 1200–1000 cm⁻¹) at higher temperatures, resulting from aliphatic bond decomposition (Fan et al., 2020). Also, increasing content of compounds containing elements from group 17 of periodic table, i.e., chlorine, bromine and iodine C–Cl, C–I, C–Br and/or increasing content of silicon–oxygen bonds (sharp low-intensity peaks between 800–500 cm⁻¹) can be observed as well. The content of stretching bonds indicate the presence of methylene groups at a similar level (C–H, medium intensity peaks in the 1600–1300 cm⁻¹ range).

Residence time had little effect on the FTIR spectra (details are provided in the Supplemental Material). At 500 °C, increasing residence time led to a gradual decrease in moisture content (O–H, broad band, 3700–3200 cm⁻¹) and an increase in the content of other bonds, including C–H, C–Cl, C–I, and C–Br. Inert gas flow rate had no significant effect on the biochar composition, as confirmed by proximate, ultimate and FTIR analyses.

The specific surface areas and pore sizes of the biochars produced at different pyrolysis conditions are presented in Fig. 6. The pore sizes were generally consistent, ranging from 7 to 14 nm (all analytical results are tabulated and provided in the Supplemental Material). As temperature increased to 400 °C, the specific surface area increased due to moisture evaporation and the removal of pore-clogging components. Between 500 and 700 °C, specific surface area decreased, likely due to material plastification and volatile release forming “bubbles”. At 800 °C, the specific surface area resumed the increasing trend with temperature. High surface area can improve soil physical properties (e.g., infiltration, water retention), improve soil interaction, and reduce heavy metal and organic compound bioavailability (Brassard

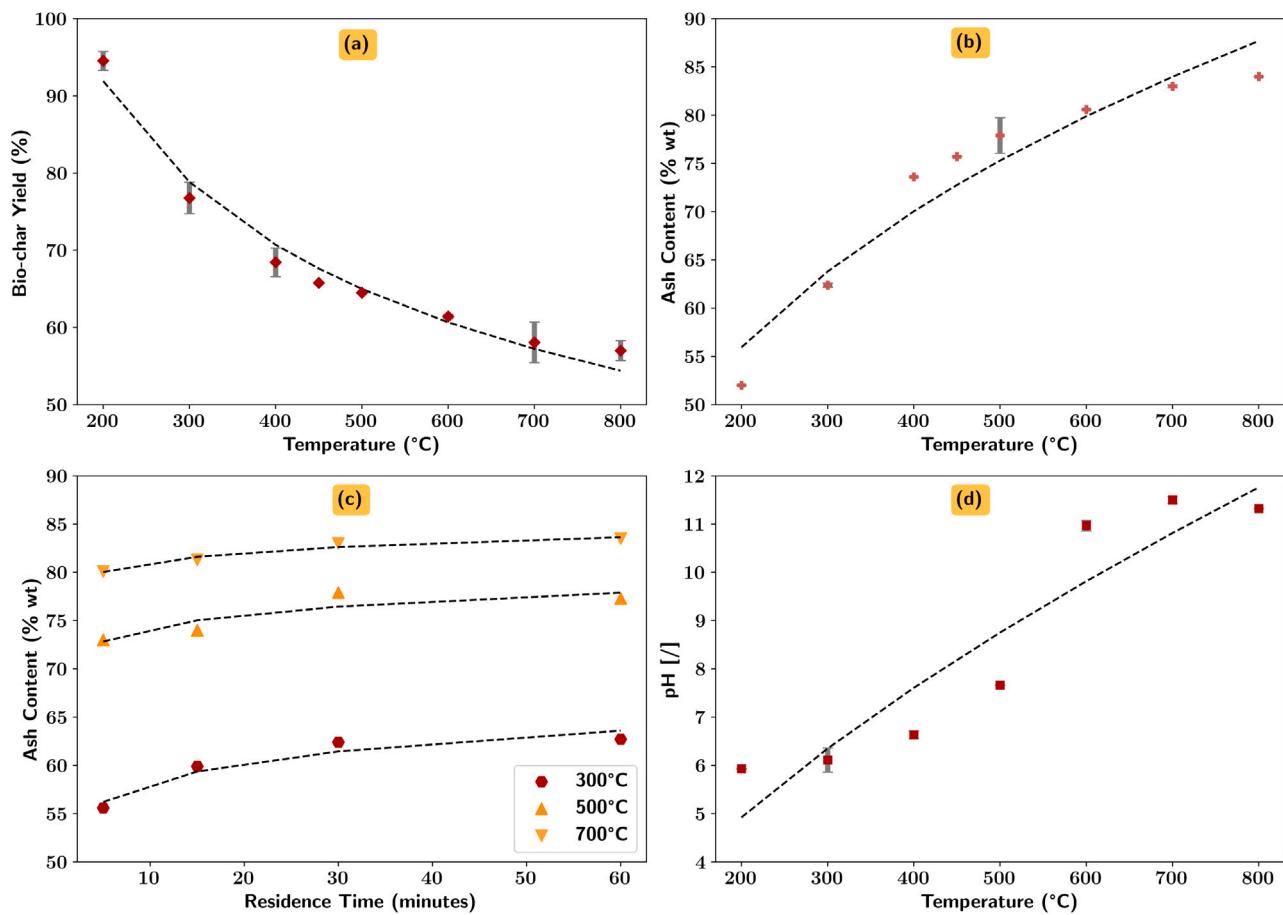


Fig. 3. Effects of pyrolysis conditions on biochar characteristics. (a) Biochar yield, (b) ash content, and (d) pH as functions of pyrolysis temperature at a constant residence time of 30 min and an inert gas flow rate of 0.5 dm³/min. (c) Ash content as a function of residence time at different pyrolysis temperatures. Error bars represent the standard deviation. The lines are fits to the data to highlight experimental trends.

