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The fate and mobility of chromium, arsenic and zinc in municipal sewage sludge during the co-pyrolysis process with organic and inorganic chlorides

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Co-pyrolysis is an efficient approach for municipal sewage sludge (SS) treatment, facilitating the production of biochar and promoting the stabilization and removal of heavy metals, particularly when combined with chlorinated materials. This study explores the impact of pyrolysis temperatures (400 °C and 600 °C) and chlorinated additives (polyvinyl chloride (PVC) as an organic chloride source and ferric chloride ($FeCl_3$) as an inorganic chloride source) at 10% and 20% concentrations, on the yield, chemical speciation, leachability, and ecological risks of arsenic (As), chromium (Cr), and zinc (Zn) in biochar derived from SS. The results revealed that increasing the pyrolysis temperature from 400 to 600 °C significantly reduced biochar yield due to enhanced volatilization of organic components, as well as the removal of heavy metals in interaction with chlorinated materials. Chlorinated additives distinctly influenced heavy metal behavior. PVC treatments at 600 °C effectively reduced the total concentrations of As and Zn by 60% and 88.3%, respectively, while $FeCl_3$ reduced Cr concentrations by up to 72.5%. Chemical speciation analysis showed that PVC treatments increased the residual fractions of As and Zn, reducing their bioavailability and environmental risk. In contrast, $FeCl_3$ promoted the transformation of Cr into oxidizable fractions, enhancing its stability. TCLP results confirmed the effectiveness of both additives in reducing heavy metal leachability, with PVC at 600 °C demonstrating superior performance for As and Zn, and $FeCl_3$ excelling in Cr stabilization. Ecological risk index assessments revealed that PVC treatments consistently resulted in lower RI values at both temperatures and concentrations, keeping them below the low-risk threshold. In contrast, $FeCl_3$ treatments exhibited elevated risk levels, especially at higher concentrations and temperatures, reaching moderate to considerable risk categories. Overall, PVC treatment at 600 °C proved to be the most effective strategy for reducing As and Zn leachability and enhancing biochar stability. While $FeCl_3$ demonstrated better performance in Cr stabilization, these findings highlight the importance of selecting appropriate chlorinated additives based on the target heavy metal for optimizing biochar production and minimizing environmental impacts effectively.

Keywords Co-pyrolysis, Heavy metal stabilization, Sewage sludge biochar, Chlorinated additives, Ecological risk assessment

The rapid growth of urban populations has led to a significant increase in the production of municipal SS, an unavoidable byproduct of wastewater treatment processes[1]. This escalation presents significant challenges for its disposal and necessitates the development of effective management strategies to enable its potential reuse. The presence of harmful pathogens, along with various organic and inorganic pollutants, makes the direct disposal or agricultural application of SS without adequate stabilization a considerable risk to human health and the environment[2]. Consequently, extensive research efforts are underway to address these risks by focusing on the degradation of organic pollutants, stabilization of heavy metals, and reduction of pathogenic agents, while simultaneously improving the agricultural applicability of SS[3].

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Common management techniques for SS include chemical stabilization, composting, anaerobic-aerobic digestion, and thermal stabilization, each with its unique advantages and disadvantages[4]. Given the increasing recognition that conventional disposal methods are neither economically sustainable nor environmentally viable, thermal processes are anticipated to become the primary strategy for SS management in the future[5].

Pyrolysis, a thermal treatment method, offers the dual advantages of reducing the volume of SS and mitigating associated environmental risks while converting SS into valuable products such as biochar, biogas, and biofuels[6]. Biochar, a carbon-rich solid generated during the pyrolysis of biomass under oxygen-limited conditions, functions as a nutrient-dense fertilizer. Its rich content of carbon, nutrients, and minerals significantly improves its effectiveness as a soil amendment[7]. This substance is highly regarded for its effectiveness in carbon sequestration, pollutant removal, and soil remediation[8,9]. Currently, biochar derived from SS is recognized as an efficient pollutant adsorbent[10] and a promising electrocatalyst for fuel cells[11].

Research has demonstrated that pyrolysis effectively eliminates organic pollutants, pathogens, and pharmaceutical residues from sludge[6] and stabilizes certain heavy metals[12,13]. While immobilizing heavy metals in biochar can mitigate their mobility and leaching[14], research indicates a considerable risk of heavy metal leaching into the soil following the application of biochar derived from SS[15]. This risk is primarily linked to alterations in soil conditions. Therefore, the removal of heavy metals, rather than their stabilization within SS, is undoubtedly a more effective and superior strategy.

The evidence suggests that the thermochemical treatment of SS and soil with chlorine (Cl) donors significantly enhances the efficiency of heavy metal removal[16–18]. Consequently, the use of chlorine donors in co-pyrolysis is unquestionably a more effective strategy compared to pyrolysis alone. Heavy metals in SS primarily exist in the form of heavy metal oxides, which are difficult to remove through thermal treatment alone because of their high boiling points and low vapor pressures[18]. In contrast, thermochemical treatment is more effective, as it converts heavy metal oxides into heavy metal chlorides, which have lower boiling points and higher vapor pressures, thereby facilitating their removal[18]. The interaction between heavy metals and chlorine occurs via two distinct pathways: direct chlorination, depicted in Eq. 1, and indirect chlorination, outlined in Eq. 2 to 5[19]. In the case of indirect chlorination, chlorine acts as a donor, reacting with either oxygen or water to produce chlorine gas (Cl_2) and hydrochloric acid (HCl). These byproducts subsequently react with heavy metals, increasing their removal, as demonstrated in Eq. 2 to 5.

$$MO + X - Cl_2 \rightarrow MCl_2 + X - O \tag{1}$$

$$X - Cl_2 + \frac{1}{2}O_2 \rightarrow X - \mathrm{O} + Cl_2 \tag{2}$$

$$M - O + Cl_2 \rightarrow M - Cl_2 + \frac{1}{2}O_2 \tag{3}$$

$$X - Cl_2 + H_2O \rightarrow X - \mathrm{O} + 2HCl \tag{4}$$

$$MO + 2HCl \rightarrow MCl_2 + H_2O \tag{5}$$

where MO: heavy metal oxides, X: metals, MCl_2: chlorinated heavy metals, X–O: metal oxides, M: heavy metals, X–Cl_2: Cl-donors, MCl_2: chlorinated heavy metals.

The production of Cl_2 or HCl during indirect chlorination is essential for the volatilization of heavy metals. A slow formation rate of these compounds can hinder heavy metal removal by decreasing the conversion rate of their chlorides[19].

Unlike previous studies that have primarily focused on the use of alkaline metal chlorides such as NaCl, $MgCl_2$, and $CaCl_2$ as chlorinating agents in thermal processes like SS pyrolysis[16], this research specifically introduces $FeCl_3$ as a chlorinating agent in the pyrolysis process. The use of alkaline metal chlorides raises concerns about salinity issues in the resulting biochar and its subsequent agricultural application. Furthermore, the pyrolysis process itself can elevate electrical conductivity[20], and the presence of alkaline metal chlorides may intensify biochar salinity. These salts can persist in the biochar matrix, leading to increased soil salinity, which may limit plant growth. In contrast, $FeCl_3$ not only acts as a chlorine donor but also adds iron to the biochar structure. The presence of iron, depending on environmental conditions, can help improve soil properties by enhancing stability and nutrient availability, thereby enhancing the quality of some soils (neutral or calcareous soils)[21]. In pyrolysis, below 300 °C, $FeCl_3$ forms ferric hydroxide ($Fe(OH)_3$) and iron oxides (FeOOH), which can become available and be absorbed by plants in the presence of siderophores and chelating agents in the root environment. Between 300 and 500 °C, $FeCl_3$ transforms into ferric oxide (Fe_2O_3) or magnetite (Fe_3O_4), which stabilize contaminants. Above 500 °C, ferric oxide reduces to FeO or metallic iron (Fe), further enhancing contaminant stabilization[22]. In addition, to minimize energy consumption during the pyrolysis process (low melting $_{(MP)}$ and boiling points $_{(BP)}$), PVC, as one of the effective chlorinated organic compounds for removing heavy metals from SS compounds, was selected alongside $FeCl_3$ in this study. Since the removal of heavy metals through chlorination depends more on the formation rates of Cl_2 and HCl than on the vapor pressure (affected by the MP and BP) of the chlorine donor[19], it seems essential to examine the effects of each chlorinated compound at each vapor pressure rate for each heavy metal. PVC has an MP of 260 °C (160–260 °C) and a BP of 240 °C, while $FeCl_3$ has an MP of 306 °C and a BP of 315 °C. Notably, these values are significantly lower than those of alkaline metal chlorides, such as $MgCl_2$ (MP: 714 °C, BP: 1412 °C), $CaCl_2$ (MP: 772 °C, BP: 1935 °C), NaCl (MP: 801 °C, BP: 1413 °C), and KCl (MP: 770 °C, BP: 1420 °C). By utilizing $FeCl_3$ and PVC, which require lower thermal energy, the pyrolysis conditions can be optimized to achieve efficient chlorination while reducing energy input. It is important to note that in recent years, significant efforts have been made in Iran and some

iron-rich countries to economically produce $FeCl_3$ from iron waste, providing an affordable and readily available source for applications such as water treatment and industrial processes.

Previous studies on urban SS from Kerman city (the SS studied in the present research) revealed elevated levels of heavy metals, particularly As and Zn, which pose significant environmental risks[23]. While conventional stabilization methods such as composting and vermicomposting reduce the bioavailability of these metals, they do not effectively lower their total concentrations[24], and changes in soil conditions upon application can lead to remobilization. Additionally, research on the co-pyrolysis of SS from Kerman city with zero-valent iron (Fe^0) demonstrated a significant reduction in the mobility and bioavailability of As and Zn, highlighting the potential of thermal treatment methods in mitigating heavy metal toxicity[23]. However, it did not lead to a decrease in the total amounts of these elements. Instead, due to the reduction in organic material during pyrolysis, the concentration of these elements increased, suggesting that co-pyrolysis with non-chlorinated elements might stabilize the metals, but it is accompanied by a relative increase in their concentrations.

The current study focuses on the removal of non-volatile heavy metals[25] such as Cr and As, as well as semi-volatile Zn[25], under pyrolysis conditions. Given the low volatility of these metals, it is possible that employing $FeCl_3$ and PVC as chlorine donors would enhance their volatilization and facilitate their removal. This research aims to evaluate the comparative efficacy of these agents in promoting the removal of As and Cr (as well as Zn), which are less responsive to conventional chlorinating agents.

Building upon previous research, which has primarily focused on the impact of $FeCl_3$ on pollutant behavior in SS during incineration[26] and combustion[27] processes, this study investigates its influence under pyrolysis conditions. Given that the the characteristics of SS and pyrolysis operating parameters significantly affect the efficiency of heavy metal removal during co-pyrolysis with chlorinating agents[16], this research examines the effects of organic (PVC) and inorganic ($FeCl_3$) chlorides. Two dosages of $FeCl_3$ and PVC (10% and 20% w/w) are tested to evaluate their impact on the behavior of As, Cr, and Zn during the co-pyrolysis of municipal SS from Kerman city at 400 °C and 600 °C. The study evaluates the total content, chemical forms, and toxicity characteristics of these metals, alongside an assessment of the associated ecological risks.

