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不同农作物秸秆原料制备生物炭特性及重金属浸出行为

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摘要: 采用水稻秆、大豆秆、小麦秆和玉米秆为原料在 550℃ 缺氧条件下制备生物炭, 考察不同原料生物炭理化性质及热解后重金属 (Cr、Ni、Cu、As、Cd 和 Pb) 迁移转化特征, 及其在不同浸出液中的浸出行为。结果表明, 4 种原料制备的生物炭的理化特性和元素组成基本一致, 其中玉米秆生物炭微孔体积 ($0.006 \text{ cm}^3 \cdot \text{g}^{-1}$) 和比表面积 ($110.120 \text{ m}^2 \cdot \text{g}^{-1}$) 低于其他原料生物炭。秸秆热解后重金属 (除 Cd 外) 含量增加了 14.04%~410.81%, 且大部分重金属 (除 Cd 和 Pb 外) 化学形态由不稳定态 (弱酸提取态和可还原态) 向稳定态 (可氧化态和残渣态) 转化。制备的生物炭中的重金属在超纯水和缓冲盐溶液中无浸出或浸出量较少, 在乙酸溶液和腐殖酸溶液中浸出量较高。其中 Cu 在乙酸溶液中浸出量较高, 为 $2.601 \sim 4.224 \text{ mg} \cdot \text{kg}^{-1}$, As 在腐殖酸溶液中浸出量较高, 介于 $0.074 \sim 0.166 \text{ mg} \cdot \text{kg}^{-1}$ 。热解后, 各种重金属的环境质量指数 (PI_i) 和内梅罗综合污染指数 (NPI) 值均不同程度增加, 但单一重金属污染等级仍为安全, 生物炭综合污染水平为清洁。由于水稻秆生物炭 Ni、Cd 和 Pb 的生态风险因子 (E_r) 较原料显著升高, 水稻秆热解后总潜在生态风险指数 RI 略有上升, 其他 3 种秸秆热解后由于重金属的稳定化, 总潜在生态风险 RI 显著降低。

关键词: 生物炭; 农作物秸秆; 重金属; 浸出; 环境风险

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Properties of Biochars Prepared from Different Crop Straws and Leaching Behavior of Heavy Metals

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Abstract: In this study, rice straw, soybean straw, wheat straw, and corn straw were chosen as raw materials, and biochars were prepared through the pyrolysis method at 550℃ under oxygen-limited conditions to investigate the physicochemical properties of biochars derived from the straws, the migration and transformation characteristics of heavy metals (HMs) (Cr, Ni, Cu, As, Cd, and Pb) after pyrolysis, and their leaching behaviors in different leaching solutions. The results showed that the physicochemical properties and elemental composition of the biochars were basically consistent. However, compared with that of biochars derived from other straws, biochar derived from wheat straw had a higher ash content (22.48%) and H/C ratio (0.06). Meanwhile, biochar derived from corn straw had a smaller micropore volume ($0.006 \text{ cm}^3 \cdot \text{g}^{-1}$) and a correspondingly smaller specific surface area ($110.120 \text{ m}^2 \cdot \text{g}^{-1}$), which was consistent with the SEM image. After pyrolysis, the content of HMs (except Cd) increased by 14.04% to 410.81%, especially that of Cu and As. However, the content of Cd in soybean straw and corn straw decreased by 20.49% and 8.20% after pyrolysis, respectively, due to the low boiling point of Cd. Furthermore, most of the HMs (except Cd and Pb) tended to transform from unstable (acid-soluble/exchangeable and reducible forms) to stable forms (oxidizable and residual forms), implying that pyrolysis facilitated the stabilization of the HMs. The HMs in biochar were not leached or were leached in small amounts in ultra-pure water and buffered salt solutions, as opposed to leaching in relatively larger amounts in acetic acid solution and humic acid solution. Cr and Ni showed low leaching capacity in all leaching solutions. Cu showed relatively high leaching capacity in acetic acid solution, with the leaching amount ranging from $2.601 \text{ mg} \cdot \text{kg}^{-1}$ to $4.224 \text{ mg} \cdot \text{kg}^{-1}$, and As showed a relatively high leaching capacity in humic acid solution, with the leaching amount ranging from $0.074 \text{ mg} \cdot \text{kg}^{-1}$ to $0.166 \text{ mg} \cdot \text{kg}^{-1}$. After pyrolysis, the environmental quality index (PI_i) and the Nemerow pollution index (NPI) values of various HMs increased by different degrees. However, the pollution of single HMs remained at a safe level, and the integrated pollution of biochars was at the level of "clean". Due to the significant increase in potential ecological risk factors (E_r) of Ni, Cd, and Pb after pyrolysis, the potential ecological risk index (RI) of biochar derived from the rice straw increased slightly. However, the potential ecological risk indexes of biochars derived from other straws significantly decreased after pyrolysis, owing to the stabilization of HMs.