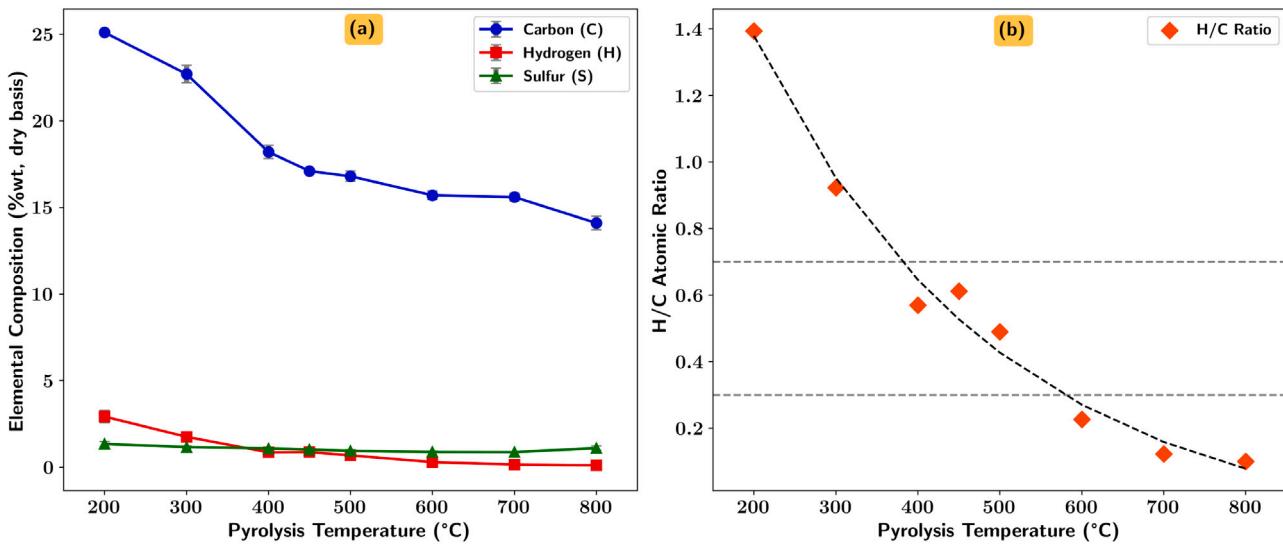


Fig. 4. Effects of pyrolysis temperature (30 min residence time, inert gas flow of 0.5 dm³/min) on biochar composition (dry basis) (a) C, H and S elemental composition, (b) H/C ratio. Error bars represent the standard deviation. The lines are fits to the data to highlight experimental trends.

et al., 2019). The N₂ adsorption–desorption isotherms and corresponding BJH pore size distribution curves of all biochars are provided in the Supplementary Material.

Reactor residence time had different effects on specific surface area at the different reactor temperatures studied. At 700 °C, longer residence times reduced specific surface area, which is linked to material

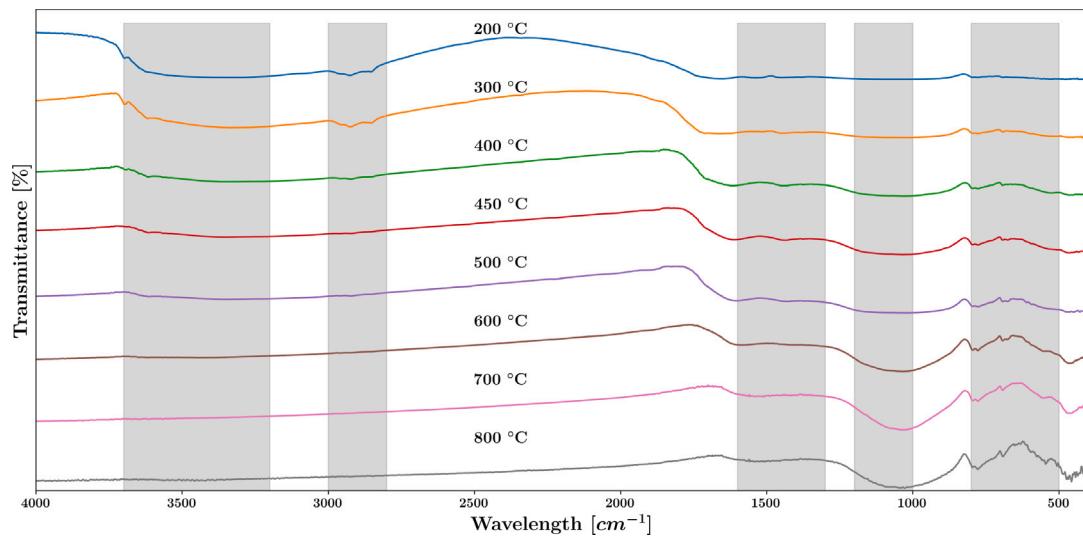


Fig. 5. Effects of pyrolysis temperature (30 min residence time, inert gas flow of $0.5 \text{ dm}^3/\text{min}$) on biochar FTIR spectra.

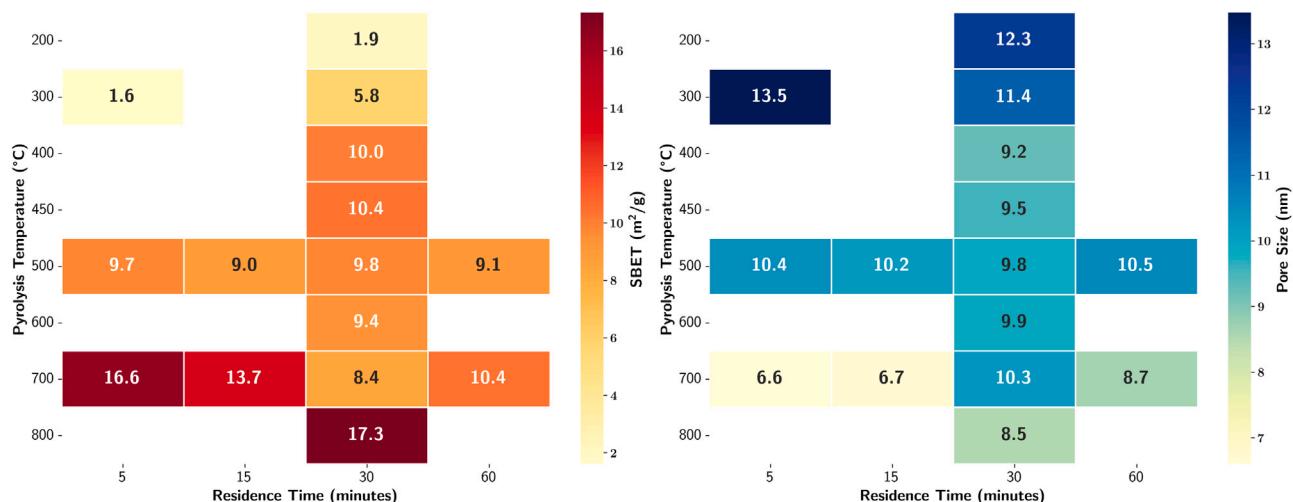


Fig. 6. Heatmap results for the effects of temperature and residence time on specific surface areas and pore sizes for fixed inert gas flow rate at $0.5 \text{ dm}^3/\text{min}$.

