

Review

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Slow pyrolysis and product utilization of heavy metal-contaminated biomass from agricultural systems

Zhengjun Wang^{1#}, Qifeng Min^{1#}, Kailin He², Ruigang Wang^{3*}, Gaoyuan Shang⁴, Dasong Lin¹ and Yajun Wang^{1*}

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Abstract

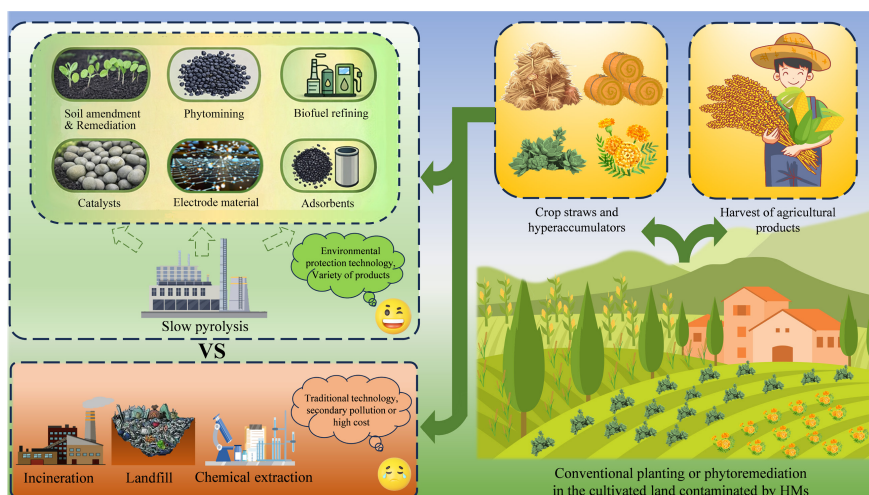
With the intensification of anthropogenic activities, cultivated soils in many regions have become increasingly contaminated with heavy metals (HMs), generating substantial quantities of biomass carrying HM burdens. Conventional disposal pathways, such as direct incineration or returning biomass to farmland, may re-release HMs and create additional environmental risks. This review summarizes the dry and wet pyrolysis treatment of HM-contaminated biomass, with an emphasis on HMs' migration, post-treatment stabilization, and product utilization pathways. To strengthen the field-level perspective of the review, a bibliometric analysis of the 2001–2025 literature was incorporated to identify major hot-spots, conceptual structures, and emerging directions. The available evidence indicates that slow pyrolysis offers a promising route to reduce the HM risk while creating carbon-rich products with potential applications in soil amendment, adsorption, catalysis, electrochemical materials, metal recovery, and energy recovery.

Keywords: HM-contaminated biomass, Slow pyrolysis, Hyperaccumulator, Harmless treatment

Highlights

- In this review, HMs are classified into mobilizable and immovable groups.
- The migration characteristics of Hg, Cd, Pb and Ni during slow dry pyrolysis of HMs-contaminated biomass were analyzed.
- Compared with ordinary biomass, the solid products obtained from the slow pyrolysis of HMs-contaminated biomass have unique utilization pathways, such as endogenous catalysts and electrode materials.

Graphical abstract



Authors contributed equally: Zhengjun Wang and Qifeng Min

* Correspondence: Ruigang Wang (3761520835@sina.com); Yajun Wang (wangyajun@caas.cn)

Full list of author information is available at the end of the article.

Introduction

Cultivated land is an indispensable resource which is intricately linked to both production and livelihood. With the advancement of global industrialization, the issue of heavy metal (HM) contamination has grown increasingly severe, posing a significant threat to human health^[1,2]. Taking China as an example, the proportion of cultivated land with excessive HMs accounted for 16.1% of the national cultivated land^[3,4]. Meanwhile, a significant amount of biomass contaminated with HMs is also generated in cultivated soil because of the presence of HMs^[5]. Herein, the major sources of HM pollution in cultivated land are crop straw and hyperaccumulators^[6].

The annual pollution of HMs in China results in the contamination of approximately 12 million tons of grain. According to the grain-to-straw ratio, the weight of contaminated crop straw reaches around 13.2–14.4 million tons^[4]. However, phytoremediation technology can be used to extract HMs from polluted cultivated land and produce a lot of waste biomass rich in HMs^[7]. These hyperaccumulators are regarded as the second major source of biomass in cultivated soil contaminated with HMs. Improper treatment of these polluted plants will cause the secondary pollution of cultivated soil and a waste of resources^[8].

The current technologies used for the treatment of HM-contaminated biomass include landfill, composting, liquid phase extraction, incineration, pyrolysis, etc.^[7,9,10]. Landfilling is a straightforward and convenient method; however, it is associated with significant drawbacks, such as land occupation and the risk of secondary contamination^[11]. Composting is the process of converting HM-contaminated plants into organic fertilizers, promoted by micro-organisms, which will not reduce the total amount of HMs and the pollution risks to farmland^[12,13]. Extraction refers to the process of transferring HMs from the biomass to a liquid phase by utilizing an extractant for their dissolution or chelation. The widespread adoption of this technology has been impeded by its limited capability to extract a specific type of HM and its relatively high cost^[9]. The process of incineration involves the combustion of plants contaminated with HMs at high temperatures, allowing for the recovery of heat energy. This method easily leads to the volatilization of HMs and air pollution^[14,15]. The abovementioned technologies are difficult to popularize on a large scale because of their defects.

Slow pyrolysis technology has gained significant attention because of its effectiveness and environmentally friendly characteristics. It usually refers to the thermal decomposition of biomass at a rate lower than 10 °C/min in an air-isolated environment, resulting in the production of biochar, bio-oil and pyrolysis gas^[16,17]. However, the significance of this technology lies not only in biomass conversion itself, but also in its capacity to link HM stabilization, management of contaminated biomass, and product valorization.

A bibliometric overview of the 2001–2025 literature was undertaken to identify research hotspots, conceptual linkages, and emerging directions, thereby providing a field-level basis for the structure and emphasis of this review. Accordingly, this review focuses on three major aspects: (1) The migration and transformation of representative HMs during dry pyrolysis, with an emphasis on Hg, Cd, Pb, Ni, As, and Cr; (2) the redistribution and stabilization of HMs during wet/hydrothermal pyrolysis, particularly the effects of temperature, the reaction medium, pH, and liquid phase transfer on metal partitioning; and (3) the utilization pathways of pyrolysis-derived products, including biochar, bio-oil, and pyrolysis gas, in soil amendment, adsorption, catalysis, electrochemical materials, metal recovery, and energy production.

Bibliometric analysis of the research landscape

To strengthen the field-level perspective of this review, we conducted a bibliometric analysis of the updated literature published during 2001–2025 using the Web of Science Core Collection. Literature was retrieved according to the search strategy described in Fig. 1, with the timespan limited to 2000–2025 and document types restricted to articles and review articles. The initial search retrieved 5,727 records. After screening and data cleaning, including the removal of irrelevant records, duplicates, and incomplete entries, the final dataset was analyzed using the Bibliometrix R package to examine publication trends, thematic evolution, and keyword co-occurrence patterns in research on the thermochemical conversion and product utilization of HM-contaminated biomass.

