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生物质炭对小白菜吸收多环芳烃的影响

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摘要:选取小麦秸秆、污泥、猪粪三种原料制备的生物质炭为研究材料,通过盆栽试验,探究不同原料生物质炭对 PAHs 污染土壤中小白菜生长情况及对 PAHs 吸收积累的影响。结果表明:三种生物质炭对小白菜吸收 PAHs 均有一定的抑制作用,与对照相比,施用生物质炭小白菜对 PAHs 的吸收量降低 14.53%~49.41%,三种生物质炭的抑制能力依次为麦秸炭>猪粪炭>污泥炭;相对于 1% 的施用量,施用 2% 的麦秸炭与猪粪炭小白菜中 PAHs 含量分别显著降低 32.02% 和 21.40%,而污泥炭不同施用量对小白菜中 PAHs 总含量的影响无明显差异;生物质炭对小白菜吸收 2~3 环的低分子量 PAHs 的降低率为 0~30.81%,对 4~6 环的高分子量 PAHs 吸收的降低率为 30.72%~68.07%;施用 2% 的麦秸炭和猪粪炭,使小白菜的生物量显著提高 20.03% 和 22.28%。因此,施用生物质炭可作为一种降低污染土壤中作物吸收 PAHs,同时保障作物产量的有效技术途径。

关键词:生物质炭;PAHs;污染土壤;小白菜;生物累积

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Effects of biochar on polycyclic aromatic hydrocarbons (PAHs) bioaccumulation in Chinese cabbage

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Abstract: Biochar technology provides a potential approach to mitigate soil pollution in agricultural production. However, limited studies have focused on the effects of different kinds of biochar on polycyclic aromatic hydrocarbons (PAHs) bioaccumulation. To address this issue, three kinds of biochar including wheat straw biochar (WBC), sludge biochar (SBC) and pig manure biochar (PBC) were prepared through the technology of oxygen limited pyrolysis, and a spot experiment was conducted to assess the mitigation effects of three kinds of biochar with the application rates of 1% and 2% on PAH transfer from contaminated urban soil to Chinese cabbage. The results showed that addition of different kinds of biochar significantly reduced the concentrations of all PAHs by 14.53%~49.41% in the Chinese cabbage compared to the control soil ($P < 0.05$), and the mitigation effectiveness was observed in order of WBC>PBC>SBC. Compared with the 1% application rate, the concentrations of PAHs were decreased by 32.02% and 21.40% under 2% WBC and 2% PBC amendments, respectively, though no significant difference was observed between the application rates of SBC. For different PAHs, the 2~3 rings and 4~6 rings PAHs bioaccumulation were reduced by 0~30.81% and 30.72%~68.07% under biochar application. In addition, the production of Chinese cabbage was significantly increased by 20.03% and 22.28% under 2% WBC and PBC, respectively. Therefore, biochar amendments could be an effective approach to reduce crop uptake of PAHs while ensuring crop yield in contaminated soil.