plastification (Lu et al., 1995). The data indicate residence times of less than 30 min released insufficient volatiles to significantly alter the surface of the biochar, but after 30 min, volatile loss has sufficient time to affect the surface of the biochar particles. The biochar samples from the 30 min pyrolysis condition showed distinct results from the other samples, indicating process interruption during intense “bubbling”. This observation is further supported by SEM images (provided in the Supplementary Material), which show a transition from rough and porous surfaces at $700 \text{ }^\circ\text{C}$ (5 to 15 min residence time) to smoother and partially-fused surfaces at $700 \text{ }^\circ\text{C}$ 30 min residence time, indicative of pore coalescence. The corresponding BJH pore size distribution curves (also provided in the Supplementary Material) show a decrease in total pore volume and a shift toward larger mesopores with increasing residence time. Whereas at $500 \text{ }^\circ\text{C}$, changes in pyrolysis residence time lacked a clear trend with respect to specific surface area, possibly due to weaker volatile release from the plastic-like structure.

The analysis of the mineral content of the biochar (from XRF analysis) results showed that potassium (K) and phosphorus (P) concentrations increased slightly with higher pyrolysis temperatures, as seen in Fig. 7. The increase in concentration is due to the breakdown and loss of organic matter and the retention of stable inorganic components. Residence time and gas flow rate affected the concentrations to a lesser extent. Similar patterns were observed for other elements like

Si, Al, Ca, Fe, and Mg (see Supplemental Material for details). The XRF spectra attributed to Cl decreased with increasing pyrolysis temperature and residence time. However, due to the high quantification limit ($QL=0.10\%$), chlorine content in the biochar could not be determined.

3.2.3. Effects of pyrolysis parameters on heavy metal content in biochar

The heavy metals concentrations of all sludge-derived biochar samples are tabulated in the Supplementary Material, along with the enrichment and residual rates. All biochars produced in this work met the International Biochar Initiative's guidelines (International Biochar Initiative, 2024), with heavy metal content within the proposed limits. ER and RR results are presented in Figs. 8 and 9, respectively, for As, Cd, Pb, Mn, Zn, Cr, Cu, and Ni. Recall, ER reflects the concentration of heavy metals in biochar, while the RR indicates the fraction of heavy metals retained after pyrolysis. ER and RR values for Pb, Mn, Zn, Cr, Cu and Ni were minimally sensitive to the different pyrolysis conditions, each showing trends similar to the Pb data presented in Figs. 8 and 9, with ER increasing from ~1 at $200 \text{ }^\circ\text{C}$ to ~1.4 to 1.7 at $800 \text{ }^\circ\text{C}$, and RR values decreasing from 100% at $200 \text{ }^\circ\text{C}$ to ~75% to 90% at $800 \text{ }^\circ\text{C}$. The ER and RR results for Pb, Mn, Zn, Cr, Cu and Ni showed low sensitivity to reactor residence time and inert gas flow rate. As and Cd were the exceptions to the other heavy metals.

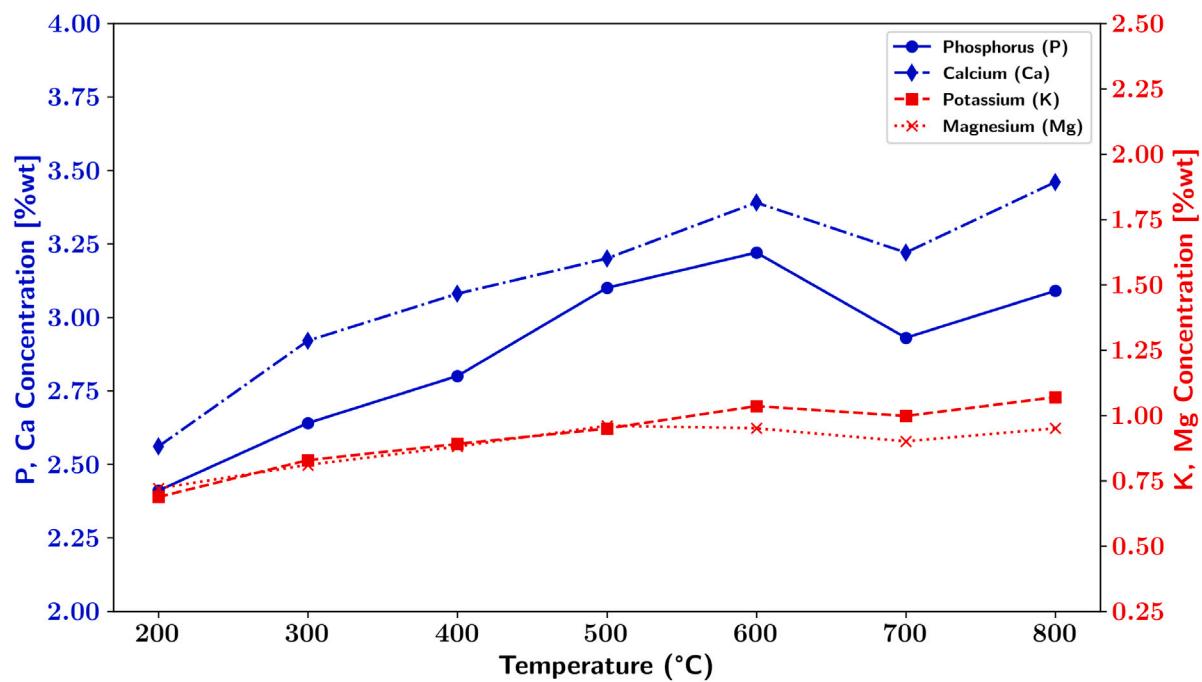


Fig. 7. Effects of pyrolysis temperature (30 min residence time, inert gas flow of 0.5 dm³/min) on mineral contents.

The residual rates of HMs in the biochar samples indicate that the majority of the heavy metals were predominantly retained in the biochar rather than distributed in other pyrolysis products, such as the bio-oil and non-condensable gas. This is consistent with observations reported in Liu et al. (2018), Li et al. (2020), where the decomposition of the organic matter in the sewage sludge into oil and syngas resulted in increased heavy metal concentrations in the biochar. HMs can also be retained in the biochar due to HM adsorption by organic matter and bio-flocs (Wang et al., 2019).