Key words: biochar; crop straw; heavy metals; leaching; environmental risk

生物炭是生物质在缺氧或无氧条件下热解炭化制备的高度芳香化的富碳产物^[1,2], 具有发达的孔隙结构、较大的比表面积和丰富的官能团^[3]。生物炭具有良好的物理和化学吸附能力, 在污染物削减和环境修复领域得到了广泛应用^[4,5]。我国是一个农业大国, 农林废弃物、禽畜粪便等生物质资源丰富, 以其为原料制备生物炭与环境领域应用相结合, 是一种极具潜力的废弃物资源化方法。

然而, 生物炭应用于环境修复领域中也存在一定的风险, 如生物炭中的内源污染物 (重金属和多环芳烃等) 在使用过程中会部分释放进入其他介质, 从而造成二次污染^[6,7]。其中, 重金属具有不可

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降解性和高度积累性,制备过程中原料里的重金属富集于生物炭中^[6,8],其生态风险和浸出特性研究对生物炭在环境修复中安全应用有重要意义.有研究发现污泥^[8,9]和粪便^[10~12]等生物质热解为生物炭后重金属含量均有不同程度的提高.同时,重金属的生物有效性和在环境中的迁移性与其化学形态密切相关.生物炭中的重金属可以离子态或化合结合态的形式进入周边环境,其中可交换的离子态重金属可以被植物直接吸收进入生物链;碳酸盐结合态和铁锰氧化物结合态重金属为不稳定态;硫化物及其有机结合态属于稳定态,此两种形态在环境中不具有生物有效性^[13,14].此外,有研究还显示热解可以使生物质中非稳定态重金属向稳定态转变^[8,9,11],一定程度上可降低重金属的浸出率和环境风险^[11,12].部分研究针对于重金属污染土壤修复的植物制备生物炭过程中重金属形态转化、浸出特性和生态风险进行了分析^[15~17].但针对农作物秸秆制备生物炭过程中重金属迁移转化及风险评估的相关研究有限^[18].Liu等^[19]发现玉米芯生物炭释放的重金属对土壤微生物活性具有一定的抑制作用;Yin等^[20]在投加水稻秆生物炭的土壤中检出了较高含量的酸溶性铅.开展不同农作物秸秆制备生物炭过程中重金属的迁移转化和环境风险研究对其应用安全性保障是非常必要的.

水稻秆、大豆秆、小麦秆和玉米秆是我国常见的农业废弃物,在环境修复领域得到广泛应用^[21~23],本研究在550℃下采用这4种秸秆为原料制备了生物炭,对其理化特性进行了表征,并考察了重金属(Cr、Ni、Cu、As、Cd和Pb)的迁移转化特性,包括原料与制备的生物炭重金属含量、化学形态、浸出行为和环境风险,以期为生物质资源化和生物炭安全应用提供参考.

1 材料与方法

1.1 生物炭制备

本实验用的水稻秆(SD)、大豆秆(DD)、小麦秆(XM)和玉米秆(YM)购自江苏连云港市,4种秸秆粉碎之后过40目筛备用.称取一定质量的原料置于鼓风干燥箱105℃烘干至恒重.干燥后的原料放入坩埚置于马弗炉,采用氮气充分置换马弗炉中的空气,在550℃下热解2h^[11,24~28],冷却至室温后研磨过筛(40目),制得的生物炭分别记作SDBC、DDBC、XMBC和YMBC.

1.2 生物炭分析表征

生物炭pH在固液比为1:10(g·mL⁻¹)的条件下测定^[29];生物炭灰分含量测定方法参照《固体生

物质燃料工业分析方法》(GB/T 28731-2012);生物炭表面形貌及元素组成采用场发射扫描电子显微镜(JSM-7800F,日本电子)测定;生物炭样品元素构成采用元素分析仪测定(Vario EL Cube,德国Elementar);生物炭样品比表面积和孔隙结构参数采用比表面积及孔隙分析仪(nova3000e,美国Quantachrome)测定;生物炭样品表面官能团采用傅里叶红外光谱仪(TENSOR-27,德国Bruker)测定.

1.3 重金属

1.3.1 重金属含量及化学形态分析

将0.50g的样品(原料、生物炭)加入2mL的H₂O₂(30%)和6mL的HNO₃,采用微波消解仪消解30min,消解后液体经0.45μm水系滤膜过滤,采用电感耦合等离子体质谱仪(ICP-MS,Agilent 7700)测定重金属总含量;重金属形态测定采用改进的BCR顺序提取法^[30],该方法将重金属形态分为弱酸提取态(FA)、可还原态(FB)、可氧化态(FC)和残渣态(FD).