Keywords: biochar; PAHs; contaminated soil; Chinese cabbage; bioaccumulation

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多环芳烃(PAHs)是环境中普遍存在的一类持久性有机污染物(POPs),主要源于化石燃料的不完全燃烧。PAHs可通过大气沉降和污水灌溉进入土壤而被植物吸收,进而通过食物链进入人体。PAHs具有较强的“三致”(致癌、致畸、致突变)作用^[1-2],会对人体健康造成严重威胁,治理PAHs污染土壤以减少PAHs在作物体内的累积已成为大家关注的热点^[3-5]。生物质炭(Biochar)是生物质在限氧条件下,250~750℃之间发生热裂解作用而得到的固态物质^[6]。生物质炭具有的特殊的多孔性结构赋予了其较强的吸附性能,作为一种新型环境修复材料已广泛应用于重金属及有机污染物的修复^[7-8]。目前已有许多关于生物质炭用于多环芳烃吸附的研究,如史兵方等^[9]研究了麻疯树籽壳生物质炭对4种PAHs的吸附效果及机理,结果表明在25℃、添加生物质炭0.15g、吸附时间60min的条件下,萘、蒽、芘和菲的去除率均高达90%以上。Beesley等^[10]研究发现,经过60d场地试验,加入生物质炭吸附后土壤中PAHs生物有效性含量显著降低。目前,虽然已有一些关于生物质炭抑制植物对多环芳烃吸收的研究,如花莉等^[11]研究发现生物质炭的输入使黑麦草中多环芳烃的累积量显著减少了27%~34%。但此类研究多是将一种或几种有机污染物人为添加到土壤中进行的^[12-13],而长期污染的土壤中多环芳烃的迁移转化特性与人为添加的短期效应存在着很大的差别^[14-15],且不同原料的生物质炭对多环芳烃的吸附能力也存在差异^[16-17]。孙璇等^[18]研究发现,玉米秸秆炭对芘的饱和吸附量分别是麦秸炭和花生壳炭的2.3倍和4.5倍。因此,本文选取作物秸秆、畜禽粪便及污泥等不同种类的生物质原料,以工业区周边长期污染土壤为对象,通过盆栽试验研究麦秸炭、猪粪炭和污泥炭对小白菜生长及富集PAHs的影响,以期降低污染土壤中作物PAHs吸收提供有效途径。

1 材料与方法

1.1 供试材料

供试土壤于4月中旬在南京市郊某工业园区周

边菜地采集, GPS定位点为31°54'21"N, 118°37'37"E, 采土深度为0~20cm。采集的土壤于室内自然风干,剔除植物残根、砂石后,粉碎过5mm筛混匀备用。土壤为黄棕壤,土壤pH 8.36,有机质37.07g·kg⁻¹,全氮1.11g·kg⁻¹,速效磷24.09mg·kg⁻¹,速效钾161.55mg·kg⁻¹。土壤中PAHs总含量为2.57mg·kg⁻¹,其中萘(Nap)301.38μg·kg⁻¹、芘(Ace)315.67μg·kg⁻¹、芴(Flu)4.00μg·kg⁻¹、菲(Phe)162.85μg·kg⁻¹、蒽(Ant)41.17μg·kg⁻¹、荧蒽(Fla)352.82μg·kg⁻¹、芘(Pyrene)379.00μg·kg⁻¹、蒽(Chry)141.33μg·kg⁻¹、苯并(b)荧蒽(BbF)191.33μg·kg⁻¹、苯并(k)荧蒽(BkF)177.81μg·kg⁻¹、苯并(a)芘(BaP)99.2μg·kg⁻¹、二苯并(a,h)蒽(DahA)214.03μg·kg⁻¹、茚并(1,2,3-c,d)芘(InP)191.09μg·kg⁻¹。

根据Maliszewska^[19]对土壤PAHs污染状况的分级方法,供试土壤属于严重污染土壤。三种生物质炭分别由小麦秸秆、猪粪、污泥在450℃下便携式炭化机中(编号:SSBP-5000,江苏银鼎生物质科技有限公司)限氧热裂解而成,分别标记为WBC、PBC、SBC,其基本性质见表1。

1.2 试验设计

试验共设七个处理,每个处理三个重复。将粉碎后过20目筛的三种生物质炭分别按0%、1%、2%比例与土壤混合均匀,每盆装土2kg。各处理分别标记为CK、1%WBC、2%WBC、1%SBC、2%SBC、1%PBC、2%PBC。装盆结束后,沿盆壁加入去离子水,使得土壤湿度达到最大田间持水量,静置24h后播种。本试验在南京农业大学资源与环境学院温室大棚中进行,供试小白菜品种为四月蔓。2016年5月2日播种,待出苗一周后间苗,每盆保留5株,45d后采收。小白菜生长期定时浇水,使之保持在田间持水量的70%左右。随机调整盆栽摆放位置。

1.3 试剂和仪器

Waters 1525 高效液相色谱仪, 配备 Waters-PAHs 专用色谱柱 C18(4.6×250 mm, 5 μm)及 Waters 474FLD、Waters 2487UVD 双检测器。KH-300DB 医