Alcock et al. (1984) classified heavy metals into three volatility categories: low-volatile (Ni, Cr, Co and Cu), semi-volatile (As, Pb, Zn, and Ti), and highly volatile (Cd). Heavy metal volatilization predominantly occurs at temperatures exceeding 600 °C (Lane et al., 2020). At around 900 °C, Pb and Cd show volatilization rates from 80 to 100%, while Zn and Cu volatilize at slightly lower rates, ranging from 40% to 80% above 1000 °C (Lane et al., 2020; Han et al., 2024). In this work, heavy metal residual rates during pyrolysis were approximately constant for all metals tested except for As and Cd.

Lower ER values were observed for As at both lower and higher pyrolysis temperatures, indicating a tendency of As to migrate during pyrolysis. As temperatures increased, especially above 500 °C, more As transported out of the biochar. The residue rate of As decreased to about 30% at 800 °C, indicating that nearly 70% was transformed to liquid and non-condensable gas phases during sewage sludge pyrolysis. Han et al. (2016) reported that 24.8–63.1% of As escaped during sewage sludge pyrolysis at temperatures of 450–850 °C. In other studies of sludge pyrolysis in the range of 250–850 °C (Zhang et al., 2021), similar As behavior was observed, with the maximum release rate reaching more than 80% (at 850 °C). As₂O₅ and to As₂O₃ volatilize at low temperatures during pyrolysis due to the low melting point of 300 °C. A similar pattern was observed for ER and RR of Cd, which showed low values particularly at higher temperatures, consistent with the high volatility of Cd. Previous work indicated a substantial reduction in Cd concentration at temperatures exceeding 600 °C (Wang et al., 2016). The behavior is attributed to Cd predominantly existing in carbonate form, which readily volatilizes during pyrolysis at temperatures above 600 °C (Udayanga et al., 2018). Research on the fast and slow pyrolysis of various sludges also showed significant levels of Cd release at temperatures above 650 °C (Han et al., 2017). Longer residence

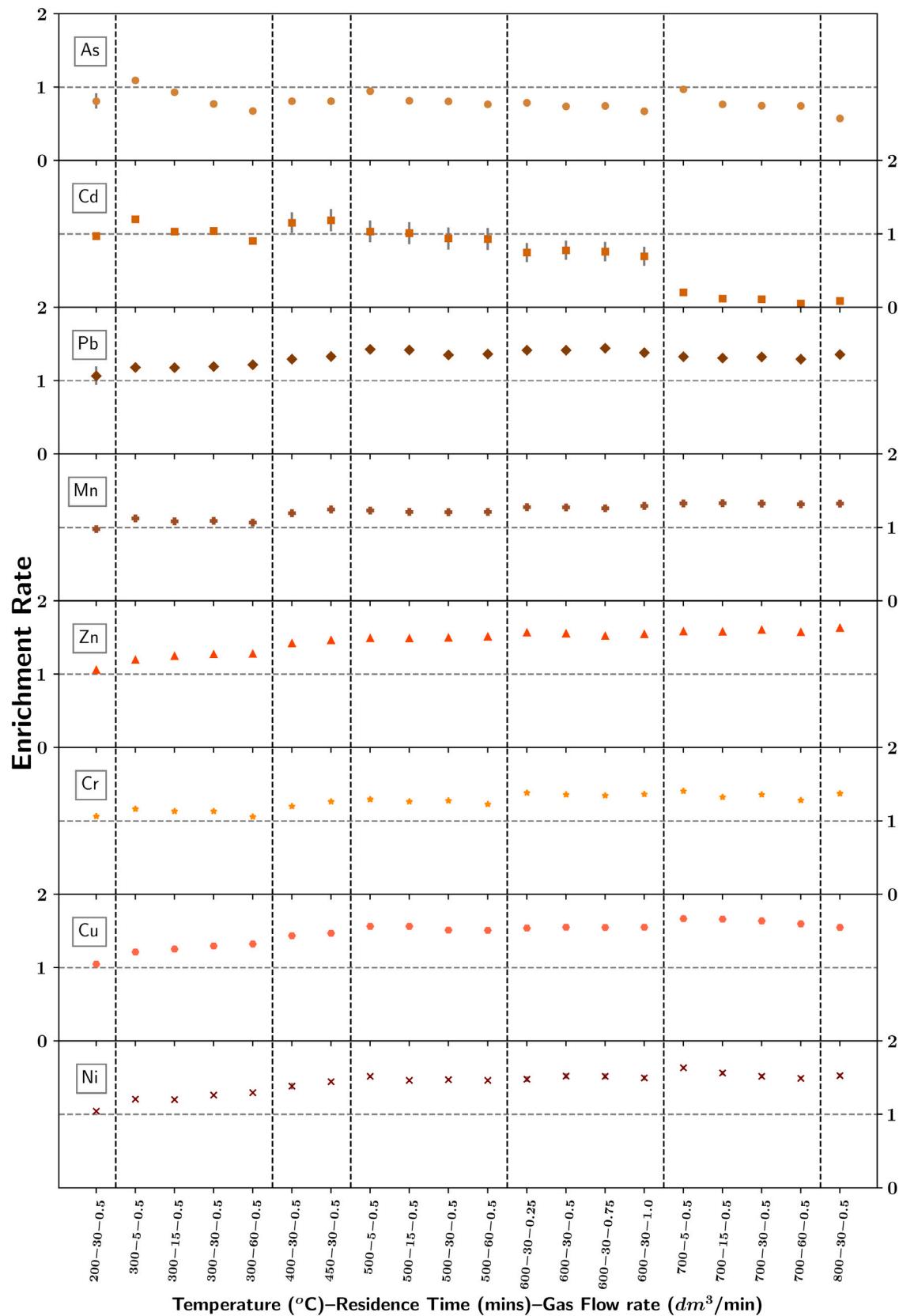
times slightly improved the volatilization of As and Cd, resulting in marginally lower ER and RR values.

While the ER and RR data for the other HMs studied did not show strong sensitivity to the pyrolysis conditions studied in the current work, there are some key observations. Zn exhibited the highest retention in the biochar with RR of 93% at 800 °C. Cu, Ni, Cr and Mn exhibited consistently high ER values across varying pyrolysis temperatures, residence times, and gas flow rates. These metals showed strong thermal stability, with their ER values typically exceeding 1, even at temperatures as high as 600–700 °C. The high ER suggests that these metals are more likely to remain concentrated in the biochar, making them less volatile and more stable during pyrolysis. Similar levels of Pb in the 450–850 °C range were obtained for slow pyrolysis, while fast pyrolysis was characterized by much higher Pb release at 850 °C (Han et al., 2017). Similar levels of Cr, Mn, Ni and Cu were obtained in other studies of sludge pyrolysis (Zhang et al., 2021). These metals are known for their stability, ensuring that a significant portion remains in the biochar post-pyrolysis (Kistler et al., 1987) and their high RR values observed here corroborate this characteristic.