Materials and methods

Preparation and characterization of SS

To generate biochar samples from SS, dried sludge was collected from the sludge-drying lagoons at the Kerman wastewater treatment facility in Kerman city, Iran. The sludge sampel was dried at 70 °C, and heavy metal concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS, Agilent model 7500, Agilent, USA) following aqua regia digestion. The results revealed the following heavy metal concentrations in the dried SS: Zn, 670.8 mg kg^{-1}; As, 55.6 mg kg^{-1}; Cd, 0.37 mg kg^{-1}; Pb, 36 mg kg^{-1}; Ni, 23 mg kg^{-1}; Cu, 142 mg kg^{-1}; and Cr, 74 mg kg^{-1}. Additionally, the SS characteristics were analyzed, showing an organic carbon content of 28.3%, a pH of 6.8, an electrical conductivity (EC) of 7.2 dS m^{-1}, and a cation exchange capacity (CEC) of 48.6 cmol(+) kg^{-1}. To ensure uniform mixing and reduce heat transfer variations caused by differing particle sizes, the sludge was crushed and screened. The particles within the 30–50 mesh range were stored in jars for future use.

Biochar production

The dried sludge samples were placed in a specially designed reactor (40 cm in length and 20 cm in internal diameter) and mixed with chlorinated compounds—PVC powder (Sigma-Aldrich) and $FeCl_3$ ($FeCl_3{\cdot}6\ H_2O$, Merck)—at concentrations of 10% and 20% (weight/weight). The co-pyrolysis process was performed at two specific temperatures (400 °C and 600 °C) under anaerobic conditions, using pure nitrogen gas (N_2, 99%) flowing at a rate of 0.5 L min^{-1} for 4 h, with a controlled heating rate of 1.2 °C min^{-1}. After cooling, the biochar was collected from the reactor, weighed, and stored in glass containers for subsequent analysis. To enable a clear comparison of the effects of chlorinated compounds and pyrolysis on SS characteristics, a control sample—without the addition of these substances and without undergoing pyrolysis—was included in the analytical procedures.

Analysis of total and chemical forms of heavy metal content

To determine the total concentration of heavy metals in the produced biochars, 100 mg of the solid sample was digested in a microwave digestion system using 6 mL of HNO_3, 3 mL of $HClO_4$, and 3 mL of HF. After complete digestion, the mixture was transferred to a 25-mL volumetric flask and diluted to a final volume of 25 mL with a 5% HNO_3 solution. Each digestion solution was filtered through a 0.22 µm filter and analyzed using atomic absorption spectroscopy (AAS: Varian Spectra AA-10).

The behavior of the metals was evaluated by analyzing their chemical forms through sequential extraction methods and assessing sample toxicity via the TCLP (Toxicity characteristic leaching procedure) method. The BCR (Bureau Communautaire de Référence) sequential extraction method was used to identify four distinct chemical forms of Zn, Cr, and As: the acid-soluble fraction, the reducible fraction, the oxidizable fraction, and the residual fraction. After each extraction step, the concentrations of heavy metals were measured using AAS. These fractions reveal how metals are bound in SS. The acid-soluble/exchangeable fraction is linked to carbonates and is the most mobile and bioavailable, posing risks to water and soil quality, especially in agriculture. The reducible fraction, associated with Mn and Fe oxides, is somewhat mobile, while the oxidizable and residual fractions are largely immobile[23]. A summary of the methodologies employed in this study is provided in Table 1.

Enrichment and residual rates of heavy metals

In this study, the enrichment rate (ER) and residual rate (RR) of heavy metals in biochars were introduced as parameters to assess the degree of enrichment and immobilization of heavy metals, respectively, following pyrolysis[28]. These parameters can be calculated using the following equations (Eqs. 6 and 7):

Step	Extraction conditions per 1 g of treated samples	Targeted chemical fraction
1	40 mL of 0.11 M CH_3COOH, 22 °C for 16 h	Acid-soluble fraction (associated with exchangeable ions and carbonates)
2	40 mL of 0.5 M $NH_2OH{\cdot}HCl$ (pH 2), 22 °C for 16 h	Reducible fraction (bound to Fe-Mn oxides)
3	10 mL of 8.8 M H_2O_2 (pH 2–3), 22 °C for 16 h; then 85 °C for 1 h	Oxidizable fraction (bound to organic matter and sulfides)
4	10 mL of 8.8 M H_2O_2 at 85 °C for 1 h	Residual fraction

Table 1. Overview of the BCR sequential extraction procedure.

$$ER = {}^{Cx}/_{C} \tag{6}$$

Where:

- *Cx*: Concentration of heavy metals in biochar (mg $kg^{[-1}$).
- *C*: Concentration of heavy metals in the feedstock (mg $kg^{[-1}$).

The residual rate is calculated as follows:

$$RR = ER \times Y \tag{7}$$

Where:

Y: Yield of biochar (%), which is determined by the ratio of the mass of produced biochar to the mass of the initial feedstock.

Toxicity assessment (TCLP method)

To assess toxicity via the TCLP method, two different buffered acidic extraction liquids were employed, depending on the alkalinity and buffering capacity of the sludge samples.

- If the pH of the sample was less than 5: Extraction liquid "1", with a pH of approximately 4.93 (prepared by mixing 7.5 mL of pure CH_3CH_2OOH and 3.64 mL of 1 N NaOH solution in 1 L of water), was used.
- If the pH of the sample was greater than or equal to 5: Extraction liquid "2", with a pH of approximately 8.22 (prepared by mixing 7.5 mL of pure CH_3CH_2OOH in 1 L of water), was utilized.

The pH values of both solutions were adjusted using 1 M HNO_3 and 1 M NaOH. For each sample, 2 g of dried sample and 40 mL of the extraction solution were transferred to 100 mL plastic containers and agitated for 18 h on a horizontal shaker at a speed of 30 ± 2 RPM.

At the end of extraction period, the liquid phase was separated from the solid phase using filter paper with a pore size of 0.8 µm. The concentrations of heavy metals in the TCLP extracts were determined via AAS.

Analysis of heavy metals ecological risk

The ecological risk index (RI), developed by Ref[29]. , integrates principles from biological toxicology, environmental chemistry, and ecology to evaluate the potential risks posed by heavy metals in SS and biochar[30]. The methodology for calculating the *RI* is described in the following equations (Eqs. 8-10):

$$Cf = {}^{Ci}/_{Cn} \tag{8}$$

$$Er = Tr \times Cf \tag{9}$$

$$RI = \sum Er \tag{10}$$

In this context, *Cf* represents the contamination factor for each heavy metal, whereas *Ci* and *Cn* denote the concentration of the potentially mobile fractions (acid soluble fraction + reducible fraction + oxidizable fraction) and the stable fraction (residual fraction) of the heavy metals, respectively. *Er* indicates the potential ecological risk factor for each individual heavy metal. The toxicity factor *Tr* for each heavy metal is assigned values as follows: As (10), Zn (1) and Cr (2)[31]. Finally, the *RI* refers to the potential ecological risk index that reflects overall contamination[31].

Results and discussion

Biochar yield

Figure 1 presents the biochar yield from SS under various treatment conditions. The data reveal that both the pyrolysis temperature and the type of chlorinated material used significantly influence the biochar yield. As the temperature increased from 400 °C to 600 °C, a clear decreasing trend in biochar yield was observed, with the lowest yield recorded at 600 °C with higher concentrations of PVC (20%). This trend aligns with previous studies indicating that biochar yield generally declines with increasing pyrolysis temperature[32–35]. Ref[36]. highlight that the complex and diverse composition of SS often leads to a wide range of yields and properties during the pyrolysis process. The decrease in biochar yield at higher pyrolysis temperatures can be attributed to several interconnected factors. As the temperature increases, the thermal decomposition of primary polymeric

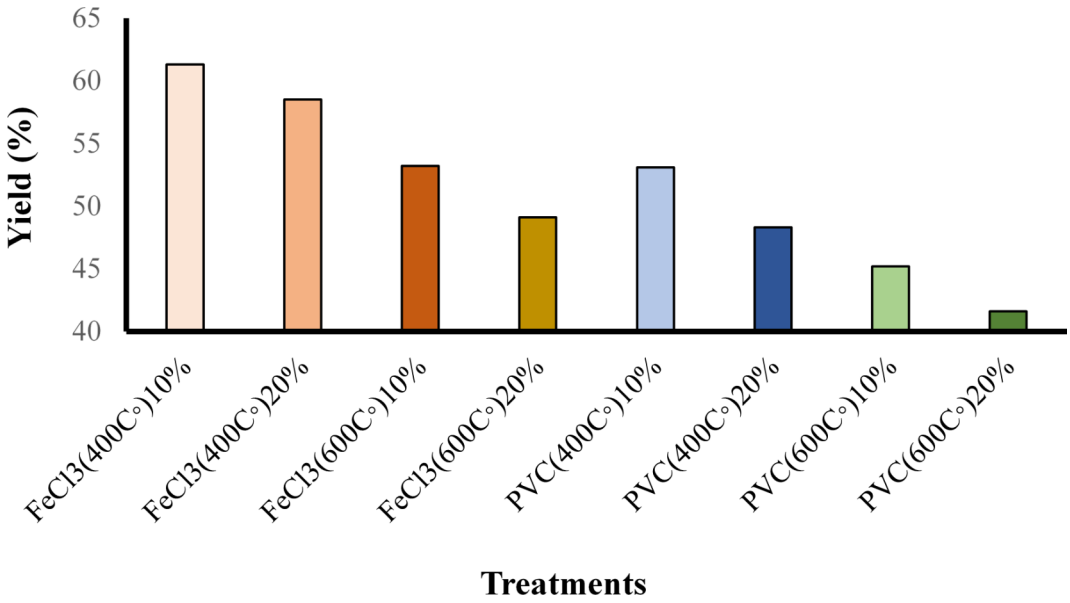

Fig. 1. Yield of SS biochars influenced by various temperatures and chlorinated materials.

components such as proteins, carbohydrates, and lipids becomes more pronounced, resulting in the release of greater amounts of volatile compounds, which in turn reduces the solid biochar content[37–39]. Moreover, higher temperatures promote the conversion of volatile substances into low-molecular-weight liquids and gases, further lowering biochar yield[40]. The dehydration of hydroxyl groups, along with the thermal degradation of celluloses, hemicelluloses, and lignin, also contributes to the reduction in yield, particularly within the temperature range of 450–600 °C[39]. Ref[41]. showed that increasing pyrolysis temperature significantly reduced biochar yield from SS. At 300 °C, the yield was 62.5%, decreasing to 28.5% at 400 °C. Between 300 and 500 °C, yields declined by 14.6–35.2%, attributed to further pyrolysis conversion and secondary reactions of the solid residue.