Rather than serving as a separate descriptive add-on, this analysis was integrated into the review to position it within the broader research landscape by clarifying the growth trajectory, conceptual core, and emerging directions of research on the slow pyrolysis of HM-contaminated biomass through annual publication trends, co-word network structures, and the trajectory of the topic's evolution. The annual publication profile shows that this field has entered a stage of sustained expansion, with rapid growth after 2017 and annual output reaching 643 papers in 2025. The co-word network indicates that the field is organized around two closely linked thematic axes: Biomass conversion and process regulation, represented by terms such as pyrolysis, biomass, temperature, and bio-oil; and environmental control and product functionality, represented by biochar, adsorption, removal, and HMs. This structure suggests that slow pyrolysis is increasingly studied not merely as a disposal technique, but as a strategy linking the management of contaminated biomass, stabilization of HMs, risk reduction, and the production of value-added carbon material. Analysis of the topic's evolution also shows the recent emergence of lifecycle assessment, the circular economy, machine learning, carbon capture, composite materials, and synergistic effects, indicating a shift toward process integration, multifunctional material design, sustainability assessment, and data-assisted optimization.

Taken together, these bibliometric results provide the rationale for the structure of the following sections. They show that the field is organized around two connected questions: How HMs migrate and transform during dry and wet pyrolysis, and how the resulting products can be used in environmentally meaningful ways. The field-level analysis also helps contextualize individual metals. Although Hg, Cd, Pb, and Ni remain the most frequently discussed metals, the weaker visibility of As- and Cr-related studies indicates that these metals remain less systematically examined, which partly explains why the current evidence base is uneven across different contaminants.

Migration characteristics of HMs under slow pyrolysis

HMs refer to metals with a density greater than 4.5 g/cm³ in the strict sense, of which there are about 60 types^[18,19]. Nevertheless, Cd, Hg, Pb, Cr, Ni, Cu, and Zn are the main HMs that exist in large quantities or may enter the farmland system. Arsenic (As) is regarded as a metalloid^[20]. Guided by the bibliometric patterns identified above, the following sections focus on the metals and process pathways that currently define the core of the field and also indicate where the evidence remains comparatively limited.

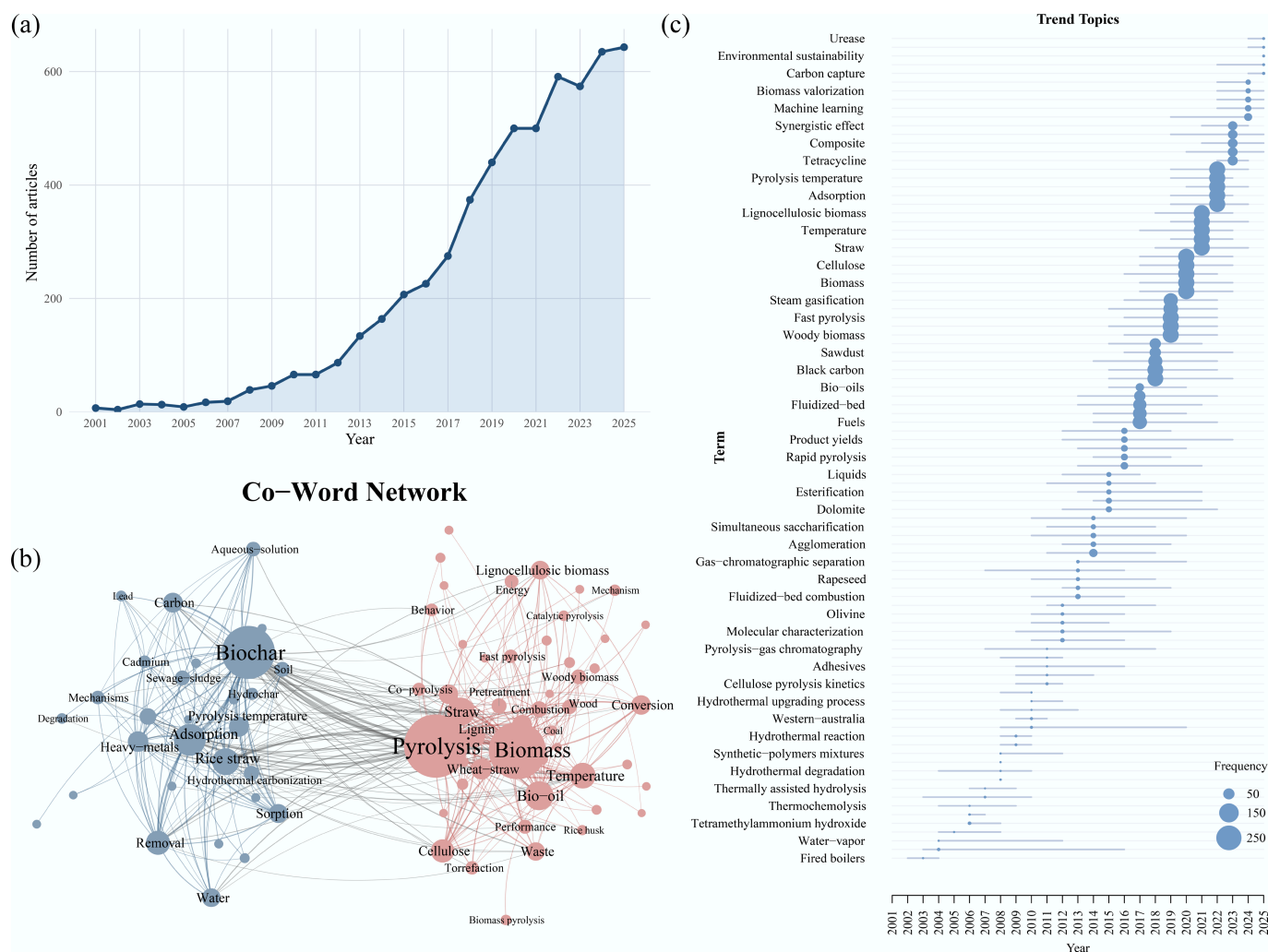


Fig. 1 Bibliometric overview of research on slow pyrolysis and product utilization of HM-contaminated biomass during 2001–2025. **(a)** Annual scientific production; **(b)** co-word network showing the main conceptual structure of the field; **(c)** evolutionary trend of the topic, highlighting recent and emerging themes.

The migration characteristics of HMs are determined by the slow pyrolysis process. In this review, mobilizable metals refer to those that can be released from biomass, whereas immovable metals are those that remain in significant amounts in solid residues after slow pyrolysis. Generally, as the temperature of the dry pyrolysis process increases, different HMs gradually diffuse from the biomass to the carrier gas. The diffusion order is as follows: Hg (350 °C) < Cd (400–500 °C) < As (600 °C) < Pb and Zn (700 °C). Meanwhile, Cu and Ni can all be significantly retained in the solid residues^[21–24]. However, the migration characteristics of HMs under wet slow pyrolysis conditions are very different from those under dry slow pyrolysis. As shown in Fig. 2, except for Ni and Cr, most HMs are very difficult to stabilize in the solid residue under wet pyrolysis conditions^[25–27].