The experiments conducted at three different temperatures (300, 500 and 700 °C) with varying residence times (5, 15, 30 and 60 min) made it possible to estimate the HM kinetics assuming first-order homogeneous decomposition with an asymptote dependence on time and temperature (see Eq. (4)). The metal removal rates are provided in the Supplementary Material. The kinetic parameters are presented in Table 3. The activation energies indicate the energy barrier for reaction, and the results show Cd requires significantly higher energy than metals such as Cr. However, the high pre-exponential factor for Cd indicates the frequency of effective reactions is high when the energy threshold is met.

3.2.4. Effects of pyrolysis parameters on chemical form of heavy metals in biochar

The bioavailability and ecotoxicity of heavy metals in the environment depend on their concentrations and on their chemical speciation (Leng et al., 2014). The acid-soluble/exchangeable fraction (F1) demonstrates high bioavailability for associated metals. Following F1, the reducible fraction (F2) ranks second in metal mobility due to its thermodynamic instability, allowing the metals in this fraction to be



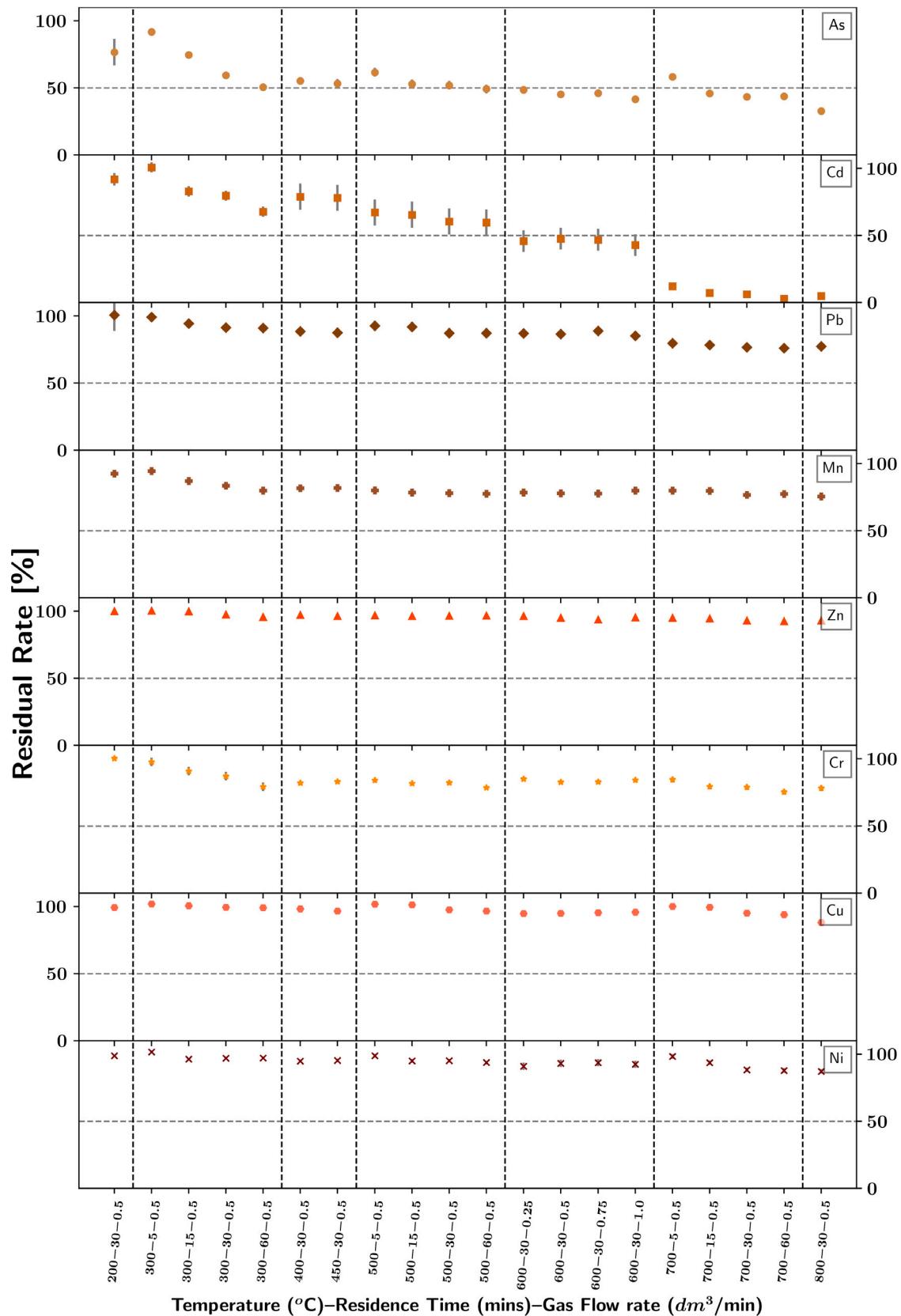


Fig. 9. Effects of pyrolysis conditions on the residual rates of heavy metals: As, Cd, Pb, Mn, Zn, Cr, Cu, and Ni. Error bars represent the standard deviation.

Table 3

Kinetic parameters of heavy metal removal during sewage sludge pyrolysis.

Element	E_m [kJ/mol]	A_m	Coefficient of determination (R^2)
As	11.64	0.154	0.976
Cd	31.17	4.099	0.921
Pb	13.76	0.053	0.907
Mn	10.75	0.046	0.878
Zn	17.08	0.029	0.866
Cr	9.56	0.028	0.825
Cu	10.43	0.005	0.969
Ni	11.32	0.015	0.977

mobilized under anoxic conditions. So, F1 and F2 are recognized as fractions with direct environmental impact. In an oxidizing atmosphere, the oxidizable fraction (F3) can be readily transformed and mobilized, categorizing F3 as a potential impact fraction (Leng et al., 2014; Li et al., 2023). Meanwhile, metals bound to the residual fraction (F4) are predominantly held within primary and secondary minerals, integrating metals into stable crystal structures that resist release under typical natural conditions, thus identifying F4 as a stable fraction. To confirm the accuracy of the BCR results, the recovery of the heavy metals in the current work was evaluated by determining the ratio of the sum of the mass fractions (i.e., F1 + F2 + F3 + F4) obtained from the sequential extraction procedure to the pseudo-total content of the metals in the sludge and biochar samples.