1.3.2 重金属的浸出特性

分别选用超纯水(HJ557-2009)^[11]、缓冲盐溶液(0.10g·L⁻¹MgCl₂·6H₂O、0.53g·L⁻¹NH₄Cl、0.075g·L⁻¹CaCl₂·2H₂O、0.10g·L⁻¹Na₂S·9H₂O、2.77g·L⁻¹K₂HPO₄、2.80g·L⁻¹KH₂PO₄和0.02g·L⁻¹FeCl₂·4H₂O)^[31]、乙酸溶液(5.00g·L⁻¹)^[15]和腐殖酸溶液(称取1.00g腐殖酸加入RO水1000mL,50℃水浴溶解12h,用0.45μm滤膜滤除不溶物,测定滤液TOC计算腐殖酸浓度223mg·L⁻¹)^[32]作为浸出液.称取1.00g制备的生物炭分别置于250mL的锥形瓶中,向其中加入200mL的浸出液,放置于水浴加热振荡器(150r·min⁻¹,35℃)中充分振荡24h,实验平行进行3次,并设置空白对照组,浸出液过0.45μm滤膜后采用ICP-MS测定重金属含量.

1.4 环境风险评价方法

原料与制备的生物炭重金属污染程度和生态风险采用内梅罗综合污染指数法(NPI)和Hakanson^[33]提出的潜在生态风险因子(E_r)进行计算.

NPI的计算公式如下:

$$NPI = \sqrt{(PI_{\text{Max}}^2 + PI_{\text{Average}}^2)/2} \quad (1)$$

$$PI_i = C_i/S_i \quad (2)$$

式中,PI_i为样品中污染物*i*的环境质量指数;C_i为污染物*i*的实测含量(mg·kg⁻¹);S_i为污染物*i*的环境质量标准(mg·kg⁻¹).PI_{Max}为污染物最大值,PI_{Average}为污染物平均值.NPI分为四类^[34],即NPI≤

1,清洁; $1 < NPI \leq 2$,轻微污染; $2 < NPI \leq 3$,中度污染; $NPI > 3$,严重污染. PI_i 分为五类^[35]: $PI_i < 1$,安全; $1 \leq PI_i < 2$,轻度污染; $2 \leq PI_i < 3$,中度污染; $3 \leq PI_i < 5$,重度污染; $PI_i \geq 5$,极重污染.

E_r 的计算公式如下:

$$C_f = C_i / C_n \tag{3}$$

$$E_r = T_r \cdot C_f \tag{4}$$

$$RI = \sum E_r \tag{5}$$

式中, C_f 为单个重金属污染指数; C_i 为弱酸提取态组分、可还原态组分和可氧化态组分浓度的总和, C_n 为残渣态组分浓度, E_r 为单项潜在生态风险因子, T_r 为重金属毒性反应因子. T_r 值分别为: Cr (2)、As (10)、Ni (5)、Cu (5)、Cd (30) 和 Pb (5)^[33,36], RI 为所有重金属引起的总潜在生态风险指数. 基于 C_f 、 E_r 和 RI 的潜在生态风险分类标准见表 1^[37].

表 1 潜在风险评价的指数分级

Table 1 Index grading of potential risk assessment

C_f	单个金属污染程度	E_r	单个金属潜在风险	RI	综合潜在生态风险
$C_f \leq 1$	无污染	$E_r \leq 40$	轻微污染	$RI \leq 150$	轻微污染
$1 < C_f \leq 3$	轻微污染	$40 < E_r \leq 80$	中度污染	$150 < RI \leq 300$	中度污染
$3 < C_f \leq 6$	中度污染	$80 < E_r \leq 160$	较重污染	$300 < RI \leq 600$	较重污染
$6 < C_f \leq 9$	较重污染	$160 < E_r \leq 320$	重污染	$RI > 600$	重污染
$C_f > 9$	重污染	$E_r > 320$	极重污染		

2 结果与讨论

2.1 不同原料生物炭基本性质

表 2 为不同原料制备的生物炭的理化特性. 由于不同秸秆原料中纤维素、半纤维素和木质素等组分含量类似, 4 种生物炭产率和主要元素组成差别不大. XMBC 的灰分较高, 可能是由于小麦秸秆所含无机矿物组分较高^[38]. 热解后秸秆原料高沸点物质挥发, 无机矿物含量增加, 4 种生物炭 pH 均呈碱性. O/C 表示生物炭的亲水性, 裂解过程中憎水性有机官能团的消失使生物炭具有了较高的碳化程度; H/C 表示生物炭的芳香化程度, H/C 越低芳香化程度越高, 生物炭越稳定^[39,40].