Comparing the two chlorinated treatments, it is evident that PVC exhibits a more pronounced effect on reducing biochar yield compared to $FeCl_3$, especially at higher concentrations (20%). At 400 °C, biochar yield in $FeCl_3$ (10%) was 61.3%, while in PVC (10%), it was significantly lower at 53.1%, representing a 13.4% reduction. Similarly, at higher concentrations (20%), $FeCl_3$ yielded 58.5%, whereas PVC recorded only 48.3%, reflecting a 17.5% decrease. At 600 °C, the differences became even more pronounced. The $FeCl_3$ (10%) treatment resulted in a biochar yield of 53.2%, while the PVC (10%) treatment showed a lower yield of 45.2%, indicating a 15% reduction. For the 20% concentration at 600 °C, $FeCl_3$ achieved a yield of 49.1%, whereas PVC dropped significantly to 41.6%, highlighting a 15.3% reduction. These numerical comparisons underscore the greater stability of $FeCl_3$-treated biochar across both temperature and concentration gradients. $FeCl_3$ demonstrates relatively higher biochar yields across both temperature ranges (400 °C and 600 °C) and concentration levels (10% and 20%). This suggests that $FeCl_3$ has a comparatively lower impact on the volatilization of organic and inorganic components, allowing for better retention of solid biochar mass. In contrast, the higher volatility of heavy metal chlorides formed in PVC treatments results in greater mass loss during pyrolysis, thereby reducing biochar yield more significantly. Overall, the observed reduction in biochar yield can be attributed to two primary factors: enhanced volatilization of organic components and the removal of heavy metals through interaction with chlorinated materials. As the temperature rises, the rate of organic matter decomposition accelerates, leading to the release of volatile compounds and a subsequent decrease in the final biochar mass. Simultaneously, elevated temperatures facilitate the interaction between heavy metals (As, Cr, Zn) and the chlorinating agents ($FeCl_3$ and PVC), promoting their removal from the biochar matrix. This synergistic effect contributes to the observed reduction in biochar yield while simultaneously enhancing the removal of targeted heavy metals. Ref[18]. investigated the co-pyrolysis of SS with PVC and/or CaO and found that increasing the pyrolysis temperature from 500 °C to 900 °C generally led to a reduction in biochar yield due to enhanced decomposition of both organic and inorganic components. Additionally, the combination of 25% PVC and 75% SS at different temperatures resulted in a 14–15% reduction in biochar yield compared to SS pyrolyzed without PVC. Ref[42]. , in a study on the effectiveness of co-pyrolysis of SS and PVC microplastics, found that biochar yield was significantly influenced by the presence of metal additives. Co-pyrolysis of metal-free PVC with sludge resulted in lower biochar yields, with the lowest yield (36.38%) observed at a reduced sludge ratio. In contrast, the highest biochar yield (73.79%) was achieved when the sludge addition was minimal in co-pyrolysis with metal-loaded PVC. The decrease in biochar yield was attributed to the volatilization of cellulose and hemicellulose in the sludge, while the increase in yield with metal-loaded PVC was likely due to the neutralization of HCl released from PVC by the metal additives.

Total heavy metals concentrations in the produced SS biochars

Figure 2 presents the trends in the total concentrations of As, Cr, and Zn in SS and the biochars derived from them, as influenced by chlorinated materials at two different pyrolysis temperatures. The results indicate that the

application of both chlorinated materials at the specified pyrolysis temperatures resulted in a reduction in heavy metal levels compared to the control. Specifically, the use of $FeCl_3$ at concentrations of 10% and 20% at 400 °C led to reductions in As of 24% and 31%, respectively, compared to the control sample. At 600 °C, these reductions increased to 46% and 50.6%, respectively, relative to the control. In comparison, the application of 10% PVC resulted in a 33.6% reduction in As at 400 °C and a 59.7% reduction at 600 °C. At 20%, PVC achieved reductions of 42.7% (at 400 °C) and 69.8% (at 600 °C), respectively, compared to the control.

The trends in Zn reduction mirrored those observed for As, with PVC demonstrating a more pronounced effect than $FeCl_3$. At 400 °C, the application of 10% and 20% PVC resulted in Zn reductions of 59.4% and 67.2%, respectively, compared to the control. At 600 °C, these reductions increased to 81.2% and 88.3%, respectively, relative to the control sample. In contrast, the application of $FeCl_3$ at 400 °C at 10% and 20% resulted in Zn reductions of 31% and 36%, respectively, while at 600 °C, the reductions were 48.5% and 54%, respectively, compared to the control. Based on the results, the removal of As was lower than that of Zn in the presence of chlorinating agents, which aligns with the findings of Ref[19]. , where it was shown that As, being one of the least volatile heavy metals, had negligible removal during thermochemical treatment, even in the presence of chlorine donors. Given that As is a non-volatile heavy metal and Zn is a semi-volatile heavy metal[25], it was anticipated that the removal efficiency of As would be lower than that of Zn.

The reduction in Cr levels, influenced by pyrolysis and chlorinated materials, exhibited a different pattern from those of Zn and As, showing a stronger response to $FeCl_3$ than to PVC. The application of 10% and 20% $FeCl_3$ at 400 °C resulted in Cr reductions of 30.6% and 36.3%, respectively, relative to the control. At 600 °C, these reductions increased to 71% and 72.5%, compared to the control sample. In contrast, the application of PVC at 400 °C and 600 °C at a 10% concentration led to reductions of 32.1% and 50.4%, respectively, whereas at a 20% concentration, the reductions were 44% and 57.4%, respectively, compared to the control sample.

Ref[43]. identified three distinct reactions that take place when Cl-donors are added to SS for the volatilization of heavy metals via chlorination. The first reaction involves the formation of Cl_2 or HCl through the interaction of Cl-donors with O_2 and H_2O. In the second step, Cl_2 or HCl reacts with heavy metals to produce metal chlorides. Finally, heavy metals interact with SiO_2 or Al_2O_3, leading to the formation of stable, inactive compounds that remain in the SS and are not removed during the thermochemical treatment. On the basis of these results, the mechanisms underlying the reduction in total concentrations of the studied heavy metals can be elucidated as follows[16]. The addition of PVC during pyrolysis leads to the release of chlorine gas (Cl_2) and HCl, which can react with heavy metals, facilitating their volatilization. This process can be represented by the following reactions (Equations: 11-18):

$$PVC = R - CH + Cl_2 \tag{11}$$

$$PVC = R - CH + HCl \tag{12}$$

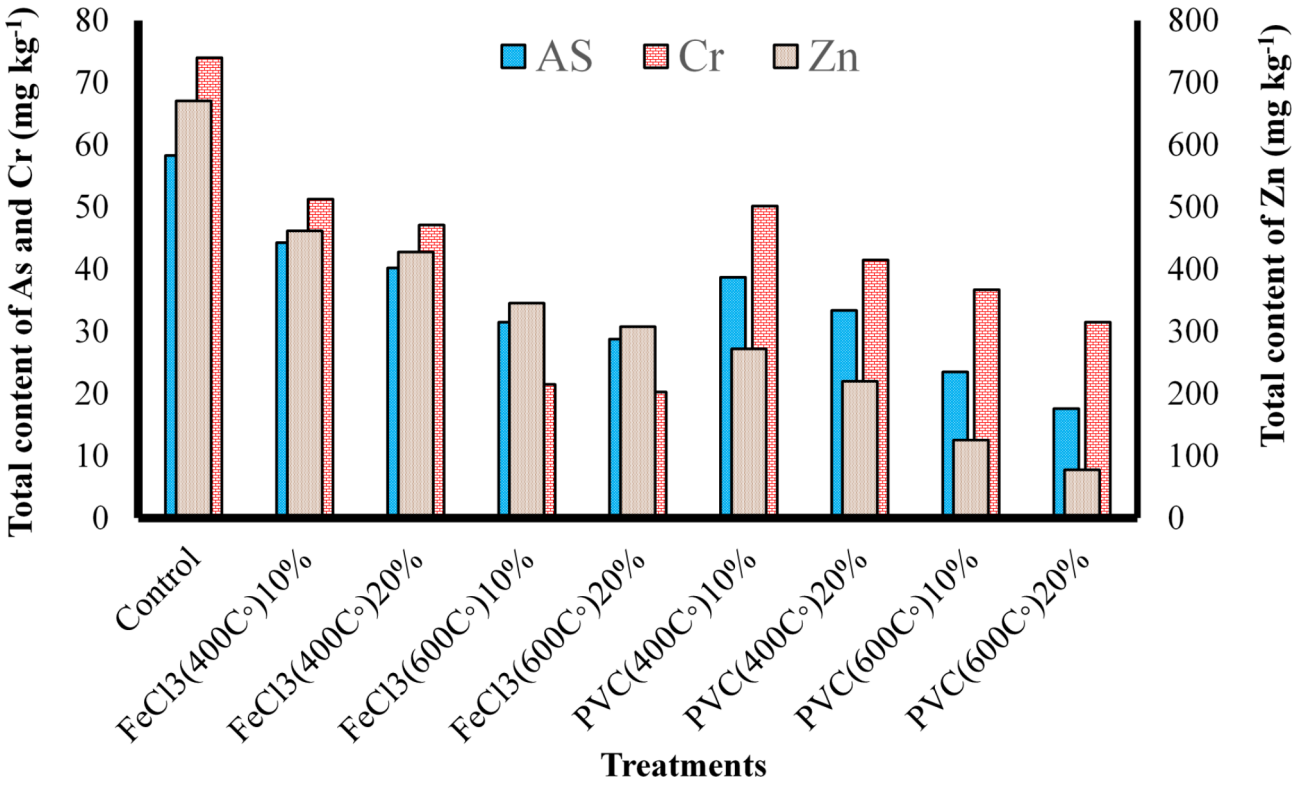

Fig. 2. Total concentrations of As, Cr, and Zn in SS biochars influenced by various temperatures and chlorinated materials.

$$M^{2+} + Cl_2 + 2e^- = MCl_2 \quad (13)$$

$$M^{2+} + 2HCl = MCl_2 + 2H^+ \quad (14)$$

$$M^{3+} + Cl_2 + 3e^- = MCl_3 \quad (15)$$

$$M^{3+} + 3HCl = MCl_3 + 3H^+ \quad (16)$$

$$M^{3-} + Cl_2 = MCl_3 + 3e^- \quad (17)$$

$$M^{3-} + 3HCl = MCl_3 + 3H^+ + 6e^- \quad (18)$$

Here, M represents the heavy metals As (As^{3+}), Zn (Zn^{2+}), and Cr (Cr^{3+}) in their respective oxidation states. The reactions of the Cl_2 and HCl produced during PVC decomposition with As and Cr lead to the formation of volatile compounds, specifically $AsCl_3$ and $CrCl_3$, respectively. The formation of metal chlorides significantly increases the volatility of these metals, leading to their reduction in the biochar matrix. As highlighted by Ref[44]. , heavy metals typically exist as oxides under pyrolysis conditions. The addition of chlorine-containing gases, such as HCl and Cl_2, facilitates the transformation of these oxides into more volatile metal chlorides, which are more readily released during pyrolysis (Eqs. 13 and 14). This process is a fundamental mechanism driving the observed reductions in heavy metal concentrations. Conversely, $FeCl_3$ acts as a potent chlorinating agent, facilitating the transformation of heavy metals into less stable forms and promoting their removal from the solid phase. This process involves the following reactions with heavy metals (Equations: 19-20):

$$M^{2+} + FeCl_3 \rightarrow MCl_2 + Fe^{3+} \quad (19)$$

$$M^{3+} + FeCl_3 \rightarrow MCl_3 + Fe^{3+} \quad (20)$$

The reaction between divalent and trivalent heavy metals with $FeCl_3$ leads to the formation of volatile metal chlorides (MCl_2 for divalent metals and MCl_3 for trivalent metals), which can be released during pyrolysis, thereby reducing their concentrations in the biochar. Additionally, when $FeCl_3$ is heated, it decomposes into iron(II) chloride and chlorine gas. At higher temperatures, it may also breakdown into iron(III) oxide and chlorine gas or vaporize into gaseous iron(III) chloride. If water is present, it can react with $FeCl_3$ to produce HCl. The generated Cl_2 and HCl then react with heavy metals, such as As, Zn, and Cr, forming volatile compounds like $AsCl_3$, $ZnCl_2$, and $CrCl_3$.