Dry pyrolysis

Migration characteristics of Hg

China is the largest emitter of Hg in Asia, with annual Hg emissions accounting for one-third of all countries. The area of cultivated land contaminated by Hg is approximately 3.2×10^4 hectares^[28]. In recent years, with the wide application of phytoremediation technology for

the treatment of contaminated soil, a large amount of Hg-rich biomass has been produced, and the issue of its subsequent safe disposal has become increasingly prominent. During the slow pyrolysis of biomass contaminated with Hg (defined as a mobilizable metal in this paper), it is necessary to control the processing parameters to regulate the migration of Hg by analyzing the existing form of Hg (inorganic mercury, organic mercury, or a combined state).

Through previous research, it has been observed that under slow pyrolysis conditions, significant quantities of Hg can volatilize prior to reaching 450 °C^[21]. In our experiments, we performed slow pyrolysis on corn stalk and wheat straws contaminated with Hg. In Fig. 3a, b, it can be seen that as the temperature rises, the mercury content in the resulting biochar diminished. When the pyrolysis temperature reached 550 °C, the Hg removal rates of wheat straw and corn stalk biochar were 94.0% and 93.2%, respectively, and the effective Hg in the biochar dropped to an extremely low level (Fig. 3c). "Effective Hg" refers to the forms of mercury in biomass or biochar that are environmentally mobile, bioavailable, or easily leachable (mobilizable mercury). Unlike total mercury, which includes all mercury species (e.g., inorganic mercury, organic mercury, and bound states), "effective Hg" specifically denotes the mercury

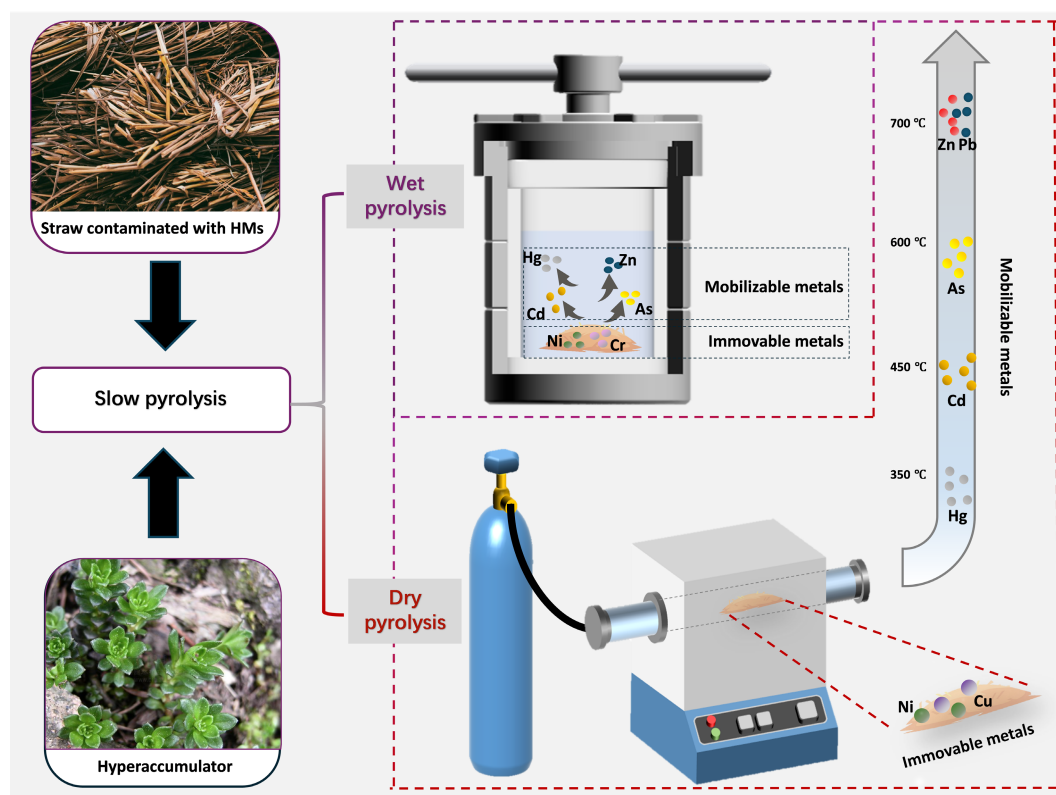


Fig. 2 The migration characteristics of HMs treated by slow pyrolysis.

fractions that are prone to be released into water, soil, or air under natural conditions, or to be absorbed by organisms. In light of the strong volatility of mercury, this experimental process involved the absorption of Hg from flue gas using a specialized absorbing solution. Concurrently, the mercury content in both the pyrolysis liquid and gas phases was quantified and subsequently translated into the recovery percentage. The experiment revealed that when the pyrolysis temperature was elevated to 550 °C, the concentration of Hg in the noncondensable gas phase exceeded 50%, as shown in Fig. 3d. In contrast, the oil phase exhibited a lower range of 24.90% to 31.41% Hg content. This indicates that after the slow pyrolysis of Hg-contaminated biomass, the recovery of Hg from the pyrolysis gas is a necessary accompanying technology to avoid the risk of air pollution caused by the release of Hg.

Migration characteristics of Cd

Industrial emissions and mining activities are usually the primary sources of Cd pollution. Wastewater, waste gas, and waste residue generated from metal smelting and mining operations can enter cultivated soil through atmospheric deposition or irrigation. In addition, phosphorus fertilizer applied in agricultural production is also one of the important sources of Cd in farmland^[29]. In addition to crop straw contaminated by Cd, plants which can accumulate Cd include *Sedum alfredii*^[30], *Myriophyllum verticillatum* L.^[31], *Celosia argentea* Linn.^[32], *Silphium perfoliatum* L., *Helianthus annuus*, and so on.

In the slow pyrolysis of *Avicennia marina* contaminated with HMs, He et al. observed that the volatilization of Cd occurred at a lower temperature. With an increase in the pyrolysis temperature from 400 to 500 °C, the Cd content in the resulting biochar decreased significantly, dropping from 84.73% to 9.32%. Furthermore, at a pyrolysis temperature of 600 °C, the Cd content in the biochar was found to be only approximately 1%^[33]. In Zong's study^[34],

diethylenetriaminepentaacetic acid (DTPA)-Cd showed significant positive and negative correlations with multiple indicators in biochar. DTPA-extractable Cd was positively correlated with cation exchange capacity (CEC), negative surface charge, and atomic ratios (H/C, N/C), but negatively correlated with pH, specific surface area (SSA), ash content, and carbon content, indicating that oxygen-containing functional groups promote Cd's bioavailability, whereas mineral components and structural properties favor its immobilization. As the pyrolysis process progresses, the proportion of aromatic carbon in biochar increases through the conversion from alkyl and O-alkyl C to aryl C. The reduction in oxygen-containing functional groups leads to a decrease in the ability to form complexes with HMs. Consequently, significant quantities of HMs are released into the noncondensable gas^[34].