The results for the effects of the pyrolysis conditions on the fractionation of the heavy metals in the biochar are provided in Fig. 10. The composition fractions for each metal in the sewage sludge (SS) feedstock are provided for reference. The sewage sludge data show different levels of environmental mobility and potential bioavailability for the different metals. Arsenic in the sludge was primarily in the exchangeable (F1, 30.4%) and reducible (F2, 34.3%) fractions, with only 21.4% in F4. Cd in the sludge had high bioavailability, with 68.4% in F2 and only 2.8% in F4. The sewage sludge data indicate As and Cd in sewage sludge have higher potential for leaching and ecological impact. In contrast, Pb and Cr were more stable in the sewage sludge, with 56.9% and 75.0% in F4, respectively. Mn and Zn were moderately mobile in the sewage sludge, with 41.2% of Mn and 38.3% of Zn in F1, suggesting potential environmental risks if untreated.

Results from the current work show pyrolysis significantly affected the fractionation of the metals, shifting the content toward more stable forms as reactor temperatures increased. For As, the residual fraction (F4) increased to 70.9% at 200 °C, reaching 88.7% by 800 °C. The increase indicates a major reduction in As bioavailability, immobilizing the metal in a more stable form. The changes in the mode of As occurrence correspond with the As retention rate, suggesting some arsenic species volatilized at low temperatures. Cd shows a significant transformation, with the F4 fraction increasing from 2.8% in SS to 94.2% at 800 °C, demonstrating effective stabilization through pyrolysis (however, the retention rate data indicate most of the Cd is not retained in the biochar). The results confirm As and Cd become significantly less mobile and less bioavailable after pyrolysis, especially at temperatures above 500 °C.

Lead, already somewhat stable in the sewage sludge, shows further immobilization with pyrolysis, with the Pb F4 residual fraction peaking at 95.0% at 300 °C, and maintaining high stability at higher temperatures. Cr, already largely stable in the sewage sludge, maintains a high F4 proportion, reaching 89.0% at 800 °C. The findings show that Pb and Cr have low environmental mobility and availability in the sewage sludge, and remain high after pyrolysis. Wong et al. (2001) observed that over 90% of Cr was bound to organic and residual phases, while Pb was mainly associated with minerals in sludges from treatment plants in Hong Kong. Walter et al. (2006) found that more than 95% of Cr in sewage sludge was concentrated in the last two fractions (F3 and F4). The results of the current work are consistent with the prior studies, where during pyrolysis, the breakdown and transformation of organic

materials likely cause Pb and Cr to shift from organic-bound phases (F3) to more stable, less extractable forms in the residual phase (F4).

For Mn and Zn, the stabilization effects of pyrolysis were more moderate. The F4 fraction of Mn increased from 16.0% in the sewage sludge to 42.3% at 500 °C and remained steady around 41.2% at 800 °C, suggesting partial but incomplete immobilization. Zn showed a similar trend, with the residual fraction increasing from 3.5% in the sewage sludge to 48.5% at 800 °C, showing increased stability but some remaining potential for mobility. For Cu, pyrolysis significantly improved stability, with the residual fraction (F4) increasing from 7.7% in untreated sludge to 75.3% at 800 °C, indicating effective immobilization and reduced bioavailability. In contrast, Ni remained predominantly stable across all temperatures, with the residual fraction (F4) consistently high (55.4–68.3%). However, the exchangeable fraction (F1) increased slightly at some pyrolysis conditions suggesting some potential for mobility. The fractionation of heavy metals in the biochar samples for pyrolysis at 300 °C at a range of residence times is provided in the Supplementary Material. For all metals considered, as the pyrolysis time increased, the share of the F4 fraction increased. In particular, large changes (increases of > 10%) were observed for Zn and Cu, moderate changes (2%–6%) were observed for Cd, As, Ni, and Cr, and the smaller changes (< 1%) were noted for Pb and Mn. Similar trends for Cr, Cu, Ni, Pb, and Zn in terms of the relationships between the source sewage sludge and processed biochar have been reported in the prior pyrolysis study by Chen et al. (2015) where heavy metals were intentionally added to sewage sludge.

3.2.5. Risk assessment of heavy metals in pyrolysis biochars

The contamination and potential ecological risk factors and the potential ecological risk index were calculated from the heavy metal analysis, and the results are shown in Fig. 11. The untreated sewage sludge contained high levels of heavy metals, which pose significant ecological and environmental risks. Particularly, Cd and Zn exhibit high toxicity and contamination levels, with C_f values of 34.0 and 27.4, respectively. These metals also dominate E_r for sewage sludge, with Cd contributing an extremely high risk ($E_r=1022$) and Zn posing a considerable risk ($E_r=27.4$). Cu, As, and Pb also showed moderate to high contamination of the unprocessed sludge. The PERI of the sewage sludge feedstock was alarmingly high, showing the need for effective remediation strategies.

The results of the current work are consistent with prior studies that demonstrate pyrolysis as a promising solution to mitigate metal contamination in sewage sludge (Jin et al., 2016; Li et al., 2022). Specifically, the results presented here show significantly reduction in the contamination and ecological risks of toxic metals. For example, Zn transitions from very high contamination in sewage sludge to clean levels ($C_f < 1.1$) at temperatures above 500 °C. Also, Cd, which contributes the most to ecological risk, has a high reduction in E_r , effectively lowering its classification from very high to moderate risk. Cu and As contamination also decreased, with C_f values dropping to less than one at 700 °C. Pb contamination decreased even more significantly, reaching negligible levels ($C_f < 0.2$) by 500 °C. The results demonstrate the effectiveness of pyrolysis in stabilizing or volatilizing heavy metals.

It is well known that the temperature and residence time determines the effectiveness of pyrolysis. The higher temperatures studied in the current work were particularly effective in reducing the contamination and ecological risks of the volatile metals Zn, Cd, and Pb. Significant risk reduction for Cd occurred between 500 °C and 600 °C, with E_r decreasing to manageable levels. Zn achieved a “clean” classification above 500 °C due to the high immobilization. Residence time further influenced the extent of risk reduction. At 300 °C, longer residence times showed greater reductions in C_f and E_r compared with shorter durations. However, the effect of residence time became less pronounced at higher temperatures, where thermal decomposition and volatilization of metals dominated the risk mitigation process.