Additionally, the results indicate that higher pyrolysis temperatures contribute to a greater reduction in heavy metals. As the temperature increased, the thermal decomposition of both PVC and $FeCl_3$ increased, leading to increased availability of reactive chlorine species. This increase in temperature also results in the production of more Cl_2 and HCl, which aligns with findings of Ref[45]. Furthermore, the elevated kinetic energy at these higher temperatures facilitates stronger interactions between heavy metals and chlorinated species, leading to more significant reductions in their concentrations. Ref[19]. in their study demonstrated that the efficiency of heavy metal removal varies significantly depending on the type of heavy metal and the chlorine donor used. They found that $MgCl_2$ and $CaCl_2$ were the most effective in removing heavy metals, except for Cr and Ni. Pb was almost completely removed, and other heavy metals such Cd, Zn, and Cu were also removed to a greater extent than in the control group. The removal efficiency for Cr was low, and thermodynamic calculations revealed that Cr formed a very stable compound, CrO_2Cl_2, when a chlorine donor was present[19]. Ref[19]. stated that the formation reaction of Cl_2 or HCl after adding chlorinating agents is likely the rate-limiting step for the removal of heavy metals. If the formation of Cl_2 or HCl is not the rate-limiting step, then the chlorination of the heavy metals must be the rate-limiting step. In this case, the chlorination rate of heavy metals should only depend on the type of heavy metal. However, as indicated by the results of both the present study and the study by Ref[19]. , this is not the case. Therefore, it can be inferred that the production rate of Cl_2 or HCl in PVC is faster than in $FeCl_3$. Consequently, PVC demonstrates better performance in removing As, Zn, and even Cr (at 400 °C) compared to $FeCl_3$.

The findings of the current study support previous research, which indicates that chlorides have differing effects on various metals[16,27]. Specifically, PVC had a more pronounced impact on Zn, which is consistent with existing research suggesting that chlorides are generally more effective for metals like Zn due to their higher volatility and greater tendency to form volatile chloride complexes[16]. In contrast, $FeCl_3$ exhibited a stronger influence on Cr, aligning with its known ability to stabilize certain metals in less volatile and more thermodynamically stable forms, thereby aiding their removal from the biochar matrix. These results highlight the unique chemical interactions between different chlorides and specific metals, driven by their distinct volatility and reactivity profiles.

Furthermore, As, despite being classified as a non-volatile element, exhibited a more pronounced interaction with PVC compared to $FeCl_3$. This observation suggests that the behavior of As in the presence of PVC deviates from typical trends observed for other metals, highlighting the nuanced effects of different chlorinating agents on As speciation and volatility during pyrolysis. Ref[45]. investigated the behavior of Cd, Cr, Mn, Ni, Pb, and Zn during SS incineration to compare the effects of chlorinated organic compounds on the volatilization of heavy metals. These findings indicated that PVC outperformed $MgCl_2$ in the removal of Cd, As, Cr, and Ni when various mass ratios of chlorinating agents were utilized. Conversely, another study reported that while PVC was more effective in removing Zn, Mn, As, and Cr, $MgCl_2$ exhibited superior performance for Cd, Cu, Pb, Ni, and Co during the pyrolysis of sludge[16].

Enrichment and residual rates of heavy metals in the produced SS biochars

The ER serves as a critical metric for evaluating the extent of heavy metal retention in biochar relative to the original feedstock concentration. As illustrated in Fig. 3, the ER values for As, Cr, and Zn were all less than one, indicating a net reduction in these heavy metals in the biochar compared to their concentrations in the feedstocks prior to pyrolysis.

The highest ER for As (0.76) was observed at 400 °C with 10% $FeCl_3$, while the lowest ER (0.30) occurred at 600 °C with 20% PVC. A gradual decrease in ER values was noted with increasing temperature and concentration of both chlorinating agents. Specifically, when temperature increased from 400 °C to 600 °C, the ER decreased by approximately 29% for $FeCl_3$ (10% concentration) and 33% for PVC (10% concentration). This trend indicates that PVC was more effective than $FeCl_3$ in removing As from SS at higher temperatures.

For Zn, the highest ER (0.69) was recorded at 400 °C with 10% $FeCl_3$, while the lowest ER (0.12) was observed at 600 °C with 20% PVC. A consistent decline in ER values was evident with increasing temperature and concentration for both agents. The reduction in ER from 400 °C to 600 °C was approximately 25% for $FeCl_3$ (10% concentration) and 54% for PVC (10% concentration). This pronounced reduction suggests that PVC is significantly more effective than $FeCl_3$ in facilitating Zn volatilization at elevated temperatures. The trends observed for As and Zn were consistent with findings in other studies, where the migration of these metals to the gas phase at elevated temperatures led to lower ER values[18].

The behavior of Cr differed significantly from As and Zn. The highest ER (0.69) was achieved at 400 °C with 10% $FeCl_3$, while the lowest ER (0.27) was recorded at 600 °C with 20% $FeCl_3$. Interestingly, $FeCl_3$ consistently showed lower ER values at higher temperatures, with a 61% reduction from 400 °C to 600 °C (10% concentration). Conversely, PVC demonstrated less pronounced declines, with a 27% decrease from 400 °C to 600 °C (10% concentration). This suggests that $FeCl_3$ acts as a more significant enhancer for Cr, leading to its higher volatility, while PVC has a lesser effect on Cr's volatility, resulting in greater retention of Cr in biochar. In a study where PVC was used alongside CaO, the dilution effect attributed to PVC addition was noted to enhance the ER of certain metals, such as Cr, Cu, and Ni, indicating a possible stabilization effect on their retention in biochar[18]. However, the negative impact of high ER values on the practical utilization of biochar containing elevated concentrations of heavy metals has also been acknowledged.

The degree of immobilization (RR) of heavy metals in biochar, as shown in Fig. 4, reflects the effectiveness of different treatments at various pyrolysis temperatures. An inverse relationship was observed between pyrolysis temperature and RR values across all chlorinated samples, indicating reduced immobilization efficiency at

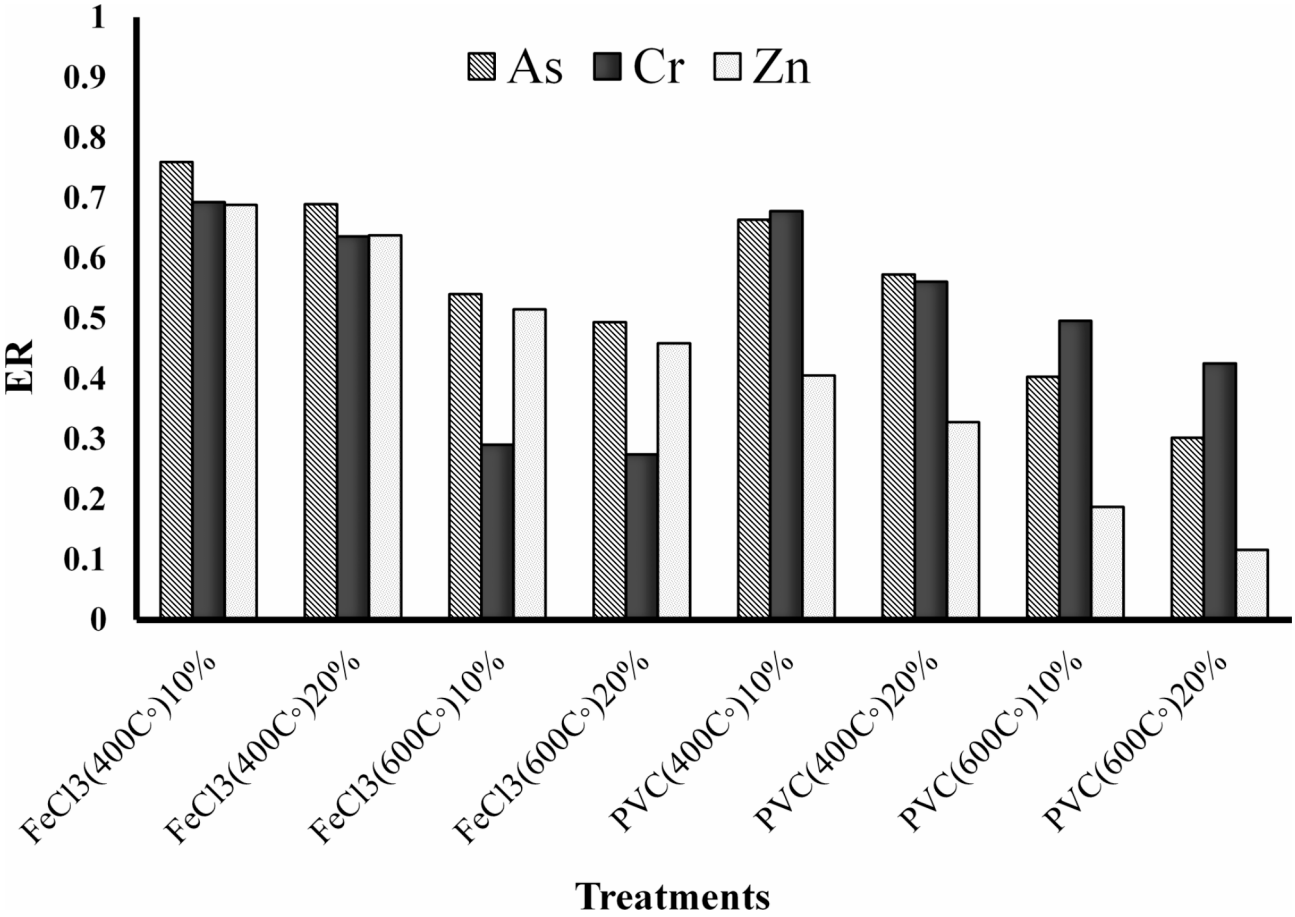

Fig. 3. The ER of As, Cr, and Zn in SS biochars influenced by various temperatures and chlorinated materials.

higher temperatures. This behavior aligns with previous studies[19], which suggest that elevated temperatures promote the volatilization and migration of heavy metals into the gas phase during pyrolysis.

For As, the highest RR (46.58%) was achieved with 10% $FeCl_3$ at 400 °C, while the lowest value (12.56%) was recorded with 20% PVC at 600 °C. In $FeCl_3$-treated samples, increasing the temperature from 400 °C to 600 °C caused a reduction of approximately 38.29% (10% concentration) and 39.90% (20% concentration) in RR values. In PVC-treated samples, the decline was more pronounced, with reductions of 48.31% (10%) and 54.61% (20%). These observations suggest that PVC significantly enhances the volatilization of As at elevated temperatures, likely through the formation of volatile As chlorides[18,46]. Conversely, $FeCl_3$ demonstrates greater stabilizing effects at lower temperatures, but its efficiency diminishes as the temperature increases.

Cr exhibited a distinct immobilization pattern compared to As and Zn. The highest RR (42.50%) was observed with 10% $FeCl_3$ at 400 °C, while the lowest RR (13.47%) occurred with 20% $FeCl_3$ at 600 °C. Temperature elevation led to a reduction in RR values of approximately 63.63% (10%) and 63.83% (20%) for $FeCl_3$-treated samples. In contrast, PVC-treated samples showed less dramatic reductions of 37.77% (10%) and 34.63% (20%). The relatively lower volatility of Cr, compared to As and Zn, supports previous findings highlighting its stability in solid matrices during pyrolysis[16].

For Zn, the highest RR (42.22%) was recorded with 10% $FeCl_3$ at 400 °C, while the lowest RR (4.83%) was observed with 20% PVC at 600 °C. In $FeCl_3$-treated samples, temperature elevation resulted in reductions of approximately 35.10% (10%) and 39.60% (20%) in RR values. However, PVC-treated samples experienced significantly sharper declines, with reductions of 60.66% (10%) and 69.48% (20%). These results suggest that PVC strongly promotes Zn volatilization, likely due to the formation of volatile $ZnCl_2$ during pyrolysis[16,46]. In contrast, $FeCl_3$ shows lower removal effects for Zn at lower temperatures, but its efficiency increases with rising temperature, resulting in a decrease in RR.