Researchers have also discovered that elevated temperature facilitates the transformation from an unstable state to a stable state of HMs in biochar, thereby diminishing the leaching toxicity^[35]. Because of this phenomenon, two optimization routes can be considered for the slow pyrolysis of Cd-contaminated plants. The first route involves setting the final pyrolysis temperature above 500 °C to ensure a low concentration and stable speciation of HMs in the solid product. Additionally, various methods can be used to capture HM ions that may escape with the pyrolysis gas. The second route aims to produce biochar with the highest possible HM content, while simultaneously generating cleaner bio-oil and pyrolysis gas, as illustrated in Fig. 4.

Migration characteristics of Pb

Pb mainly enters the agricultural system through traffic exhaust, smelting dust, and organic fertilizers. It adversely affects plants through multiple avenues, encompassing energy processes, metabolic functions, structural integrity, and genetic expression, ultimately

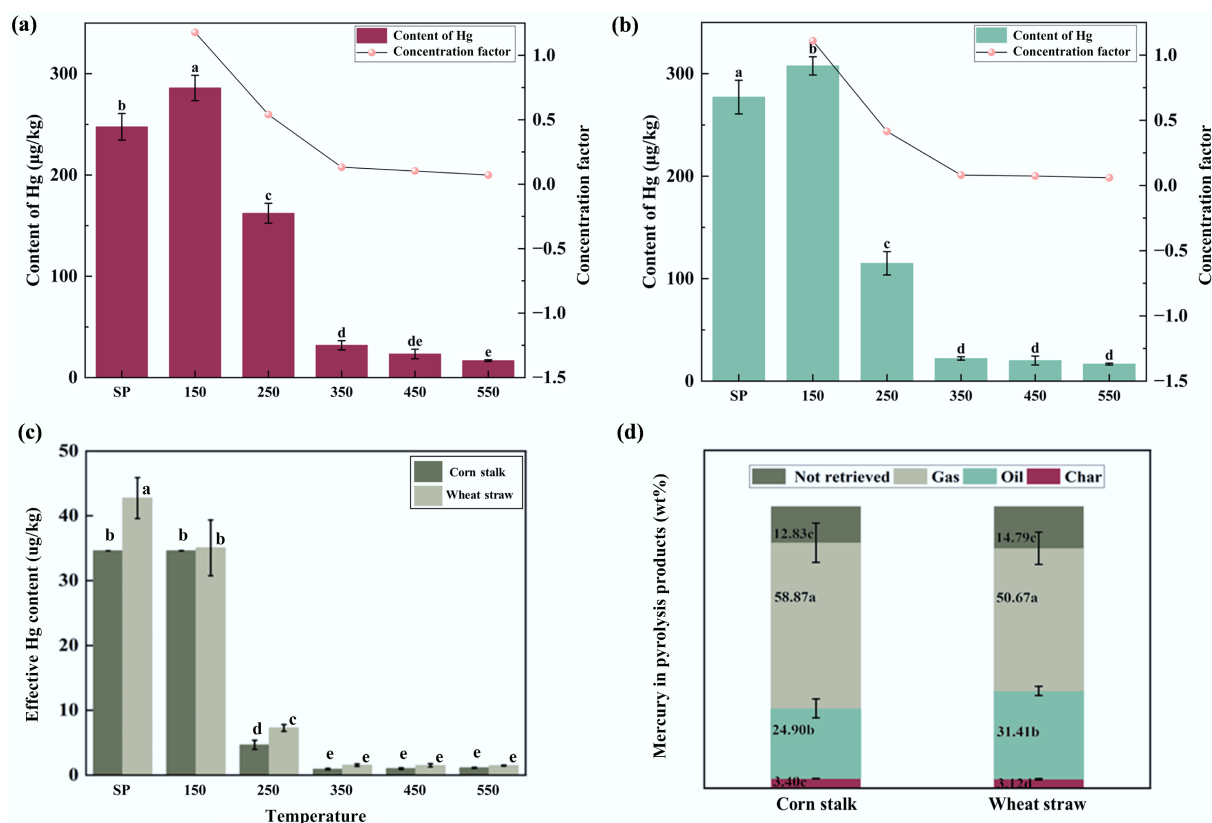


Fig. 3 The migration characteristics of Hg during slow pyrolysis. (a) The content and concentration factor of Hg in corn stalk biochar. (b) The content and concentration factor of Hg in wheat straw biochar. (c) The effective Hg content in biochar. (d) The distribution of Hg in the three phases.

manifesting as slow growth, decreased biomass, reduced photosynthetic efficiency, and impairment of the antioxidant system^[36]. The hyperaccumulators of Pb include *Silphium perfoliatum* L., *Pogonatherum crinitum*^[36], and *Solanum nigrum*^[37].

Pyrolysis temperature is a key parameter affecting the stabilization of lead. Compared with Cd, the escape temperature of Pb is higher during slow pyrolysis, and it is still a mobilizable metal. Studies have found that at lower temperatures (300–400 °C), slow pyrolysis of contaminated biomass can reduce the bioavailability of Pb, but its escape potential increases with a rise in the pyrolysis temperature^[38]. Du et al. observed that Pb showed enrichment at temperatures below 550 °C^[39]. Similarly, Bian et al. pyrolyzed contaminated wheat straw collected from metal-contaminated fields with contrasting Pb levels at 350 and 550 °C, and found that pyrolysis could stabilize Pb in the resulting biochar^[40]. However, when the pyrolysis temperature exceeds a certain range (500–700 °C), Pb begins to escape from the solid, while the lead remaining in the biochar can be effectively stabilized^[41]. In addition, a higher heating rate also promotes the release of Pb. Sun et al. conducted a study on the rapid pyrolysis of centipedegrass (*Eremochloa ophiuroides*) and found that the concentration of Pb in biochar decreased from 229.4 to 89.0 mg/kg as the pyrolysis temperature increased from 500 to 600 °C^[42].

Conversely, the presence of lead can alter the pyrolysis kinetics and product distribution of biomass. Studies have shown that Pb can reduce the reaction activation energy in the main thermal degradation stage of biomass^[43]. When water hyacinth (*Pontederia crassipes*) biomass is pyrolyzed, the presence of lead can increase the yield of pyrolyzed bio-oil by up to 56%, whereas the yields of

biochar and gas are reduced^[44]. It proves that endogenous Pb plays a catalytic role in the slow pyrolysis of biomass.

Migration characteristics of Ni

The main pathways for Ni to enter the farmland system are industrial emissions and its inherent presence in the parent material of the soil. Its bioavailability is controlled by the type of parent rock, carbonate content, and pH of the soil. Owing to its substantial market value and the ample availability of super-rich plant resources, Ni has emerged as the sole metal to have successfully achieved commercial-scale phytomining at present^[45]. Studies have shown that nickel-enriched plants such as *Odontarrhena chalcidica* have been cultivated on a large scale in places like Albania, Greece, and Malaysia. Their low carbon emissions (reducing 80–100 tons of carbon per ton of nickel producing compared with traditional Ni smelting) meet the sustainable development needs of the electric vehicle industry. Other Ni-hyperenriched plants include *Alyssum corsicum*^[46], *Berkheya coddii*^[47], *Pistia stratiotes*^[48], etc.