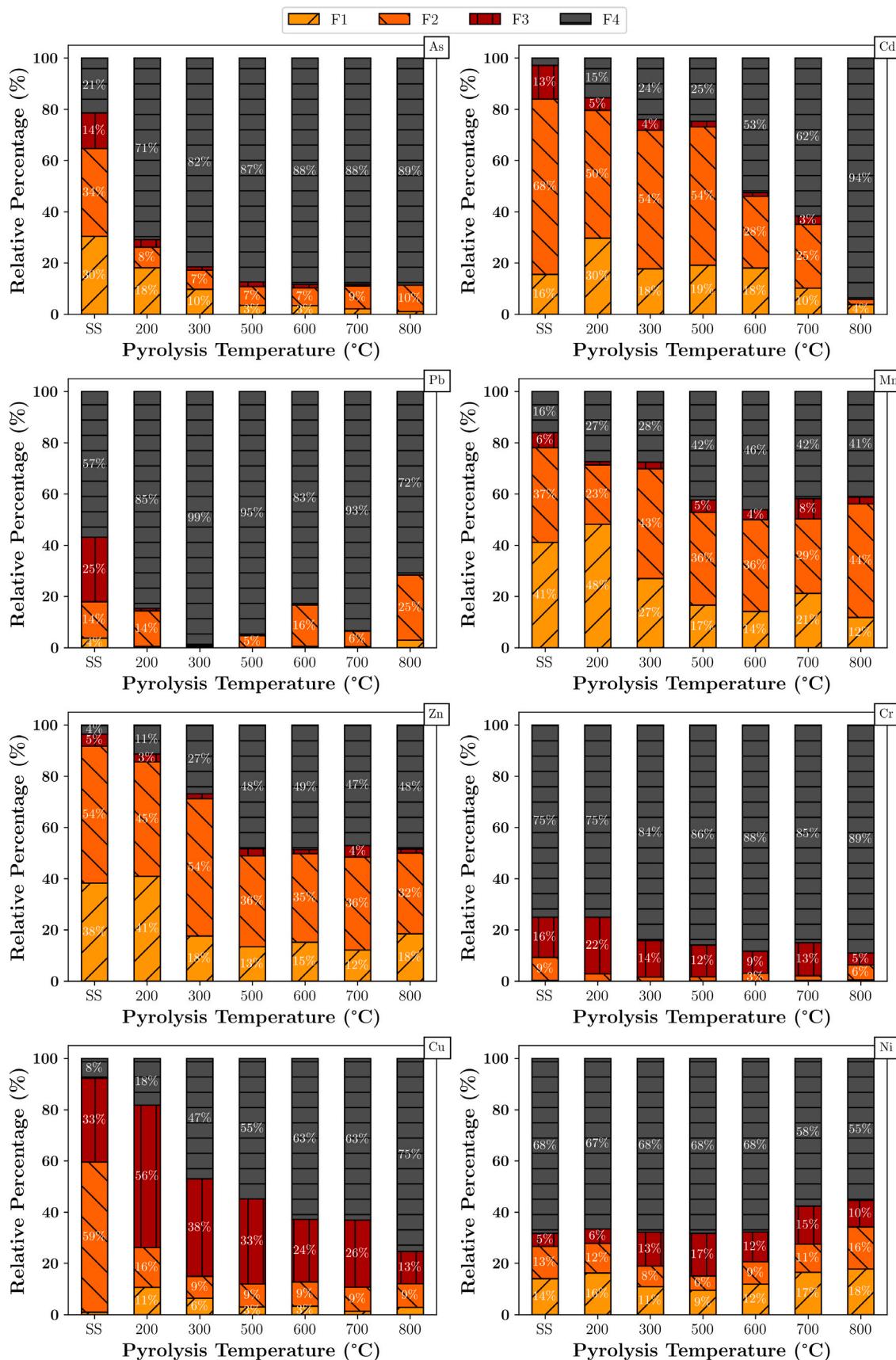


Fig. 10. Effects of pyrolysis temperature (0.5 dm³/min inert gas flow rate, 30 mins residence time) on fractionation and bioavailability of heavy metals in biochar. The values for the sewage sludge (SS) feedstock are provided for comparison.