表1 供试生物质炭的基本性质

Table1 Basic properties of biochar

生物质炭 Biochar	pH	灰分 Ash/g·kg ⁻¹	有机碳 Organic carbon/g·kg ⁻¹	全氮 Total N/g·kg ⁻¹	全磷 Total P/mg·kg ⁻¹	全钾 Total K/mg·kg ⁻¹	比表面积 BET/m ² ·g ⁻¹
WBC	10.17	242.91	534.34	10.35	3.26	24.92	20.62
SBC	7.86	805.93	309.83	13.21	11.83	8.68	4.99
PBC	9.67	399.98	393.48	9.82	16.14	15.73	18.44

用数控超声波清洗器,RE52-98 旋转浓缩蒸发仪。

试剂二氯甲烷、正己烷、丙酮均为分析纯,乙腈为色谱纯。多环芳烃标准物质为美国 EPA 要求的 16 种优先检测的 PAHs 混合标样,包括萘(Nap)、萘(Ace)、萘烯(Acy)、芴(FI)、菲(Phe)、蒽(Ant)、荧蒽(Fla)、芘(Pyr)、苯并(a)蒽(BaA)、蒽(Chry)、苯并(b)荧蒽(BbF)、苯并(k)荧蒽(BkF)、苯并(a)芘(BaP)、二苯并(a,h)蒽(DahA)、苯并(g,h,i)芘(BghiP)和茚并(1,2,3-c,d)芘(InP),购自美国 Supelco 公司。

1.4 分析项目和方法

小白菜生物量采取直接称量法,生物质炭灰分含量的测定参照农业行业标准 NY/T 1881.5—2010^[20],土壤、其余生物质炭性质测定按鲍士坦推荐方法^[21]。土壤、小白菜中 PAHs 的提取、纯化参见文献^[22-23]。在样品分析过程中进行方法空白、平行样以及加标回收率测定,土壤加标回收率为 79%~112%(萘为 64%),植物加标回收率为 70%~104%,符合样品分析要求。高效液相色谱分析条件参见文献^[23],流动相为乙腈和水,初始乙腈:水=60:40,经 15 min 后变为 100:0,再经 6 min 后又回到初始状态。紫外检测器检测波长设置为 254 nm。荧光检测器程序设置为 0~6.5 min: $\lambda_{Ex}=270$ nm, $\lambda_{Em}=330$ nm;6.5~14.5 min: $\lambda_{Ex}=245$ nm, $\lambda_{Em}=390$ nm;14.5~26 min: $\lambda_{Ex}=290$ nm, $\lambda_{Em}=430$ nm。

1.5 数据分析

采用软件 Microsoft Excel 2013 对试验数据进行统计处理,采用 SPSS 13.0 进行单因素方差分析和多重比较(LSD 检验),显著性检验在 $\alpha=0.05$ 概率水平下进行。

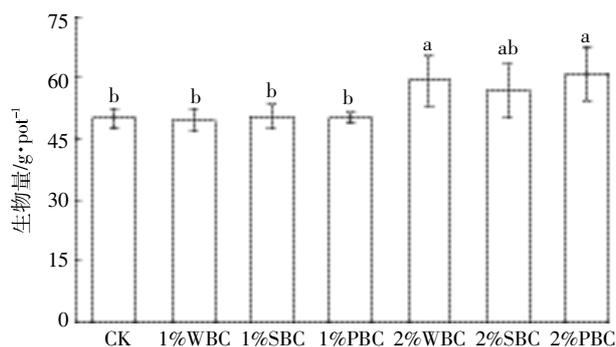
2 结果与分析

2.1 生物质炭对小白菜生物量的影响

各处理小白菜生长 45 d 后每盆生物量在 49.71~61.19 g 之间(图 1),三种供试生物质炭对盆栽小白菜生物量的影响与其施用量有关。与 CK 比较,施炭量在 1%水平下,三种供试生物质炭对小白菜生物量均无显著性影响,施用 2%的麦秸炭和猪粪炭小白菜的生物量分别提高 20.03%和 22.28%,而施用污泥炭没有显著性差异。