表 3 为生物炭的孔隙结构参数. 热解后原料有机质的分解和挥发性组分的释放会造成大量孔隙的产生, 有机质组成、结构和材料的疏密程度是影响产物比表面积的主要因素^[41]. DDBC 和 XMBC 的 BET 比表面积较高, 分别达到 $231.20 \text{ m}^2 \cdot \text{g}^{-1}$ 和 $222.54 \text{ m}^2 \cdot \text{g}^{-1}$, 且微孔体积与比表面积之间有显著的相关性 ($R > 0.93$), 微孔体积较小也造成 YMBC 的 BET 比表面积较低, 这与前期的研究结果一致^[29]. 图 1 为生物炭的扫描电镜图像, 不同原料制备的生物炭均有丰富的孔隙结构, 同时可以看出 YMBC 的孔隙与其他原料生物炭相比较大, 大孔体积占孔隙总体积比重较高 (表 3), 张伟明^[42]的研究也发现类似的现象.

表 2 4 种生物炭的产率、灰分、pH 值和元素组成¹⁾

Table 2 Yield, ash, pH, and element composition of four biochar species

样品	产率/%	灰分/%	pH	元素组成 (ω)/%								原子比	
				C	N	O	H	K	Na	Mg	Ca	O/C	H/C
SDBC	26.43	12.62	10.61	25.11	1.61	10.89	0.83	—	—	0.48	1.10	0.43	0.03
DDBC	23.13	13.39	10.13	27.12	0.89	12.26	1.02	0.13	—	—	—	0.45	0.04
XMBC	24.67	22.48	10.42	25.13	1.62	8.83	1.41	0.87	—	—	0.18	0.35	0.06
YMBC	28.75	10.81	10.88	24.41	1.03	11.36	1.04	0.12	0.06	0.12	0.29	0.47	0.04

1) “—”表示未检测到

表 3 生物炭的比表面积和孔隙结构

Table 3 Specific surface area and pore structure of biochar

样品	BET 比表面积 $/\text{m}^2 \cdot \text{g}^{-1}$	微孔体积 $(< 2 \text{ nm})/\text{cm}^3 \cdot \text{g}^{-1}$	中孔体积 $(2 \sim 50 \text{ nm})/\text{cm}^3 \cdot \text{g}^{-1}$	大孔体积 $(> 50 \text{ nm})/\text{cm}^3 \cdot \text{g}^{-1}$	孔隙总体积 $(1.7 \sim 377.9 \text{ nm})/\text{cm}^3 \cdot \text{g}^{-1}$
SDBC	188.950	0.008	0.028	0.010	0.046
DDBC	231.200	0.009	0.030	0.010	0.049
XMBC	222.540	0.008	0.029	0.010	0.047
YMBC	110.120	0.006	0.015	0.009	0.029

2.2 FTIR 光谱分析

图 2 为不同原料制备生物炭的傅里叶变换红外

光谱图, 4 种生物炭均含有羧基、羟基和羰基等官能团. 3430 cm^{-1} 处的峰对应于水分子、醇、羧酸或

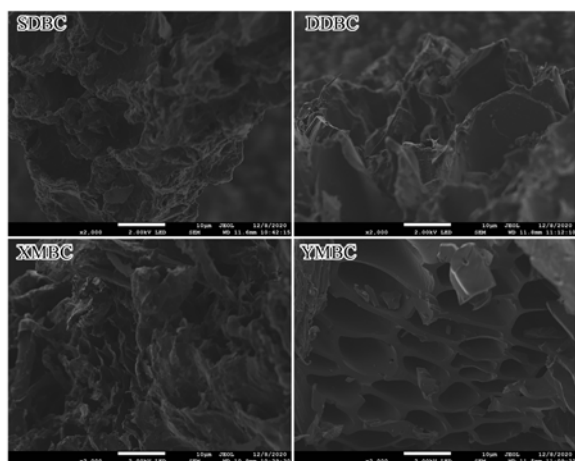


图1 不同秸秆制备的生物炭的扫描电镜图

Fig. 1 SEM of biochar derived from the straws

金属氢氧化物中—OH 的振动, $2\,920 \sim 2\,855\text{ cm}^{-1}$ 处的峰代表脂肪族 C—H 和 C=O 的特征吸收峰^[37], 波数在 $1\,630\text{ cm}^{-1}$ 处的吸收峰是芳香碳上的 C=C^[43], $1\,385\text{ cm}^{-1}$ 处的峰代表羧基碳酸酯和脂肪族—CH, $1\,100\text{ cm}^{-1}$ 附近是 C—O 键的振动^[44], $600 \sim 800\text{ cm}^{-1}$ 附近峰代表芳香族和杂芳香族化合物的存在^[45,46], 669 cm^{-1} 附近的峰代表与有机、无机化合物有关的金属卤化物^[37,47]. 4 种生物炭在 $3\,430\text{ cm}^{-1}$ 处出现了吸收峰, 表明生物炭中醇羟基和酚羟基的存在, YMBC 在 $2\,920 \sim 2\,855\text{ cm}^{-1}$ 处的微弱吸收峰表明有长链的饱和烷烃和—COOH 的存在, 以及在 $1\,100\text{ cm}^{-1}$ 处显示的 C—O, 说明 YMBC 含有较多的含氧官能团, 对应较高的 pH. DDBC 和

XMBC 在 $2\,920 \sim 2\,855\text{ cm}^{-1}$ 处无吸收峰, 在 $1\,100\text{ cm}^{-1}$ 处代表的 C—O 峰强度较弱, 一般表现出较低的 pH.