Distribution of chemical forms and mobility factor of heavy metals in the produced SS biochars

Figures 5, 6 and 7 illustrate the chemical speciation values and relative percentages of Zn, As, and Cr in the studied SS samples, highlighting significant changes in both the control and treated samples due to the application of chlorinated materials and the pyrolysis process.

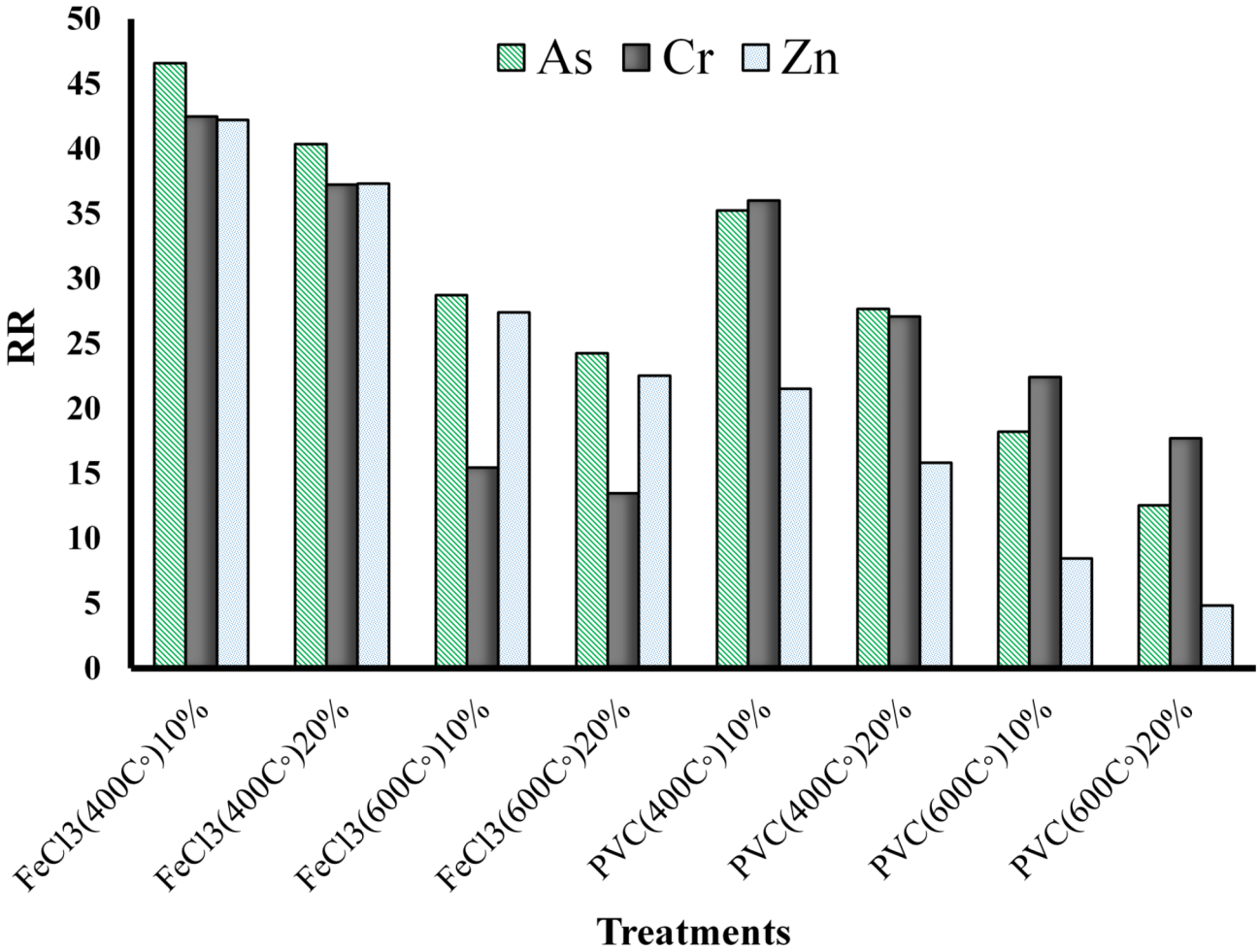

Fig. 4. The RR of As, Cr, and Zn in SS biochars influenced by various temperatures and chlorinated materials.

The chemical speciation of As in SS treated with $FeCl_3$ and PVC shows distinct shifts depending on treatment type, concentration, and pyrolysis temperature. In the control sample, As was mainly found in the acid-soluble fraction (59.35%), indicating high bioavailability and ecological risk. This distribution indicates a high bioavailability and ecological risk, consistent with previous studies[23]. $FeCl_3$ treatment generally increased the reducible fraction, especially at higher concentrations (20%) and temperatures (600 °C), with the acid-soluble fraction decreasing moderately (57.29%) and the reducible fraction rising significantly (29.86%). However,

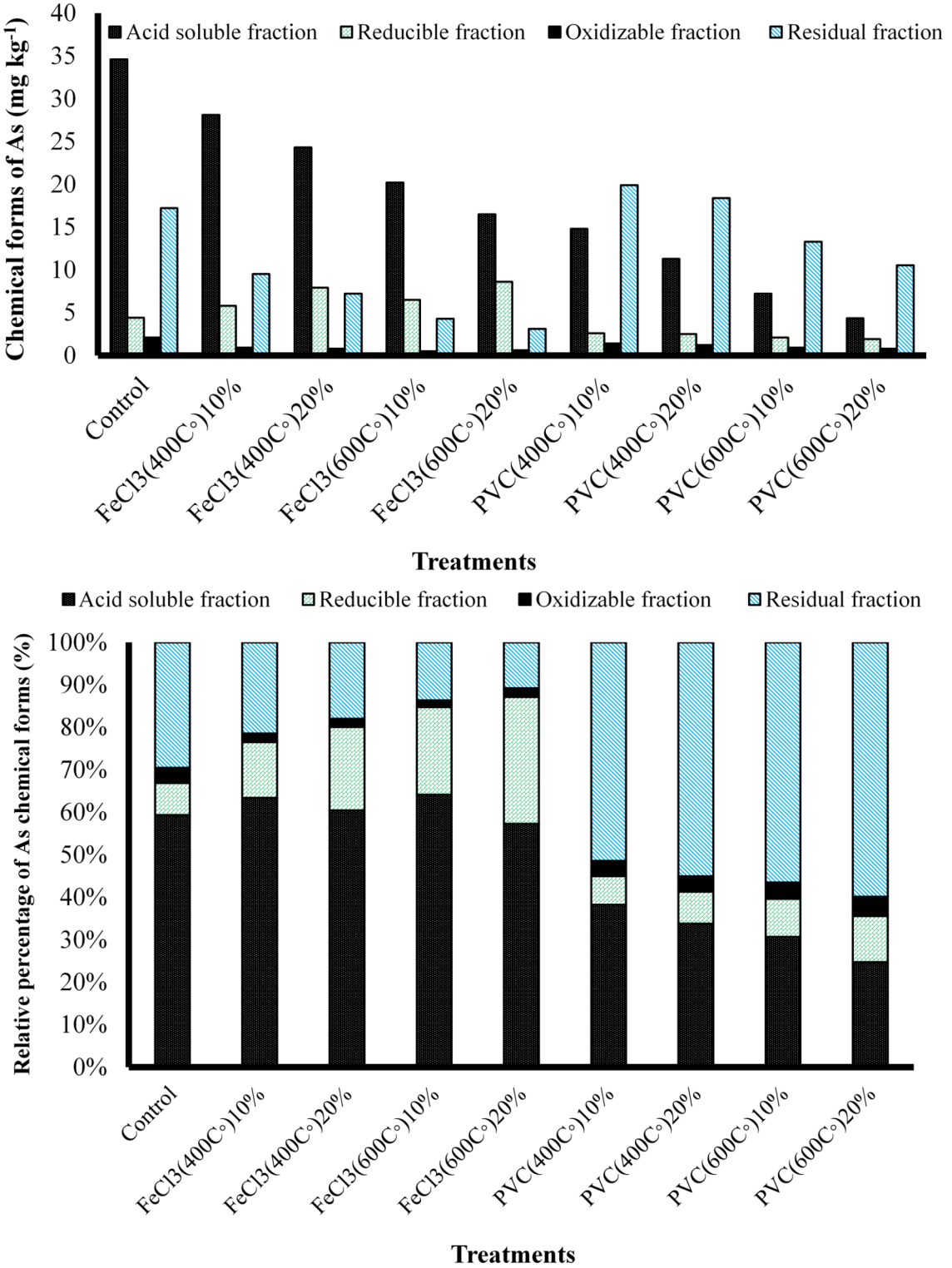

Fig. 5. Quantities and relative distribution of chemical forms of As in SS biochars influenced by various temperatures and chlorinated materials.

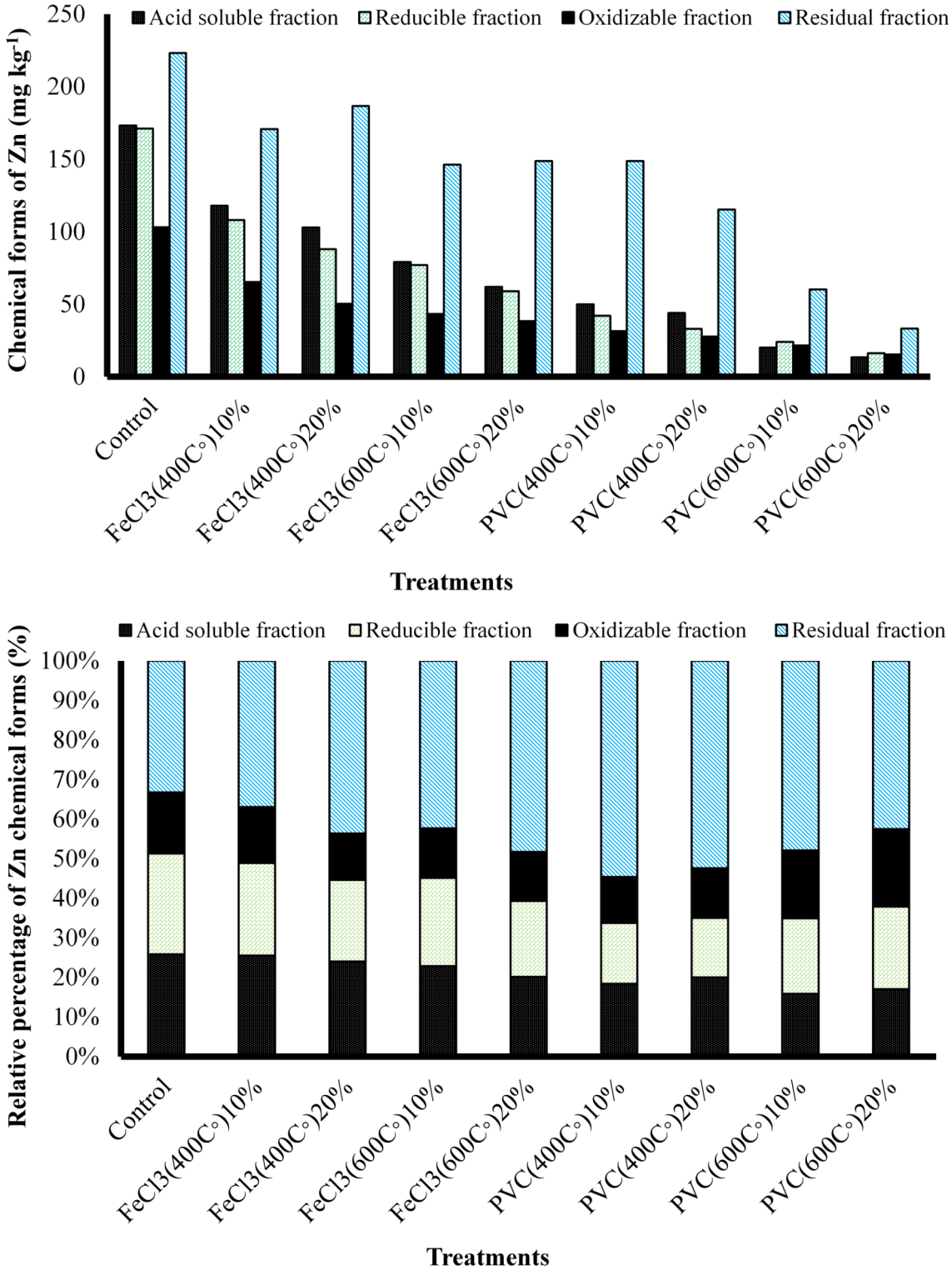

Fig. 6. Quantities and relative distribution of chemical forms of Zn in SS biochars influenced by various temperatures and chlorinated materials.