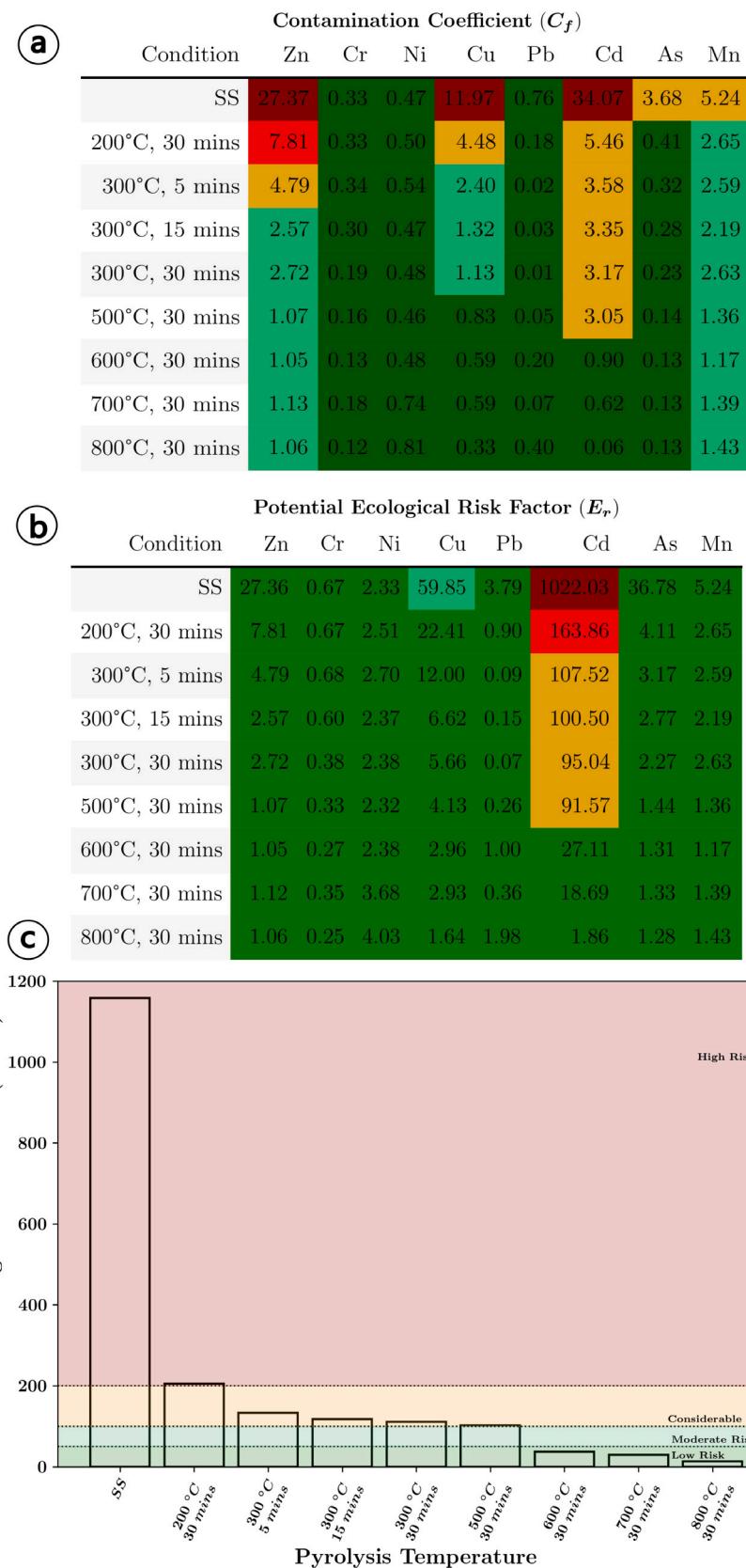


Fig. 11. Results for assessment of the heavy metals in the pyrolysis biochars for (a) Contamination factor, (b) potential ecological risk factor, and (c) potential ecological risk index (PERI). Values for the feedstock sewage sludge (SS) are provided for comparison. The color coding in the table ranges from dark green (no risk) to dark red (high risk).

Untreated sludge had an alarming PERI of 1158, indicating significant ecological hazards primarily due to the toxic metals cadmium and zinc. The PERI gradually decreased with higher pyrolysis temperature and longer residence time. At moderate temperatures, e.g., 200 °C and 30 mins residence time, the biochar heavy metal PERI decreased, moving the risk classification from very high to high. Higher temperature combined with extended residence times, reduced the PERI further. However, the most significant decrease in PERI values was observed for temperatures above 500 °C. The results demonstrate higher temperatures are crucial to achieve low-risk levels, making biochar safer for potential environmental applications.

4. Conclusions & future work

Disposal of sewage sludge, a key byproduct of wastewater treatment, can pose significant challenges, particularly when the sludge contains high concentrations of regulated contaminants. Pyrolysis offers a sustainable solution for managing sludge and producing value-added products like biochar. This study systematically evaluated the influence of pyrolysis parameters, including temperature (200–800 °C), residence time (5–60 min) and inert gas flow rate (0.25–1.0 dm³/min), on the properties of biochar derived from sewage sludge, including important characteristics for environmental applications like soil amendment. The biochars produced at temperatures above 600 °C had H/C ratios below 0.57, improving their suitability for environmental applications like soil remediation. The biochars produced at temperatures above 600 °C also exhibited high pH levels (> 11) and nutrient content, including more than 3.0% total phosphorus, 3.2% calcium and approximately 1.0% potassium and magnesium. Higher pyrolysis temperatures contributed to increased surface area, potentially further improving biochar functionality. It should be noted that the conclusion regarding the negligible influence of the inert gas flow rate applies only to the tested conditions (600 °C, 30 min). Additional experiments at varied temperatures and residence times are needed to comprehensively assess the impact of inert gas flow rate on the properties of the resulting biochar.

Analysis of the heavy metal content of the sewage sludge and the biochars showed pyrolysis not only reduced harmful elements like arsenic (As) and cadmium (Cd) in the biochar, but pyrolysis also effectively increased immobilization of most of the heavy metals within the biochar matrix (except for Ni). The study also confirmed that pyrolysis was highly effective at reducing heavy metal contamination and ecological risks in sewage sludge. BCR sequential extraction showed the heavy metals in the biochar produced at temperatures above 600 °C were largely immobilized in oxidizable and residual fractions, minimizing their environmental risk. In particular, the untreated sewage sludge had a critical PERI value of 1158, mainly due to high levels of Cd ($E_r=1022$) and zinc ($C_r=27.4$), and pyrolysis significantly reduced the PERI values, e.g., to below 50 for pyrolysis at 600 °C and as low as 13.52 at 800 °C, classifying the biochar as low-risk. The results suggest that heavy metals undergo initial immobilization below 300 °C, partial release during organic matter decomposition, and eventual stabilization or volatilization above 500 °C, depending on the speciation and thermal stability. Further studies are required to clarify the transformation pathways. The findings demonstrate that pyrolysis at higher temperatures can effectively decrease the content of toxic metals in the biochar and stabilize the residual metals remaining in the biochar, making the biochar a potentially sustainable and environmentally safe material. However, additional analysis of harmful organic components, such as polycyclic aromatic hydrocarbons (PAH), persistent organic pollutants (POPs), and per- and polyfluoroalkyl substances (PFAS) should be conducted to ensure the safety of biochar for soil amendment and other applications. Optimization of the pyrolysis parameters, like heating rates and feedstock pre-treatment, may offer further improvement of the biochar quality and environmental performance.

This work demonstrated pyrolysis as a practical method for converting sewage sludge into biochar, stabilizing heavy metals within

a carbon matrix to reduce leachability and environmental risks. Adhering to safety standards, the results of this work offer a strong foundation to scale sustainable sludge management solutions, with particularly effective outcomes for volatile metals like Zn, Cd, As, and Pb at higher pyrolysis temperatures (>500 °C), making pyrolysis an attractive process for urban wastewater treatment applications. Future research should include pilot-scale or continuous pyrolysis experiments to better simulate industrial conditions. The economic feasibility of sludge pyrolysis largely depends on regional sludge disposal costs and regulatory policies. Although the process is energy-intensive, the cost-effectiveness could improve if the resulting biochar proves safe and beneficial for environmental applications, particularly given the nutrient content of the biochar (e.g., phosphorus). Regulatory constraints and environmental risk assessments will also play a critical role in determining the applicability and commercialization potential of this approach.

CRediT authorship contribution statement

Dorota Makowska: Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Manikandan Pandiyan:** Writing – original draft, Visualization, Software, Methodology, Formal analysis. **Katarzyna Kapusta:** Investigation, Formal analysis. **Karolina Kolarz:** Investigation. **Zuzanna Stypka:** Investigation. **André L. Boehman:** Writing – review & editing. **Margaret S. Wooldridge:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.jenvman.2025.127888>.

Data availability

Data will be made available on request.

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