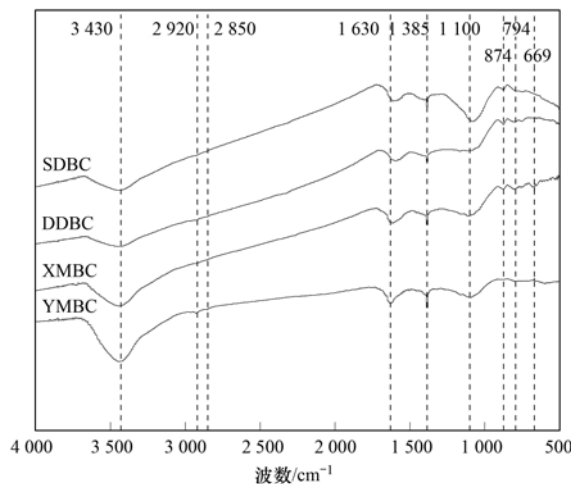


图2 4 种生物炭的红外光谱图

Fig. 2 FTIR spectra of four biochar species

2.3 重金属

2.3.1 重金属含量变化情况

图3 为不同秸秆原料及制备的生物炭重金属含量. 从中可见, 热解制备的生物炭中 Cr、Ni、Cu、As 和 Pb 的含量都有不同程度的增加, 其中 Cu 和 As 增长幅度较大, 前期采用水稻秆制备生物炭的研究中也发现 Cu 含量热解后增长较显著^[18]; 4 种秸秆中, XMBC 中 Cu 含量较原料增加 395.24%, YMBC 中 As 增加 410.81%. 生物炭重金属含量增加主要