2.2 生物质炭对小白菜 PAHs 总含量的影响

不同生物质炭及施用量对小白菜吸收 PAHs 总量的影响见图 2。与 CK 相比,施用生物质炭可显著降低小白菜中 Σ PAHs 含量,降低幅度为 13.92%~



图中不同小写字母代表各处理间差异显著($P<0.05$)。下同
Different lowercase letters indicate significant differences ($P<0.05$) among different treatments. The same below

图 1 不同生物质炭处理对小白菜生物量的影响

Figure 1 Effect of different biochar treatments on cabbage biomass

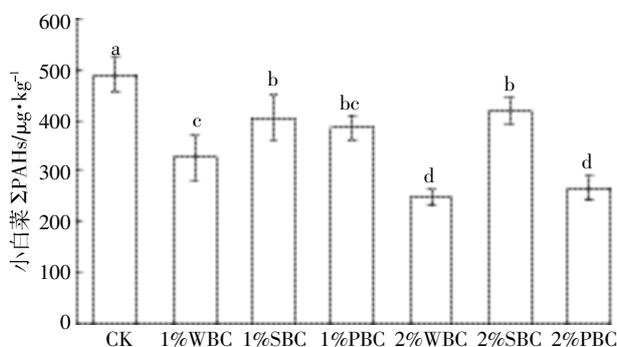


图 2 不同生物质炭处理对小白菜 Σ PAHs 含量的影响

Figure 2 Effects of biochar treatments on cabbage Σ PAHs content

49.41%。不同类型和施用量的生物质炭对小白菜 PAHs 吸收的影响不同。施用量在 1%水平时,麦秸炭对小白菜 PAHs 吸收的降低幅度最大,达 33.21%;猪粪炭和污泥炭则分别显著降低 21.35%及 17.24%,二者之间无显著差异。与 1%的施用量相比,2%施用量的麦秸炭和猪粪炭对小白菜 PAHs 吸收分别降低了 24.26%和 30.57%,而污泥炭不同施用量处理间小白菜 PAHs 的吸收无显著差异。

2.3 生物质炭对小白菜不同种类 PAHs 含量的影响

生物质炭对小白菜吸收不同种类 PAHs 的影响不同(图 3、表 2)。生物质炭施用量在 1%水平时,麦秸炭、猪粪炭对小白菜吸收所有环类的 PAHs 均显著降低,其中麦秸炭、猪粪炭和污泥炭对五环类 PAHs 的抑制率均为最高,分别达 67.13%、56.14%和 50.03%。麦秸炭和猪粪炭对二环、三环、四环和六环的抑制率分别在 23.91%~37.44%和 10.83%~27.69%之间;污泥炭显著降低小白菜中四环芳烃含量达 32.41%,而对二环、三环、六环没有显著影响。施用量在 2%水平时,

麦秸炭、猪粪炭对四环、五环类 PAHs 的抑制率相对较高,分别为 72.43%、57.16%和 68.30%、63.50%,对二环、三环、六环的抑制范围分别为 28.53%~41.27%和 19.25%~48.00%。污泥炭对四环、五环降低率分别为 29.82%、46.51%,对二、三、六环类 PAHs 均无显著影响。

从不同的 PAHs 来看,1%和 2%麦秸炭处理下小白菜的二环芳烃 Nap 含量较对照分别降低 23.85%及 34.27%,而对于 Ace,仅在 2%麦秸炭处理下,小白菜中 Ace 的含量较对照显著降低 72.53%,其余处理则均无显著差异。

从三环芳烃来看,与 CK 相比,生物质炭对 Fl、Phe 和 Ant 的吸收抑制率分别为 0~52.94%、0~16.94%和 0~81.98%。1%和 2%的猪粪炭处理下小白菜 Ant 含量显著降低 31.63%和 85.55%;1%和 2%污泥炭处理下 Fl 含量显著降低 45.00%和 52.94%;1%和 2%麦秸炭处理下小白菜的 Phe、Ant 含量分别降低