the residual fraction, representing the most stable phase, remained relatively low (10.76%), suggesting partial but incomplete stabilization. In contrast, PVC treatment consistently favored the transformation of As into the residual fraction, effectively reducing bioavailability. At 400 °C and 10% PVC, the acid-soluble fraction dropped (38.24%), and the residual fraction increased significantly (51.42%). With 20% PVC at 600 °C, the acid-soluble fraction reached its lowest (24.77%) and the residual fraction peaked (59.89%), indicating maximum stabilization. Overall, while $FeCl_3$ shifts As primarily into the reducible fraction, PVC treatment more effectively

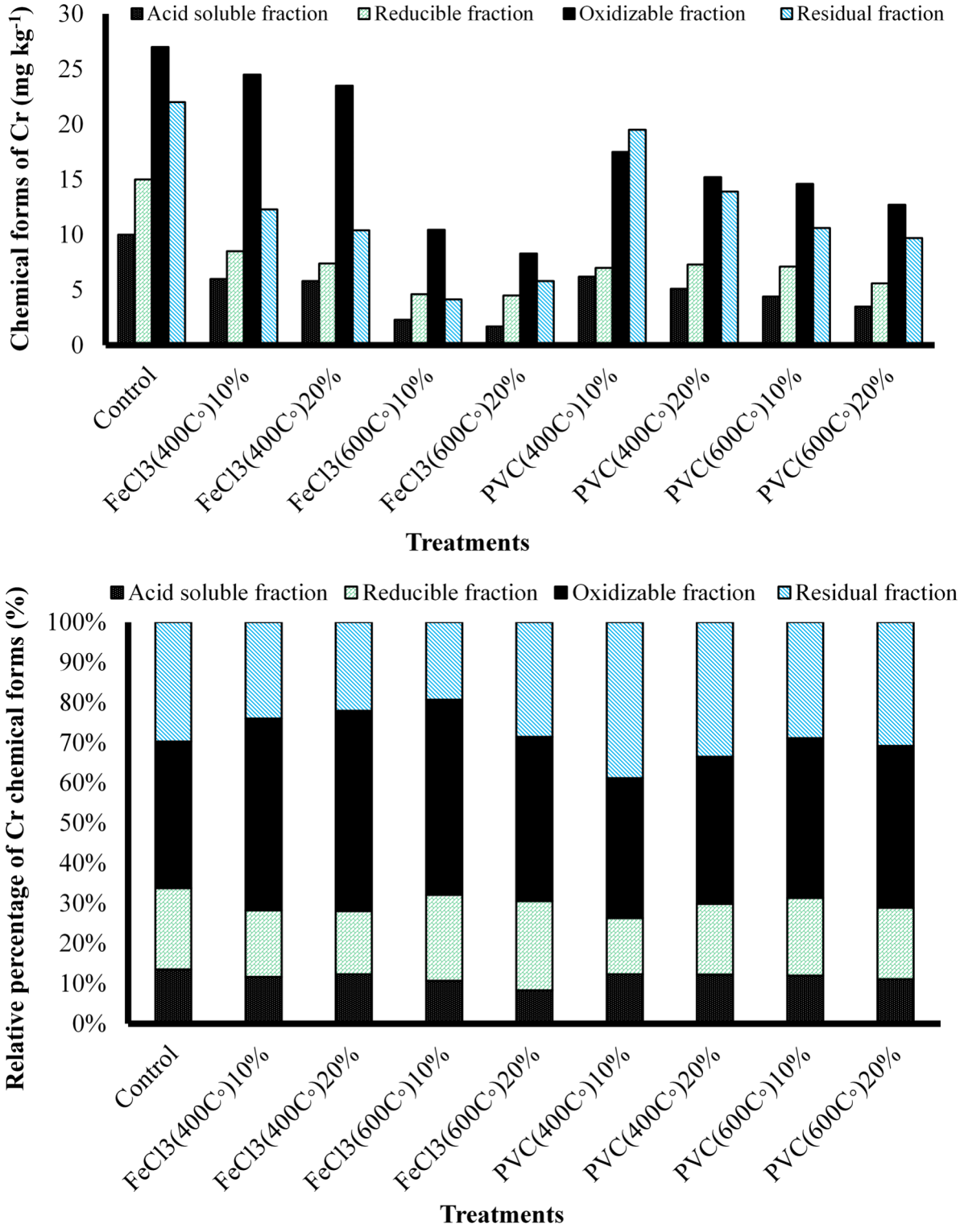

Fig. 7. Quantities and relative distribution of chemical forms of Cr in SS biochars influenced by various temperatures and chlorinated materials.

immobilizes As in the residual fraction, reducing long-term mobility and environmental risks. The combination of 20% PVC and 600 °C pyrolysis emerges as the most efficient approach for stabilizing As in SS.

Zn treatment with $FeCl_3$ and PVC at various temperatures significantly altered its chemical speciation, reducing mobility and bioavailability. In the control sample, Zn was mainly found in the residual fraction (~ 33.3%), followed by the acid-soluble (~ 25.8%) and reducible (~ 25.5%) fractions, indicating relatively high bioavailability. In the study by Ref[47]. , Zn in SS was mainly found in the reducible fraction, with smaller amounts

in the exchangeable and acid-soluble fractions. The more stable fractions (oxidizable and residual) contained 6.9–10.6% of total Zn. Ref[48]. found that in SS from a wastewater treatment plants in China, 58.5–77.5% of Zn was in the exchangeable, acid-soluble, and reducible fractions. However, Ref[49]. found that the oxidizable fraction contained the highest concentration of Zn in SS from 10 municipal plants. $FeCl_3$ treatment at 400 °C (10%) caused a slight decrease in the acid-soluble, reducible, and oxidizable fractions, with a 3.68% increase in the residual fraction, suggesting that Zn was stabilizing in less mobile forms. At 400 °C (20%), this trend was more pronounced, with the residual fraction increasing by 30.7%. $FeCl_3$ treatment at 600 °C (10%) showed a greater reduction in the acid-soluble, reducible, and oxidizable fractions, with a significant 14.03% increase in the residual fraction, indicating enhanced Zn stabilization. In comparison, PVC treatment at 400 °C (10%) resulted in a substantial reduction in the acid-soluble fraction (~ 29.3%) and a 63.4% increase in the residual fraction, indicating a strong shift toward more stable, less mobile forms of Zn. This shift was even more pronounced at 400 °C (20%), where the acid-soluble fraction decreased by 23.2%, and the residual fraction increased by 58.5%, further stabilizing Zn in the less mobile residual fraction. PVC treatment at 600 °C (10%) caused an even more significant decrease in the acid-soluble fraction (38.4%) and a 28.2% increase in the residual fraction, further reducing the mobility of Zn. The most notable stabilization occurred at 600 °C (20%), where the acid-soluble fraction decreased by 30.6%, and the residual fraction increased by 42.5%, indicating the most effective long-term stabilization of Zn. In brief, both $FeCl_3$ and PVC treatments effectively stabilized Zn, but PVC, especially at higher temperatures, emerged as the most efficient method. At 600 °C, PVC treatment drastically reduced Zn's mobility and bioavailability, transforming it into a far more stable form within the SS compared to $FeCl_3$ treatment. This makes PVC at 600 °C the optimal choice for achieving long-term stabilization of Zn in SS, significantly minimizing its potential environmental impact.

For Cr, treatment with $FeCl_3$ and PVC caused notable shifts in chemical speciation. In the control, Cr was relatively mobile, with the acid-soluble fraction at 13.51%, the reducible fraction at 20.27%, and the oxidizable fraction at 36.49%. These findings align with the study by Ref[50]. , where Cr was primarily found in the oxidizable and residual fractions of SS. This distribution suggests that Cr is strongly bound to organic matter, sulfides, and the solid matrix, making it immobile and less likely to migrate into the environment. Therefore, Cr does not pose a significant threat to the natural environment, especially when compared to more mobile metals like Zn. $FeCl_3$ treatments, especially at higher temperatures (600 °C), significantly reduced the acid-soluble fraction, indicating decreased mobility. At 400 °C and 10% concentration, the acid-soluble fraction dropped to 11.70%, while the oxidizable fraction increased substantially to 47.76%, signifying that Cr was becoming more stabilized in forms bound to organic matter and sulfides, which are less bioavailable and less mobile. The Residual fraction also increased to 23.98%, indicating further stabilization into less mobile forms. This trend was more pronounced at 600 °C, with the acid-soluble fraction falling to 8.37%, the oxidizable fraction rising to 48.60%, and the Residual fraction increasing to 28.57%, reinforcing the stabilization of Cr in more stable, less mobile forms. PVC treatments also promoted Cr stabilization, especially at higher temperatures. At 400 °C and 10%, the acid-soluble fraction decreased to 12.35%, and the Residual fraction increased to 38.84%. These results indicate a reduction in Cr's mobility and enhanced sequestration. Higher PVC concentrations and temperatures further enhanced stabilization, with the Residual fraction increasing to 33.49% at 400 °C and 20% and 30.79% at 600 °C and 20%. Overall, both $FeCl_3$ and PVC treatments shifted Cr towards more stable, less mobile forms, with $FeCl_3$ treatment showing a notable increase in the oxidizable fraction, particularly at higher temperatures. This suggests that $FeCl_3$, especially at elevated temperatures, is particularly effective in stabilizing Cr by enhancing its sequestration into less bioavailable and mobile forms, while PVC treatment, particularly at 600 °C, contributes to the stabilization of Cr in SS, it results in a slight increase in the mobile fraction, indicating that it may not be the most effective option for long-term stabilization.

To enable a clearer comparison of treatment effects on heavy metal mobility, the mobility factor[23] ([Acid-soluble fraction / Total concentration] ×100) was calculated, as shown in Fig. 8. This factor highlights the proportion of each metal present in the most bioavailable and mobile fraction, offering valuable insight into their environmental risks and the effectiveness of stabilization treatments. For Cr, the control sample exhibited a mobility factor of 13.51%, indicating moderate mobility. Treatment with $FeCl_3$ significantly reduced mobility, particularly at 600 °C with 20% $FeCl_3$, where the factor dropped to 8.37%, representing a 38% reduction compared to the control. Similarly, PVC treatments proved effective, with 20% PVC at 600 °C reducing the mobility factor to 11.11%, indicating substantial stabilization. Overall, $FeCl_3$ demonstrated slightly better performance in Cr immobilization at elevated pyrolysis temperatures, underscoring the role of heat in reducing Cr bioavailability.