A seven-year field study conducted in Albania has demonstrated the effectiveness of plant mining^[49]. The Ni hyperaccumulator *O. chalcidica*, which grows on nickel-rich soil, extracts approximately 100 kg of Ni ha⁻¹ annually. After harvest, high-purity nickel salts are recovered from the plants through ashing, indicating that Ni behaves as a relatively immobile HM. Slow pyrolysis can effectively fix Ni in hyperaccumulator biochar, thereby reducing its bioavailability and the potential risk of secondary pollution^[50]. Ziad Al Chami et al. pyrolyzed contaminated sorghum (*Sorghum bicolor*) stalks in a horizontal tube furnace and found that approximately 99% of Ni was retained in the pyrolytic carbon, and the content of HMs in the pyrolytic oil was below the detection limit^[51]. Ni also plays the role of a catalyst in the biomass pyrolysis process, profoundly

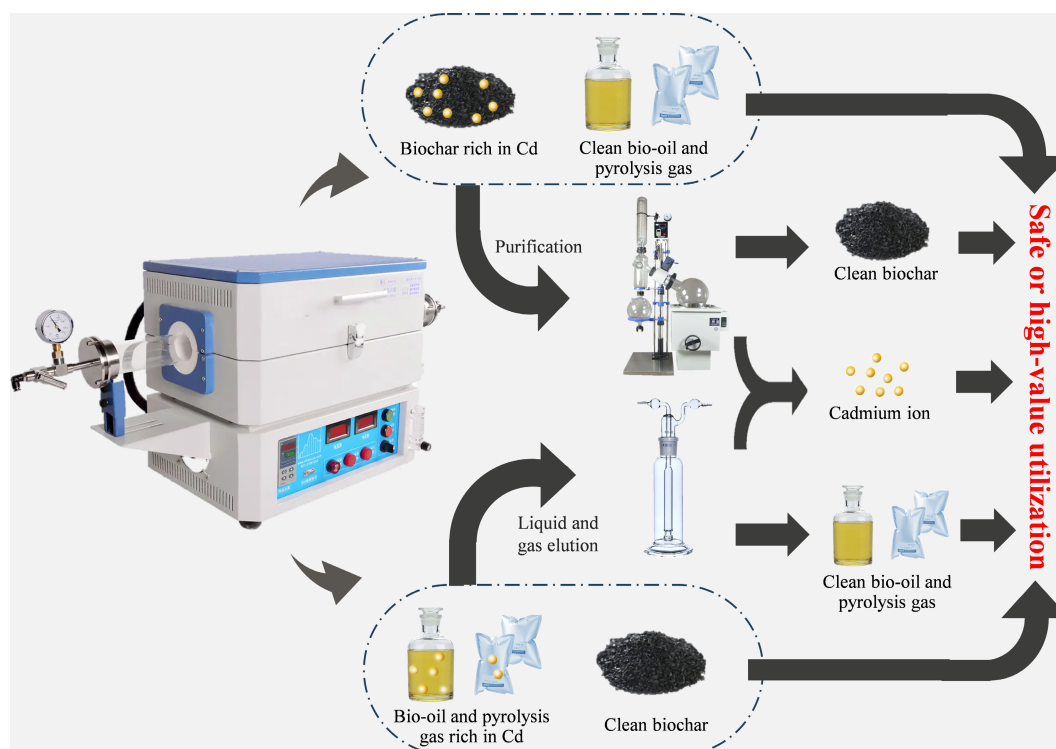


Fig. 4 Two technological routes for the slow pyrolysis of plants contaminated by Cd.

influencing the yield and composition of gas, liquid, and solid-phase products. For lignin in biomass, slow pyrolysis conducted in the presence of Ni ions results in a remarkable 180.60% increase in gas yield, accompanied by a substantial rise in the proportion of H_2 [52]. Therefore, a comprehensive understanding of the interactions between Ni and the main components of biomass is crucial for the development of efficient treatment technologies for Ni-contaminated biomass.

Migration characteristics of As and Cr

Compared with typical divalent metals such as Cd, Pb, Hg and Ni, metalloids such as As and multivalent transition metals such as Cr exhibit more complex transformation pathways during pyrolysis because of their variable oxidation states and strong interactions with mineral matrices. Their inclusion is therefore important for a more comprehensive review of HM-contaminated biomass utilization, even though As- and Cr-related pyrolysis studies remain less systematic than studies on Hg, Cd, Pb, and Ni.

Arsenic, which can be enriched in phytoremediation biomass such as *Pteris vittata*, may undergo volatilization and phase redistribution during thermochemical conversion. At elevated temperatures, part of the As can migrate into the gas phase, whereas another fraction may remain in the solid phase through the formation of metal–arsenate compounds, mineral lattice incorporation, or surface complexation[14,26]. For As-contaminated biomass, product safety depends not only on the total As retention, but also on the distribution of As among the gas, liquid, and solid phases and on the stability of As-bearing species in the final carbonaceous product.

Chromium is particularly sensitive to redox conditions. Under oxygen-limited pyrolysis, toxic and mobile Cr(VI) may be reduced to the less toxic and less mobile Cr(III) by reductive gases and electron-donating functional groups generated by decomposing biomass. The resulting Cr(III) can be immobilized in biochar through precipitation as $Cr(OH)_3$ or Cr_2O_3 , complexation with oxygen-containing

functional groups, or association with silicates, carbonates, and iron-bearing minerals[53–55]. Increasing the temperature and ash content may further favor Cr's stabilization by promoting mineral association and formation of the crystalline phase. Therefore, valence-state transformation should be considered to be a central indicator when evaluating the environmental safety of Cr-bearing pyrolysis products.

From a resource-utilization perspective, biochar derived from As- or Cr-bearing biomass may still have environmental value, but only when pyrolysis-induced changes in metal speciation and leachability are carefully controlled. In the As hyperaccumulator *P. vittata*, partial reduction of As(V) to the more volatile As(III) was observed at 200 °C, and 62.5% of the total volatilized As was released below 400 °C, indicating substantial low-temperature mobility[15]. In contrast, Dastyar et al. stated that As is generally highly volatile, whereas Cr is comparatively nonvolatile during thermochemical conversion, and that moderate pyrolysis temperatures of about 350–450 °C, and in some cases up to around 600 °C, are more favorable for As and Cr retaining in the biochar[56].

Chemical speciation of HMs before and after dry pyrolysis

Through dry pyrolysis, the final speciation of different HMs varies. However, a common trend is observed, as the vast majority of HMs in the solid phase are transformed from the unstable acid-extractable and reducible fractions to the stable oxidizable and residual fractions. Silicon, phosphorus, sulfur, calcium, and other similar elements facilitate the fixation of HMs within the solid products. The details are shown in Table 1.