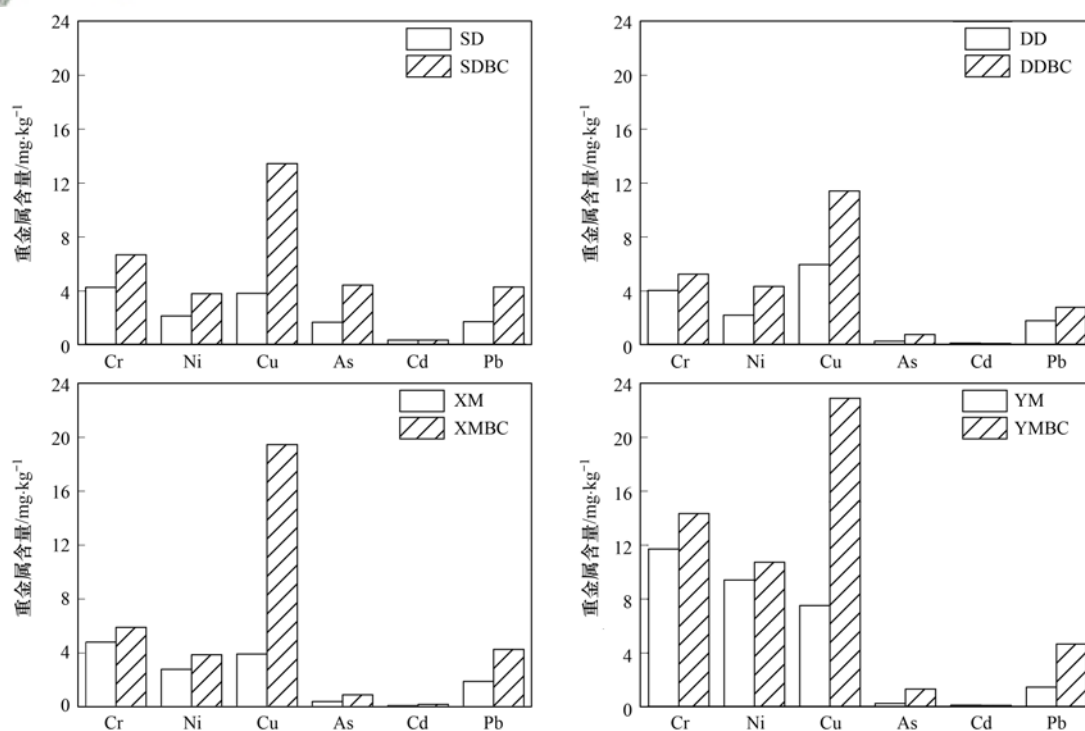


图3 4 种秸秆及其生物炭中重金属含量

Fig. 3 Heavy metal content in four types of straws and its biochar

由于热解过程中原料中有机物被分解挥发,重金属失去与有机物络合的结合位点^[48],但重金属比有机物具有更高的热稳定性^[49],虽然有少部分重金属挥发至气相,但是大部分被保留在生物炭中,导致生物炭中重金属的含量明显高于原料^[50]. DDBC 和 YMBC 中 Cd 含量较原料分别降低了 20.49% 和 8.20%,采用生物质原料制备生物炭的研究中也发现 Cd 含量热解后降低的现象^[51,52],主要是因为 Cd 的沸点较低,且可以氯化盐等易挥发性盐的形式转移至气相^[51]. 不同秸秆中重金属含量变化情况与其元素组分本身的特性及其在原料中存在的化学形态有关^[53].

2.3.2 重金属化学形态

图 4 为不同原料及其制备的生物炭中重金属的化学形态分布变化情况. 秸秆热解后制备的生物炭中大部分重金属(除 Cr、Pb)的弱酸提取态和可还原态(非稳定态)占比显著下降,相应的重金属稳定态占比上升,其稳定性得到改善,前期对重金属富集植物的研究也发现热解可显著提升生物质原料中重

金属的稳定性^[51~53]. SDBC、DDBC 和 XMBC 中可还原态 Cr 占比较原料分别增加了 12.39%、9.48% 和 8.46%,有研究发现随着热解温度的升高,热解产生的气相组分中 Cr 含量上升,这可能与热解过程中部分可氧化态和残渣态(稳定态)的 Cr 挥发至气相有关,导致可还原态 Cr 占比增大^[52]. 4 种原料热解制备的生物炭中可还原态 Pb 占比均增大,主要由于在较高的温度下部分稳定态 Pb 与挥发性热解产物一起迁移至气相所致^[54]. 此外,除 Cr 和 Pb 外,4 种原料制备的生物炭中稳定态重金属占比均显著升高. 热解后生物质表面官能团活性增强并与重金属结合,可提升 Ni 等重金属稳定态的含量^[8,9]. Cu 与有机物质的络合能力较强,在生物质中主要以有机结合态和硫化物形式存在,热解时有机物和硫化物易分解,有利于 Cu 向残渣态转化^[55]. 高温热解后,生物质中的碱金属和碱土金属元素对 As 有固定作用^[56],导致其稳定态含量增加. 此外,生物质热解后产生多种难降解有机物, Cd 与其可缩合成更加稳定的化合物^[57].