When analyzing Zn, the control sample recorded a relatively high mobility factor of 25.83%, reflecting significant bioavailability. A study by Ref[47]. assessed the mobility of Zn in SS and found that Zn exhibited medium mobility across all sludge samples. Treatment with $FeCl_3$ at 600 °C and 20% concentration reduced this value to 20.13%, marking a 22% decrease. In comparison, PVC treatments at 600 °C showed superior performance, reducing the mobility factor to 15.91% with 10% PVC and 17.07% with 20% PVC. These results suggest that PVC, particularly at elevated pyrolysis temperatures, is more effective than $FeCl_3$ in immobilizing Zn by minimizing its presence in the acid-soluble fraction.

For As, the control sample displayed the highest mobility factor among the three metals, reaching 59.35%, indicating a significant environmental risk. Treatment with $FeCl_3$ showed limited effectiveness, reducing the mobility factor to 57.29% at 600 °C with 20% $FeCl_3$. In contrast, PVC treatments demonstrated exceptional efficiency, with 20% PVC at 600 °C lowering the mobility factor to 24.77%, representing a 58% reduction compared to the control. This substantial decrease highlights PVC's superior capacity to stabilize As, especially at elevated pyrolysis temperatures.

When comparing the three elements, it becomes evident that As exhibits the highest initial mobility factor (59.35%), followed by Zn at 25.83% and Cr at 13.51%. In the study conducted by Ref[47]. , the MF was categorized into four distinct groups: low ($MF \leq 10$), medium ($11 \leq MF \leq 30$), high ($31 \leq MF \leq 50$), and very high ($MF \geq 51$).

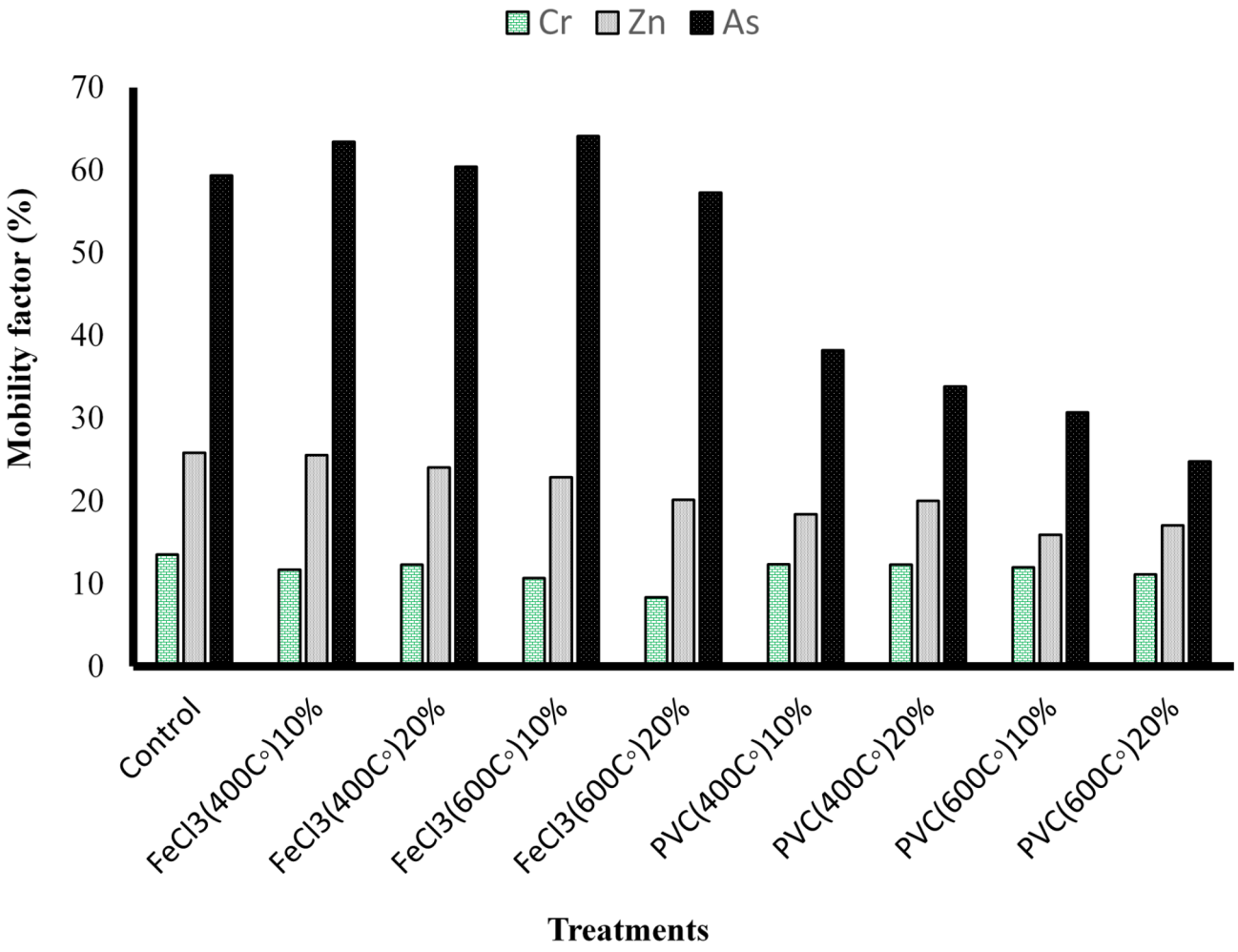

Fig. 8. Mobility factor of Cr, Zn, and As in the treated samples.

Based on this classification, the MF values calculated for the elements in the current study were categorized accordingly. For Cr, the MF values ranged from 8.37 to 13.51, placing them in the medium mobility category. Interestingly, the treatment of SS led to changes in the mobility classes for Cr, as values for $FeCl_3$-treated samples (both 400 °C and 600 °C) showed a slight reduction in MF, indicating a shift towards lower mobility compared to the control. Zn exhibited MF values between 15.91 and 25.83, which generally placed it in the medium mobility range. However, treatments with PVC, especially at higher concentrations (600 °C at both 10% and 20%), were more effective at reducing Zn's mobility, with MF values dropping to 15.91 and 17.07, respectively, indicating a shift to the lower end of the medium category compared to the control. On the other hand, $FeCl_3$ treatments resulted in only minor reductions in Zn's mobility, especially at higher concentrations (20% at 600 °C), where the MF value decreased to 20.13, still within the medium range but not as significantly as with PVC. For As, the MF values ranged from 24.77 to 64.13, with most values initially corresponding to the high and very high mobility categories, indicating greater potential for environmental mobility compared to Cr and Zn. Notably, treatments with $FeCl_3$ did not significantly alter the mobility classification for As, as the MF values remained in the very high mobility range, with the highest value observed at 600 °C with 10% $FeCl_3$ (64.13). However, treatments with PVC, especially at higher concentrations (600 °C at both 10% and 20%), were more effective in reducing the mobility of As. The MF values for PVC treatments shifted As from the very high category to the high category, with the 600 °C 20% PVC treatment resulting in a value of 24.77, a clear reduction in mobility compared to the control. Thus, while $FeCl_3$ did not significantly change the mobility class for As, PVC treatments proved to be effective in lowering its mobility.

Leaching behavior of heavy metals in the produced SS biochars

The TCLP results highlight distinct differences in the leachability of As, Cr, and Zn from SS treated with $FeCl_3$ and PVC under varying pyrolysis conditions (Fig. 9). For As, the control sample showed a concentration of 7.6 mg L^{-1}, exceeding the regulatory limit of 5 mg L^{-1}. Compared to the control, $FeCl_3$ treatments at 400 °C reduced As leachability by 27.1% and 31.8% for 10% and 20% dosages, respectively, though both remained above the acceptable limit. At 600 °C, $FeCl_3$ treatments achieved further reductions of 45.7% and 52.7%, successfully meeting regulatory standards. By contrast, PVC treatments demonstrated superior performance, with reductions

of 66.7% and 72.6% at 600 °C for 10% and 20% dosages, effectively lowering As concentrations well below the permissible limit.

For Cr, the control sample exhibited a leachate concentration of 6.58 mg L^{-1}, surpassing the standard limit of 5 mg L^{-1}. Relative to the control, $FeCl_3$ treatments at 400 °C achieved reductions of 32.4% and 36.5%, bringing Cr levels below the acceptable threshold. At 600 °C, the reductions were more significant, reaching 69.5% and 76.7% for 10% and 20% dosages, respectively. In contrast, PVC treatments at 400 °C showed limited effectiveness, with

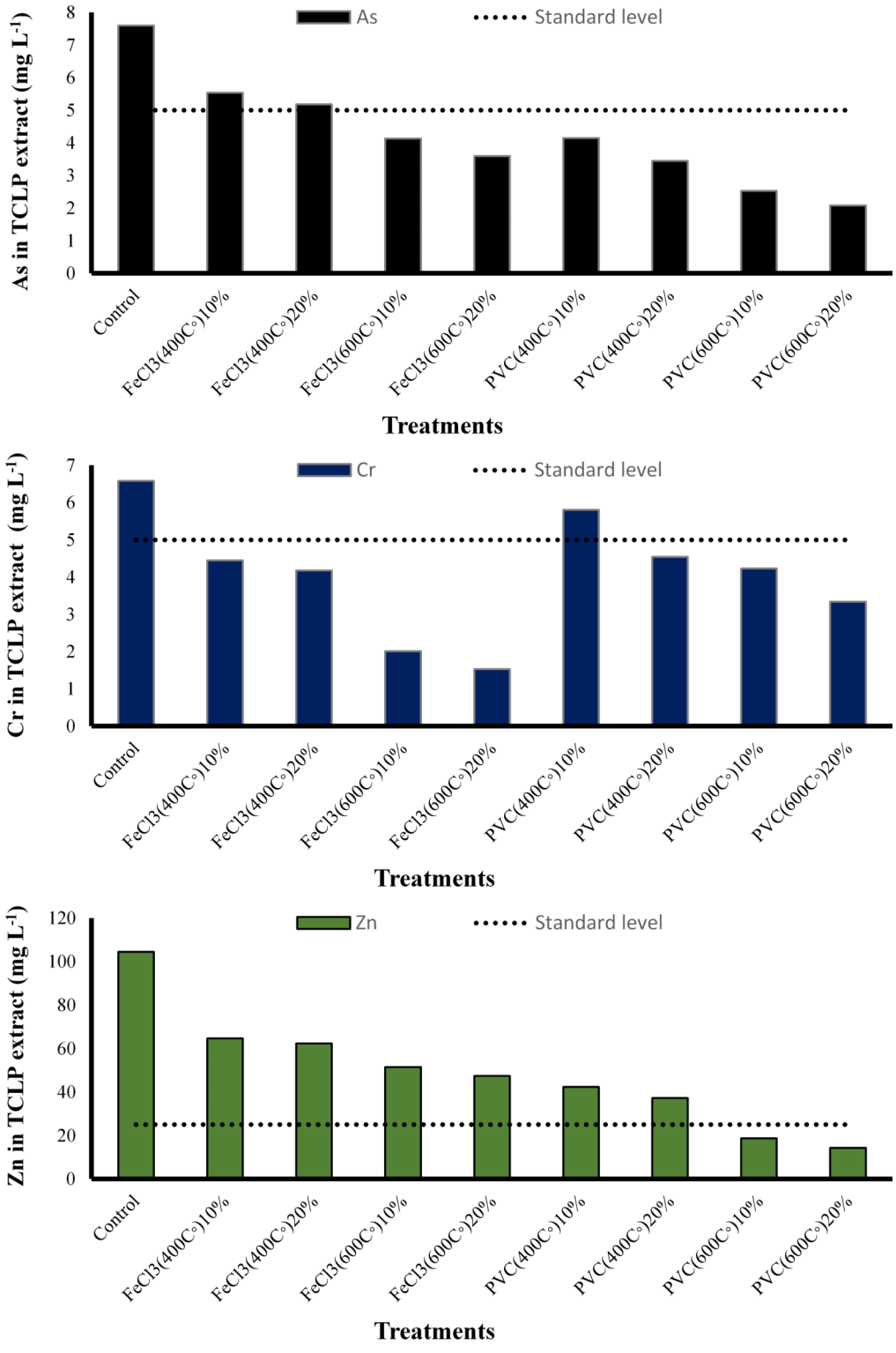

Fig. 9. TCLP results for As, Cr, and Zn in SS biochars influenced by various temperatures and chlorinated materials.

reductions of only 11.8% and 31.0% for 10% and 20% dosages. However, at 600 °C, PVC treatments improved substantially, achieving reductions of 35.7% and 49.2%, successfully meeting regulatory standards.