Wet pyrolysis

Wet pyrolysis process of HM-Contaminated Biomass

Wet pyrolysis (hydrothermal technology) is a heat conversion technique that has emerged in recent years for the recycling and utilization

Table 1 Comparative summary of HMs' behavior during dry pyrolysis of contaminated biomass

Metal	Before pyrolysis	After pyrolysis	Transformation characteristics or key influencing elements	Ref.
Hg	Organic-bound fraction	The vast majority volatilizes into the gas phase as elemental Hg, whereas in the solid phase, Hg mainly occurs in F4 form and may exist as HgS	S promotes fixation → HgS	[57]
Cd	Mainly F1 and F2 fractions	In the solid products, Cd mainly occurs in the F3 and F4 fractions, and may exist as stable CdSiO ₃ and Cd ₃ (PO ₄) ₂ species	Cl promotes volatilization → CdCl ₂ S promotes fixation → CdSP promotes fixation → Cd ₃ (PO ₄) ₂	[58–60]
Pb	Mainly F1 and F2 fractions	In the solid products, Pb mainly occurs in F3 (oxidizable) and F4 (residual) fractions. Pb bound to Fe/Mn oxides may be released at high temperatures through mineral phase reorganization and then transformed into F3 or F4	P promotes fixation → Pb ₃ (PO ₄) ₃ Cl/ Si promotes fixation → PbSiO ₃	[41,61]
Ni	Mainly F1 and F2 fractions, or mainly exchangeable, organic-bound, and carbonate-bound fractions	Mainly occurs in the F3 and F4 fractions. Nickel tends to react with mineral components in biomass ash, such as SiO ₂ and CaO, forming more thermodynamically stable nickel silicates (e.g., Ni ₂ SiO ₄) or perovskite-like minerals	Si and Ca promote fixation → Ni ₂ SiO ₄ , et al.	[62,63]
As	Mainly present as oxyanions (AsO ₄ ^{3−} , AsO ₃ ^{3−}), predominantly in organic-bound form	In the solid phase, As mainly occurs in F4 form. Under the reducing atmosphere of pyrolysis, As(V) may be reduced to As(III) and form As ₂ O ₃ ; it may even be further reduced to elemental As or As ₂ S ₃ in sulfur-rich systems	Fe and S promote fixation → FeAsS, As ₂ S ₃ , or FeAsO ₄	[64,65]
Cr	Mainly exchangeable, organic-bound, and carbonate-bound fractions	At high temperatures, Cr(VI) can be effectively reduced to Cr(III) by biomass pyrolysis products such as carbon, H ₂ S, H ₂ , and CO. Cr(III) can further form stable mineral phases with Si, Al, Fe, and P in biomass	Cr(III) is relatively harmless and less mobile, whereas Cr(VI) is highly toxic and mobile. It can form stable mineral phases with Si, Fe, and P → Cr-Si-O complexes or spinel structures such as CrFe ₂ O ₄ and CrPO ₄	[66,67]

In the BCR sequential extraction method, F1 is the acid-extractable fraction, F2 is the reducible fraction, F3 is the oxidizable fraction, and F4 is the residual fraction. In TCLP-based environmental risk assessments, the fractions include exchangeable, carbonate-bound, Fe/Mn oxide-bound, organic-bound, sulfide-bound, and residual forms.

of plant resources contaminated with HMs. It involves the thermal decomposition of biomass under specific temperature and pressure conditions within a closed water medium^[50,68]. Most wet pyrolysis processes typically operate within a temperature range of 180–360 °C, while maintaining a saturation pressure of 2–10 MPa. The preparation process is straightforward, and the conversion cost is acceptable for producing hydrothermal carbon. This technology is not limited by the water content of the raw material, thus indicating its potential for widespread application in the treatment of HM-contaminated biomass^[69].

Migration characteristics of HMs during wet pyrolysis

In addition, the type of liquid phase has a significant influence on the migration characteristics of HMs during wet pyrolysis. Zhang et al. used H₂O and HCl as solvents for hydrothermal carbonization of *S. alfredii* containing Cd and Zn, and found that low temperatures and HCl promoted the transfer of Cd and Zn from the solid phase into the processing liquid, thereby improving HMs' separation during hydrothermal treatment^[70]. This distinction is important because the reduced escape risk under wet pyrolysis should not be interpreted as the disappearance of metals but as the suppression of uncontrolled volatilization together with more directed redistribution into hydrochar or the liquid phase. Additional studies on *Sedum*-type hyperaccumulators demonstrate that metal partitioning can be tailored by the temperature, residence time, pH, and additives. Hydrothermal upgrading of *S. alfredii* Hance at high temperature and pressure achieved almost complete removal of Zn, Pb, and Cu into the aqueous phase^[71], whereas milder hydrothermal conversion enriched most Cd, Cu, Pb, and Zn in the solid residue^[72]. During subcritical hydrothermal liquefaction of *Sedum plumbizincicola*, HMs were mainly distributed in hydrochar and the aqueous phase, but less than 10% entered the heavy oil fraction; notably, more than 96% of As migrated into the aqueous phase^[73]. Other work showed that Zn released from *Sedum plumbizincicola* could catalyze hydrothermal reactions and increase bio-oil production^[25], and KOH-modified hydrochar from Cd/Zn hyperaccumulator biomass could be used for aqueous Cd(II) removal^[74]. These findings indicate that wet pyrolysis of *Sedum*-type

hyperaccumulators should be understood as a controllable separation, stabilization, and resource recovery process rather than a single removal event.

Main products of wet pyrolysis

The main products of wet pyrolysis include hydrothermal carbon and carbonized liquid, with minimal production of gaseous byproducts. The bio-oil generated by this process has a significantly higher calorific value (higher heating value, HHV). Jiang et al. conducted wet pyrolysis of *P. vittata* used to remediate contaminated farmland, and produced bio-oil with a calorific value of 28.51 MJ/kg. The main components of the bio-oil were phenols, ketones, hydrocarbons, aldehydes and so on, and the aqueous phase was mainly acetic acid (17.21–24.77 mg/mL)^[75]. Zhang found that the hydrothermal carbon yield first increased and then decreased with the increase in the reaction's intensity, and the carbonized liquid yield first decreased and then stabilized, whereas the gas-phase product yield continued to rise. However, the products were dominated by hydrothermal carbon (40.4%–52.1%) and carbonized liquid (38.3%–57.5%) regardless of the reaction's intensity, and only a small part was transferred to the gas phase (2.1%–13.3%)^[70].

In addition to the wet pyrolysis temperature, the HMs inside the biomass also catalyze the wet pyrolysis reaction, affecting the final products. Zhu et al. found that the presence of Pb in the remediation plant *Rhus chinensis* increased the yield of formic acid and acetic acid, but decreased the yield of levulinic acid. On the basis of the abovementioned research results, it can be concluded that wet pyrolysis greatly simplifies the types of products compared with slow pyrolysis. It can be used to convert HM-contaminated biomass into a large amount of clean hydrothermal carbon^[76].