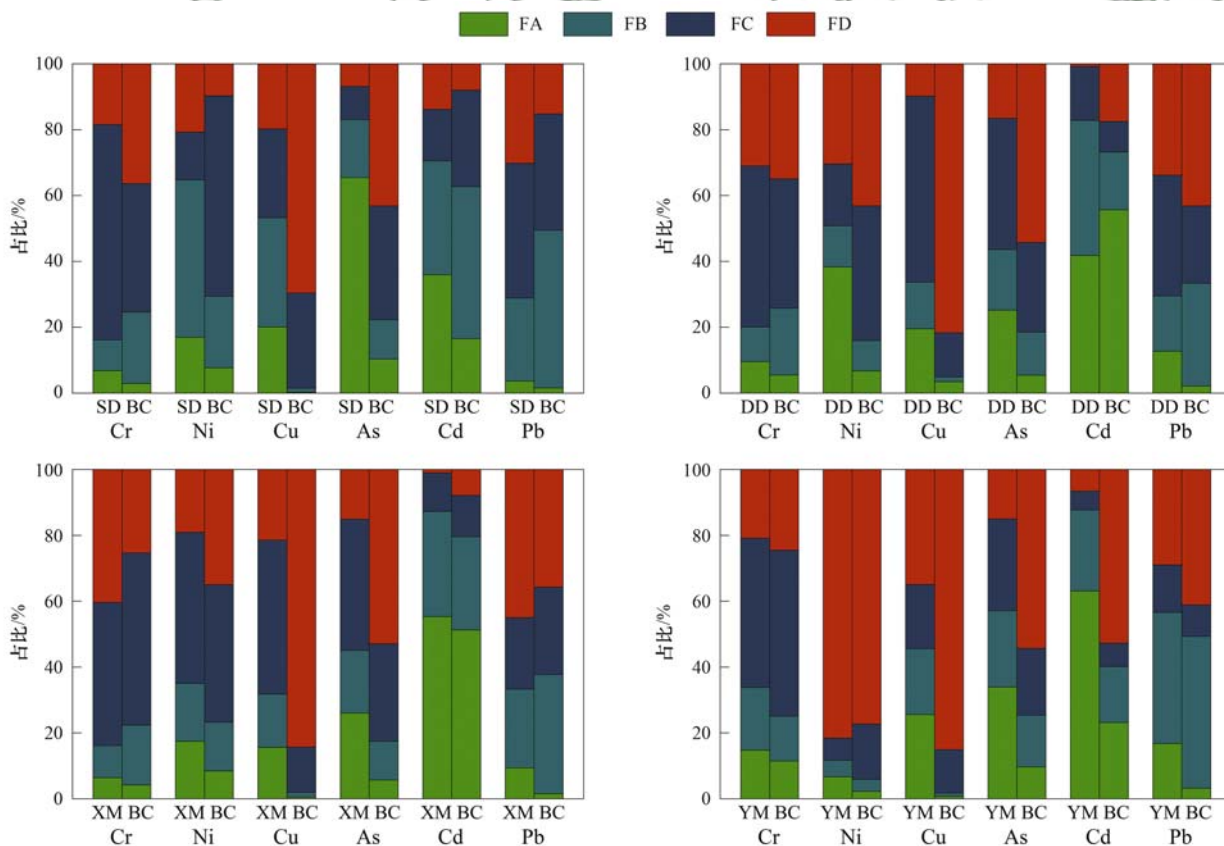


图 4 4 种秸秆及其制备的生物炭中重金属形态分布

Fig. 4 Chemical speciation distributions of HMs in four straws and its biochar

2.3.3 重金属浸出特性

表 4 为生物炭中重金属在 4 种浸出液中的浸出量. 以超纯水为浸出液时,生物炭中的 As 和 Cd 均有少量浸出,浸出量分别为 0.003 ~ 0.227 $\text{mg} \cdot \text{kg}^{-1}$

和 0.001 ~ 0.020 $\text{mg} \cdot \text{kg}^{-1}$,其他金属均未检测到浸出. 以缓冲盐溶液为浸出液时,4 种生物炭中 Cr 和 Ni 均未检测到浸出; SDBC 中 Cu 浸出量为 0.134 $\text{mg} \cdot \text{kg}^{-1}$; 4 种生物炭中的 As、Cd 和 Pb 的浸出量分

别介于 0.024 ~ 0.165、0.006 ~ 0.014 和 0.009 ~ 0.083 $\text{mg}\cdot\text{kg}^{-1}$. 以乙酸溶液为浸出液时,4 种生物炭浸出液中 Cr 均未检出; SDBC 和 YMBC 的浸出液中有 Ni 检测到,含量分别为 0.110 $\text{mg}\cdot\text{kg}^{-1}$ 和 0.030 $\text{mg}\cdot\text{kg}^{-1}$; Cu、As、Cd 和 Pb 在 4 种生物炭的浸出液中均有检测到,含量分别介于 2.601 ~ 4.224、0.047 ~ 0.297、0.037 ~ 0.191 和 1.067 ~ 1.484 $\text{mg}\cdot\text{kg}^{-1}$. 以腐殖酸溶液为浸出液时,4 种生物炭中 Cr 和 Ni 均未浸出; SDBC 中 Cu 浸出量为 0.082 $\text{mg}\cdot\text{kg}^{-1}$; 4 种生物炭的 As 浸出较多,浸出量为 0.074 ~ 0.166 $\text{mg}\cdot\text{kg}^{-1}$; Cd 和 Pd 的浸出量分别为 0.001 ~ 0.191 $\text{mg}\cdot\text{kg}^{-1}$ 和 0.001 ~ 1.067 $\text{mg}\cdot\text{kg}^{-1}$.

表 4 4 种生物炭中重金属在不同浸出液中的浸出量¹⁾/ $\text{mg}\cdot\text{kg}^{-1}$

Table 4 Leaching amount of HMs in four biochars in different leaching solutions/ $\text{mg}\cdot\text{kg}^{-1}$

生物炭	浸出液	Cr	Ni	Cu	As	Cd	Pb
SDBC	超纯水	—	—	—	0.080	0.002	—
	缓冲盐	—	—	0.134	0.165	0.006	0.040
	乙酸	—	0.110	2.894	0.297	0.191	1.067
	腐殖酸	—	—	0.082	0.166	0.002	0.007
DDBC	超纯水	—	—	—	0.003	—	—
	缓冲盐	—	—	—	0.024	0.008	0.083
	乙酸	—	—	4.224	0.088	0.048	1.484
	腐殖酸	—	—	—	0.111	—	0.001
XMBC	超纯水	—	—	—	0.004	0.001	—
	缓冲盐	—	—	—	0.041	0.014	0.009
	乙酸	—	—	3.702	0.064	0.037	1.359
	腐殖酸	—	—	—	0.085	0.001	0.001
YMBC	超纯水	—	—	—	0.227	0.001	—
	缓冲盐	—	—	—	0.063	0.006	0.014
	乙酸	—	0.030	2.601	0.047	0.040	1.238
	腐殖酸	—	—	—	0.074	0.001	—

1) “—”表示未检测到

2.4 环境风险评价

从表 5 可以看出,4 种秸秆热解后各种重金属的 PI_i 值均不同程度增加,但是 4 种秸秆及其制备的生物炭的单一重金属污染指数均小于 1,说明其单一重金属污染等级为安全. 热解后生物炭的综合污染指数均有所上升,但是 NPI 值都小于 1,甚至小于 0.1,污染水平为清洁.