In the case of Zn, the control sample recorded a TCLP value of 104.5 mg L^{-1}, far exceeding the regulatory threshold of 25 mg L^{-1}. When compared with the control, $FeCl_3$ treatments at 400 °C achieved reductions of 38.1% and 40.4%, which were insufficient to meet the standard. At 600 °C, these reductions increased to 50.7% and 54.6%, and still fell short of compliance. On the other hand, PVC treatments displayed exceptional efficacy, particularly at 600 °C, where reductions of 82.1% and 86.3% were achieved for 10% and 20% dosages, respectively, successfully bringing Zn concentrations well below the acceptable limit.

Overall, the TCLP results reveal distinct trends in metal leachability reduction. Compared with the baseline sample, $FeCl_3$ treatments demonstrated notable efficiency in reducing Cr leaching, especially at higher temperatures and dosages. In contrast, PVC treatments exhibited superior performance in controlling As and Zn leachability, with maximum efficiency observed at 600 °C. These findings highlight the differential behavior of the two chlorinated materials, emphasizing PVC's advantage in addressing As and Zn leaching risks, while $FeCl_3$ remains a strong candidate for Cr stabilization under pyrolysis conditions.

Ref[51]. investigated the leaching of heavy metals from fast pyrolysis residues produced from different particle sizes of SS. Their results indicated that the TCLP-leaching contents of heavy metals from SS residues were lower than 2.0 mg kg^{-1} dry weight, which is less than 1% of the total content of heavy metals. This met the maximum content of contaminants for the toxicity characteristic, suggesting that the heavy metals in the pyrolysis residues were not highly mobile under the TCLP conditions. Ref[41]. studied heavy metal leaching from biochar produced by pyrolyzing SS. They applied the TCLP method to raw sludge and three biochar samples. Results showed minimal leaching of heavy metals from the biochar, with concentrations ranging from near zero to 17.96 mg kg^{-1}. The release of metals from the raw SS sample accounted for about 1–3% of the total heavy metal concentration, with Ni being the exception, reaching 9.8%. Biochar without impregnation significantly suppressed leaching, while biochar impregnated with K_2CO_3 showed higher leaching, but still met EPA standards.

Heavy metal risk assessment in the produced SS biochars

The chemical speciation analysis of Cr, Zn, and As enabled the calculation of the Cf and Er, which were subsequently used to determine the overall potential ecological risk index (RI) for these metals in the SS and the resulting biochars, as shown in Fig. 10. The RI values for the treatments varied significantly depending on the type and concentration of the reagents used, as well as the temperature conditions. The control sample showed an RI of 30.63, which falls within the moderate-risk category (30–60). For the $FeCl_3$ treatments, the RI values increased with both the reagent concentration and temperature. The 10% $FeCl_3$ treatment at 400 °C resulted in an RI of 44.68, indicating a 46% increase compared to the control. The 20% $FeCl_3$ treatment at 400 °C showed an even higher increase, with an RI of 54.06, a 77% rise compared to the control. At 600 °C, the $FeCl_3$ treatments led to even more substantial increases in the RI, with the 10% $FeCl_3$ treatment at 600 °C showing a 138% increase (RI = 72.98) and the 20% $FeCl_3$ treatment at 600 °C reaching an RI of 88.97, representing a 190% increase relative to the control.

In contrast, the PVC treatments resulted in a significant reduction in RI. The 10% PVC treatment at 400 °C led to an RI of 13.43, showing a decrease of 56% compared to the control, while the 20% PVC treatment at 400 °C further reduced the RI to 13.03, representing a 57% decrease. At 600 °C, both the 10% and 20% PVC treatments showed similar reductions, with RI values of 13.71 and 12.55, indicating a 55% and 59% decrease, respectively, relative to the control.

The results indicate that most of the treatments, except for the PVC treatments, exceeded the low-risk threshold, primarily due to the high Er for As. The $FeCl_3$ treatments, especially at higher concentrations and temperatures, resulted in moderate to considerable ecological risks, whereas the PVC treatments consistently reduced the RI, demonstrating their potential to lower heavy metal risk in biochar. The 10% and 20% PVC treatments at both 400 °C and 600 °C show the most significant reductions, making them preferable in terms of minimizing the ecological impact of heavy metals. Ref[18]. assessed the RI of heavy metals in biochars derived from co-pyrolysis of SS with PVC and calcium oxide (CaO). The study found that pyrolysis conditions influenced heavy metals differently, resulting in varying Er values. While the Er values of Cr, Cu, Pb, and Zn decreased, those for As increased. The results suggested that the presence of PVC increased the RI of heavy metals in biochar, especially at lower pyrolysis temperatures. Adding CaO reduced the risk, with SA900 (95% SS + 5% CaO at 900 °C) showing the lowest RI value (6.68), indicating low ecological risk.

Conclusion

This study investigates the effects of pyrolysis temperature and chlorinated additives, with a specific focus on $FeCl_3$ in a pyrolysis environment, on the removal and stabilization of some heavy metals from SS. This work represents a novel application of $FeCl_3$ in pyrolysis conditions, with a comparative analysis conducted alongside PVC, a well-established chlorinated compound, to evaluate its performance in reducing As, Zn, and Cr concentrations. The results underscore the critical role of pyrolysis temperature, with 600 °C emerging as the optimal temperature for maximizing heavy metal removal, while also reducing biochar yield due to increased thermal degradation and volatilization. Elevated temperatures facilitated the transformation of heavy metals into less bioavailable and less leachable forms, thereby contributing to the reduction of their environmental risk. Among the chlorinated additives, PVC demonstrated superior efficacy in reducing As and Zn concentrations, particularly at both 400 °C and 600 °C. These treatments effectively minimized the leachability of these metals, with the 20% PVC treatment at 600 °C proving to be the most effective in reducing their environmental mobility. This reduction is likely attributed to the chlorination process facilitated by PVC, which promotes the formation of volatile metal chlorides, lowering the residual concentrations of these metals in biochar. In contrast, $FeCl_3$ showed stronger performance in removing Cr, particularly at higher temperatures. It formed

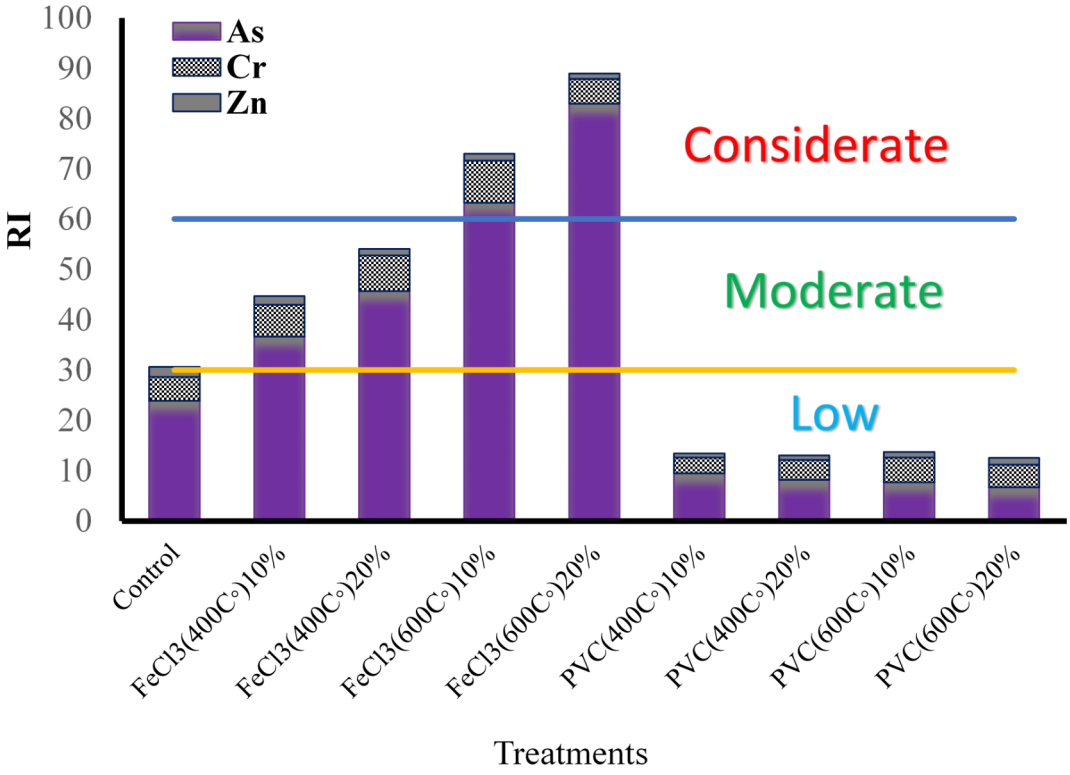

Fig. 10. The potential ecological risk index (RI) of heavy metals in SS biochars influenced by various temperatures and chlorinated materials.

non-volatile complexes that facilitated the removal of Cr, while the remaining Cr in the biochar matrix was stabilized, significantly reducing its leachability. Chemical speciation analysis confirmed that chlorinated treatments shifted heavy metals to less bioavailable forms, enhancing the residual fractions of As and Zn. TCLP tests further supported these findings, showing substantial reductions in metal leachability, particularly with the 10% and 20% PVC treatments at 600 °C. These results highlight the effectiveness of PVC in stabilizing As and Zn in biochar, making it a promising additive for environmental applications. Despite the favorable outcomes, the ecological risk assessment revealed a moderate to high risk for As, particularly with the $FeCl_3$ treatments, which exhibited a substantial increase in the risk index (RI) with higher concentrations and temperatures. This indicates the need for careful management in biochar applications where As is prevalent. In contrast, PVC treatments significantly reduced the RI, demonstrating their potential to minimize the ecological risk of heavy metals. Although $FeCl_3$ proved more effective for Cr removal and stabilization, its effectiveness in reducing the environmental impact was less pronounced compared to PVC for As. Thus, PVC is particularly recommended for scenarios requiring the reduction of ecological risks associated with As, while $FeCl_3$ remains more suitable for Cr-contaminated environments. The study suggests that further research is needed to explore the efficacy of chlorinated compounds for managing specific heavy metals in SS. A more tailored approach, considering the unique behavior of each heavy metal, is recommended for optimizing biochar production and minimizing environmental impacts.

Data availability

All data generated or analysed during this study are included in this published article.

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Mahboub Saffari: writing – original draft, methodology, formal analysis, experimental work; Masomeh Moazallahi: experimental work, review, editing; Rezvan Mashayekhi: experimental work, review, editing.

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Declarations

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