Applications of slow pyrolysis products from HM-contaminated biomass

Slow pyrolysis provides a practical route to convert HM-contaminated plants into usable materials and energy products. As depicted in Fig. 5, the utilization strategy for pyrolysis products entails integrating the

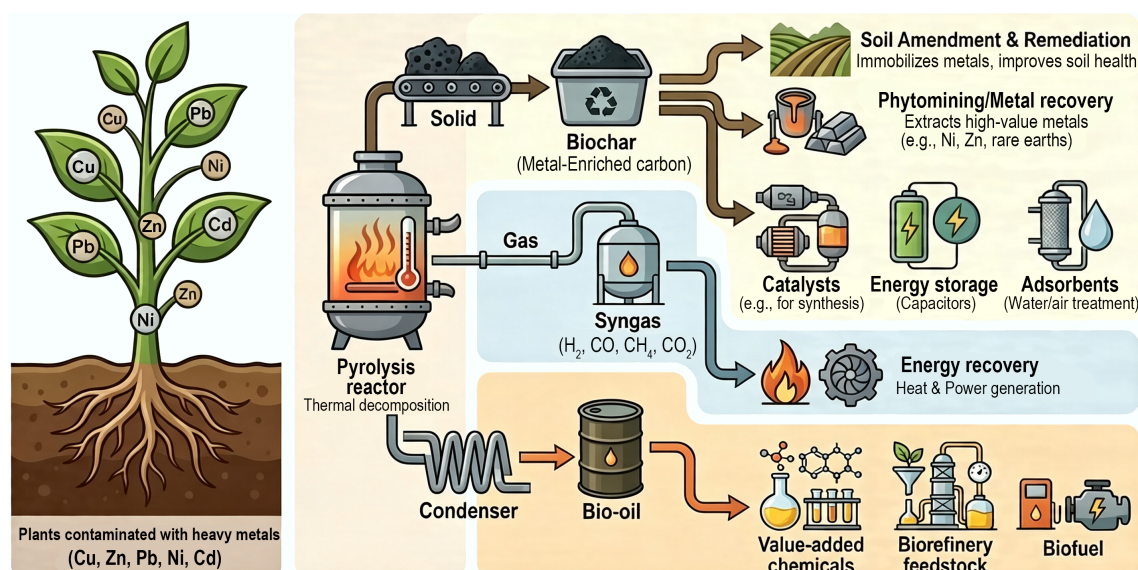


Fig. 5 Applications of slow pyrolysis products from HM-contaminated biomass.

stabilization of pollutants with the efficient harnessing of resources. The biochar product can be used for soil remediation, adsorbents, catalysts, and other functional uses, whereas syngas and bio-oil support energy recovery and fuel upgrading.

Soil amendment

The conversion of contaminated biomass into biochar offers a sustainable pathway for soil remediation and quality enhancement. Agonomically, biochar serves as an effective soil amendment by increasing the soil's alkalinity and providing a stable carbon matrix^[50,77]. The high degree of aromaticity and carbon's stability ensure long-term carbon sequestration when biochar is incorporated into the soil^[77].

Environmentally, biochar excels in the *in situ* immobilization of co-existing HMs, thereby reducing their bioavailability to indigenous plants and microbes. For instance, biochar derived from phytoremediation residues can significantly decrease the exchangeable fractions of metals like Ni, Sb, and Cd through mechanisms including surface complexation and mineral-induced precipitation^[50,78]. Specifically, the presence of carbonates and phosphates within the biochar matrix acts as a buffer that stabilizes hazardous elements, mitigating the ecological risk of secondary leaching^[46]. Consequently, the application of this type of biochar not only restores the soil's fertility but also provides a safe disposal solution for toxic biomass, facilitating the circular economy in contaminated land management^[77,78].

Adsorbents

Biochar derived from hyperaccumulators and phytoremediation residues has emerged as a high-efficiency adsorbent for the removal of HMs from aqueous solutions. For instance, biochar prepared from contaminated plant residues (*Conyza canadensis*, *Betula luminifera*, *Gahnia tristis*) at different pyrolysis temperatures (300–600 °C) showed excellent Pb(II) adsorption, with maximum capacities up to 139.16 mg/g, driven by functional group complexation, electrostatic attraction, and cation exchange mechanisms^[78]. In addition, biochar produced from the arsenic hyperaccumulator *P. vittata* demonstrates exceptional performance in capturing divalent cations, with maximum adsorption capacities reaching 98.4 mg/g for Cd(II) and 176 mg/g for Pb(II)^[79].

Moreover, the inherent alkalinity and mineral components (e.g., calcium and magnesium salts) of biochar play a synergistic role in the co-adsorption and immobilization of multiple HMs^[78,79]. Environmental safety assessments have indicated that despite the high initial metal content in some feedstocks, the resulting biochar exhibits low leaching toxicity, meeting the safety standards for water treatment applications^[80]. These studies demonstrate the feasibility of transforming hazardous biomass into environmentally friendly adsorption materials.

Electrode materials

Because of their abundant pore structure, easily adjustable pore size, and the presence of inner metals, the biochar derived from pyrolysis of HM-contaminated biomass is an ideal electrode material for fabricating supercapacitors, offering advantages of cost-effectiveness and environmental friendliness^[81–84]. Electrode materials are key components of batteries, which affect the transmission of components and the effectiveness of electrochemical reactions in batteries. Li et al.^[85] prepared ZnO/PbO porous carbon from mineral *Sedum officinalis* that contained Zn, Pb, and Cd, and found that the presence of Zn and Pb caused a microporous–mesoporous hierarchical pore structure in the material. The electrochemical performance of the porous carbon indicated that the capacitance of ZnO/PbO porous carbon could reach 145.3 F/g, whereas the capacitance of unmodified biochar prepared under the same conditions was only 51.7 F/g. Moreover, ZnO/PbO hierarchical porous carbon prepared from HM-contaminated *Sedum plumbizincicola* is also expected to be used as a supercapacitor electrode material for high-performance energy storage devices. In addition, biomass with endogenous Cd also has the potential to be an excellent electrode material. Wang et al. prepared activated carbon decorated with MnO, which was easily fabricated from hyperaccumulators cultured in a Mn(II)-rich solution. The electrode achieved an excellent specific capacitance of 436.8 F/g at a current density of 1 A/g in a three-electrode system^[50]. Liang et al. used plants enriched with metal ions to prepare supercapacitors, and found that cobalt nanospheres were uniformly dispersed in the hierarchical porous carbon skeleton after activation. The cobalt nanospheres had obvious pseudocapacitive properties, and the hierarchical porous carbon skeleton had

low impedance, which was beneficial to improving the rate performance of the product^[86]. The biochar prepared from biomass contaminated with HMs using pyrolysis technology possesses a stable structure, excellent cycling performance, high electrode capacitance, good conductivity and high efficiency, as well as ecological and environmental benefits. Consequently, it exhibits remarkable potential for applications in the field of new electrode materials or energy storage materials.