生物质和生物炭中重金属的潜在生态风险因子(E_r)及重金属风险评价指数(RI)如表 6 所示. 4 种秸秆及其制备的生物炭中 Cr 和 Pb 的 E_r 值较低,热解后小麦秆中 Cr 和水稻秆中 Pb 的 E_r 值分别增大至 5.893 和 27.891,仍属于轻微污染水平. 不同秸秆原料中 As 的 E_r 值均高于 40,呈中

度、较重或重污染水平,热解后均降低至轻微污染水平. Cd 的污染水平最高,水稻秆中 Cd 呈重污染水平,热解后 E_r 值显著升高至 344.483,呈极重污染水平;这与 Cd 的富集系数较大及其在稻田土壤中的迁移能力较强有关^[58,59],同时,前期采用重金属富集植物制备生物炭的研究中也发现热解后 Cd 的 E_r 值较高^[15]. 其他原料中 Cd 呈极重污染水平,热解后分别降低至重污染、中度污染和轻微污染水平. 热解制备的 DDBC、XMBC 和 YMBC 中重金属的潜在生态风险(RI 值)较原料均显著降低;热解后由于 Cd 的生态风险因子上升,导致 SDBC 的 RI 值略有上升,但其潜在生态风险等级未发生变化.

表 5 生物炭的重金属污染指数

Table 5 HMs pollution index of biochar

项目	Cr	Ni	Cu	As	Cd	Pb	NPI
S_i (环境值)/ $\text{mg}\cdot\text{kg}^{-1}$	500.000	100.000	500.000	30.000	3.000	300.000	
PI_i	SD	0.009	0.021	0.008	0.056	0.118	0.062
	SDBC	0.013	0.038	0.027	0.148	0.121	0.080
	DD	0.008	0.022	0.012	0.009	0.041	0.014
	DDBC	0.010	0.043	0.023	0.026	0.032	0.025
	XM	0.010	0.028	0.008	0.013	0.031	0.018
	XMBC	0.012	0.039	0.039	0.030	0.064	0.036
	YM	0.023	0.094	0.015	0.009	0.041	0.050
	YMBC	0.029	0.107	0.046	0.044	0.037	0.058

表 6 生物质及其生物炭重金属的潜在风险评价

Table 6 Potential risk assessment of HMs in straws and its biochar

项目	Cr	Ni	Cu	As	Cd	Pb	RI
SD	8.848	22.959	20.271	135.391	186.122	11.561	385.153
SDBC	3.500	55.908	2.183	13.182	344.483	27.891	447.146
DD	4.434	13.753	45.846	50.455	3 630.000	9.793	3 754.280
DDBC	3.726	7.913	1.122	8.449	141.176	6.594	168.981
XM	2.949	25.407	18.319	56.271	2 790.000	6.114	2 899.061
XMBC	5.893	11.133	0.929	8.901	352.000	9.001	387.857
YM	7.589	1.357	9.324	56.410	427.500	12.278	514.458
YMBC	6.163	1.762	0.875	8.416	26.926	7.165	51.308

3 结论

4 种秸秆制备的生物炭的产率、灰分、pH 值和元素组成基本一致,其中 YMBC 的产率和 pH 较大,为 28.75% 和 10.88, XMBC 的灰分较高为 22.48%。YMBC 微孔体积较小,相应的比表面积较小。秸秆热解后重金属(除 Cd)含量增加了 14.04% ~ 410.81%。大部分重金属的化学形态有不稳定态向稳定态转移的趋势,热解有利于重金属的稳定化,可降低生物质中重金属的迁移性和生物有效性。4 种生物炭中重金属在乙酸溶液和腐殖酸溶液中的浸出量较高,其中 SDBC 各种重金属浸出量均较高。内梅罗污染指数评价结果显示,热解后生物炭的综合污染指数均有上升,但 NPI 值都小于 1,甚至小于 0.1,污染水平仍为清洁。潜在环境风险评价结果显示,热解显著降低了 DDBC、XMBC 和 YMBC 的潜在生态风险,而 SDBC 的潜在生态风险由于重金属 Cd 的 E_r 值升高而有所提升,对易富集 Cd 等生态毒性较高重金属的生物质,其制备的生物炭的环境风险需特别关注。

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