Catalysts

In heterogeneous catalysis, metal species embedded within or introduced into biochar critically determine the catalytic activity and reaction pathways. Conventional approaches typically rely on the external loading of metal catalysts onto the surface of biochar. However, growing evidence indicates that biochar inherently containing HMs derived from contaminated biomass or hyperaccumulator plants exhibit superior catalytic behavior. For example, biochar derived from HM-contaminated straw can be directly repurposed as a multimetal-supported catalyst (e.g., containing Fe, Mn, Cu, and Zn), demonstrating excellent performance in electro-Fenton degradation of persistent organic pollutants^[5]. Compared with externally metal-loaded biochar, hyperaccumulator-derived biochar benefits from uniformly distributed endogenous metals that are stabilized within the carbon matrix during pyrolysis, resulting in enhanced catalytic efficiency. Notably, biochar prepared from the Zn hyperaccumulator *S. alfredii* enabled rapid peroxymonosulfate activation, achieving over 90% removal of the target organic pollutants within tens of minutes and exhibiting reaction rate constants several times higher than those of uncontaminated plant-derived biochar^[87]. Similarly, hyperaccumulator-derived biochar showed markedly improved degradation efficiency toward azo dyes in Peroxymonosulfate (PMS)-based systems while maintaining high catalytic stability and negligible metal leaching over multiple cycles, in contrast to externally metal-loaded counterparts^[88]. Moreover, heteroatom-engineered biochar originating from metal-enriched biomass further accelerates pollutant removal kinetics, indicating that the synergistic interaction between intrinsic metal species and tailored carbon structures favors nonradical oxidation pathways^[89].

Metal recovery

Re-enrichment or recovery of HMs through slow pyrolysis is an ideal solution, which shifts the perspective from "waste disposal" to "metal recovery". Biochar derived from pioneer plants (e.g., *Miscanthus* spp.) and hyperaccumulators acts as a concentrated "bio-ore", where HMs such as Zn, Cu, and Ni are significantly enriched compared with the original biomass^[90,91]. Co-pyrolysis of hyperaccumulator plants with polyvinyl chloride (PVC) has demonstrated the potential to extract 94.58% of Zn from hyperaccumulator-derived biochar through the formation and volatilization of metal chlorides, offering a pathway to recycle metals^[90]. He et al. reported that during the slow pyrolysis of cadmium-rich *Avicennia marina*, ferric chloride (FeCl₃) pretreatment significantly improved the cadmium extraction rate, with approximately 91% of cadmium removed to the condensable liquid phase^[92]. These studies indicate that the phytoremediation-pyrolysis system has the potential to function as a viable thermochemical separation method for extracting metals from agricultural land.

Biofuel

Energy conversion is also one of the ways to utilize the slow pyrolysis products from HM-contaminated biomass, where the inherent metals serve as *in situ* catalysts. Specifically, HMs such as Cu have been found to selectively improve bio-oil's quality by promoting the catalytic

cracking of pyrolytic lignin into low molecular weight organic matter^[92,93]. This catalytic effect significantly enhances the higher heating value (HHV) and chemical stability of the bio-oil, thereby increasing its suitability for fuel applications^[93]. In addition, bio-oil can also serve as a precursor for value-added chemicals (e.g., phenols and ketones) and as a potential biorefinery feedstock for further upgrading.

In light of this review of the migration characteristics of HMs during the pyrolysis process, it is evident that slow pyrolysis provides a practical way to convert HM-contaminated biomass into high-quality fuels, while effectively restricting the transfer of some HMs to the target energy products. Park et al. reported that pyrolysis of contaminated silvergrass (*Miscanthus sinensis*), pine (*Pinus* sp.), and *Acacia* sp. produced bio-oil yields of approximately 45 wt%–54 wt%, and the pyrolysis gas was mainly composed of CO and H₂, with HHVs ranging from about 2.3 to 16.2 MJ/kg. However, the HMs were largely retained in the solid phase, resulting in low-metal bio-oil and combustible gas products^[77]. Similarly, Zeng et al. demonstrated that solar-driven pyrolysis of HM-contaminated biomass significantly enhanced the production of high-quality gases, particularly CO and H₂, confirming that metal contamination does not hinder gas fuel generation during thermochemical conversion^[94].

Conclusions and prospects

Conclusions

Overall, slow pyrolysis and related hydrothermal routes provide a promising pathway for coupling reductions of the risk of HM-contaminated biomass with the production of carbon materials and resource recovery. Based on the current evidence, the main conclusions of this review can be summarized as follows.

(1) The migration and transformation of HMs during dry and wet pyrolysis are jointly governed by the feedstock's properties, the processing temperature, the atmosphere, the mineral composition, and the reaction medium. Therefore, the environmental behavior of HMs cannot be evaluated solely on the basis of total metal concentration.

(2) Slow pyrolysis is not merely a disposal technique for contaminated biomass but a process that can simultaneously promote HMs' stabilization, reduce environmental risk, and generate value-added products. Under properly controlled conditions, pyrolysis-derived products can be directed toward soil amendment, adsorption, catalysis, electrochemical materials, metal recovery, and energy conversion.

(3) The bibliometric results support the importance of this field. Rapid publication growth since 2017; the structural centrality of keywords such as pyrolysis, biomass, biochar, adsorption, and removal; and the emergence of topics such as lifecycle assessment, circular economy, carbon capture, and machine learning all indicate that this field has moved beyond basic descriptions of the process toward integrated evaluation and application-oriented design.

Prospects

Future research should focus on the following aspects.

(1) Greater attention should be paid to post-treatment speciation, valence state, long-term environmental stability, and the safe utilization boundaries of pyrolysis-derived products, particularly for comparatively under-represented contaminants such as As and Cr.

(2) Advanced characterization tools, including synchrotron-based methods and other high-resolution spectroscopies, should be combined with sequential extraction and leaching tests to clarify the binding environments and transformation mechanisms of HMs

in biochar and hydrochar. In parallel, novel hydrothermal systems, including deep eutectic solvents, ionic-liquid-assisted media, and co-processing strategies, may improve metal separation, recovery efficiency, and the process's controllability.

(3) At the implementation level, scale-up requires the simultaneous consideration of economic feasibility, products' safety, and regulations. Feedstock collection, transportation, drying, and size reduction can strongly influence the overall cost structure, whereas scale-up of the reactors remains constrained by heat and mass transfer efficiency and control over metal volatilization. Therefore, lifecycle assessments and techno-economic analyses should be incorporated into future process designs to evaluate whether slow pyrolysis can progress from laboratory demonstrations to environmentally defensible deployment.

Ethical statements

During the preparation of this work, the authors used Chat GPT 5.4 and Nano Banana2 for language refinement and figure enhancement. The authors reviewed and edited all content produced with the assistance of this tool, verified its accuracy, and take full responsibility for the integrity and originality of the final manuscript. This work represents the authors' own intellectual contribution, and no AI tool is credited as an author.

Author contributions

The authors confirm their contributions to the paper as follows: all authors contributed to the study conception and design; Zhengjun Wang, Qifeng Min (co-first author); Kailin He: writing-original draft; Gaoyuan Shang, Dasong Lin: literature research, format proofreading; Ruigang Wang, Yajun Wang (co-corresponding author): writing-review and editing. All authors reviewed the results and approved the final version of the manuscript.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Declarations

Competing interests

The authors declare that they have no conflict of interests.

Author details

¹Agro-Environmental Protection Institute, Ministry of Agriculture and Rural Affairs, Tianjin 300191, China; ²College of Agronomy and

Resource Environment, Tianjin Agricultural University, Tianjin 300392, China; ³National-Regional Joint Engineering Research Center for Soil Pollution Control and Remediation in South China, Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management, Institute of Eco-environmental and Soil Sciences, Guangdong Academy of Sciences, Guangzhou 510650, China; ⁴School of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an 710065, China

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