15.34%、77.34%和 16.94%、78.52%。

从四环芳烃来看,生物质炭对 Fla、Pyr 和 Chr 的吸收抑制率分别为 0~71.45%、0~85.55%和 49.48%~83.02%。三种生物质炭中麦秸炭对小白菜 Fla 和 Chr 吸收的抑制效果较好,施用量为 1%和 2%条件下小白菜中 Fla 和 Chr 含量较对照分别显著降低 48.80%、71.45%和 33.96%、76.10%。猪粪炭对小白菜 Pyr 吸收有较好的抑制效果,施用 1%和 2%猪粪炭 Pyr 的含量显著降低 61.79%和 81.98%。

从五环芳烃来看,生物质炭对小白菜 BbF、BkF、BaP、DahA 和 IcdP 的吸收与 CK 相比分别降低 55.19%~83.92%、0~45.17%、31.35%~93.73%、0~64.83%和 0~35.59%。三种生物质炭处理下小白菜 BbF 含量均显著降低,其中猪粪炭抑制率最高,1%和 2%处理水平小白菜 BbF 含量显著降低 75.50%和 83.92%。1%麦秸炭小白菜的 BkF 含量降低最高,达 45.16%。三种生物质炭对小白菜吸收 BaP 的抑制能力为麦秸炭>猪粪

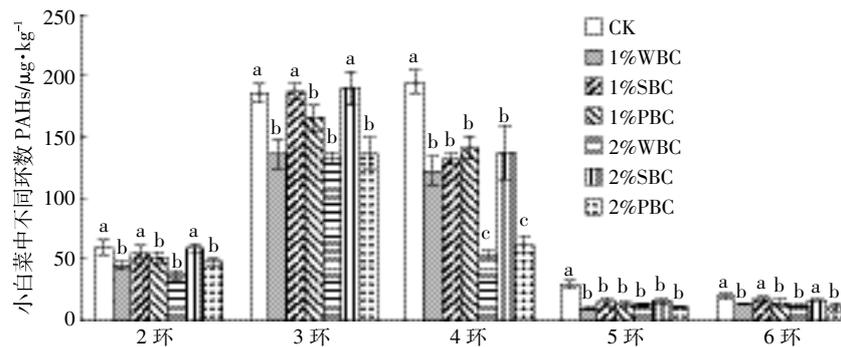


图3 不同生物质炭处理对小白菜不同环类 PAHs 的影响

Figure 3 Effects of biochar treatments on cabbage PAHs content of different species

表2 施加生物质炭处理对小白菜中 PAH 含量的影响($\mu\text{g}\cdot\text{kg}^{-1}$)

Table 2 Effects of the biochar treatments on cabbage PAH content ($\mu\text{g}\cdot\text{kg}^{-1}$)

PAHs	CK	1%WBC	1%SBC	1%PBC	2%WBC	2%SBC	2%PBC
Nap	53.84±5.56a	41.00±2.62bc	47.77±5.56ab	46.18±5.41ab	35.39±2.89c	51.01±5.75a	44.08±4.94ab
Ace	5.68±0.45bc	4.29±0.86c	6.52±0.46b	5.39±0.52bc	1.56±0.26d	7.97±0.66a	3.98±0.17cd
Fl	3.40±0.57a	3.71±0.12a	1.60±0.32c	3.89±1.06a	2.65±0.45ab	1.87±0.08c	2.54±0.07b
Phe	147.73±14.59a	125.07±6.16b	151.41±29.57a	138.08±34.94ab	122.7±4.67b	159.75±11.57a	129.28±13.05ab
Ant	34.68±2.91a	7.86±1.26d	33.94±3.82a	23.71±2.41c	7.45±2.25d	28.69±1.16b	5.01±3.33d
Fla	117.85±23.54a	60.34±3.55b	67.05±5.32b	108.94±4.62a	33.65±1.84d	73.05±3.73b	48.01±3.09c
Pyr	72.71±6.97a	58.7±3.71b	57.83±3.96b	27.78±3.41c	19.06±1.31d	59.34±9.74ab	13.1±2.48d
Chr	4.77±0.59b	3.15±0.43c	7.13±0.31a	4.53±1.2bc	1.14±0.31d	4.68±0.13b	0.81±0.02d
BbF	18.9±2.09a	5.36±0.94bc	7.24±0.54b	4.63±0.23c	6.96±0.31b	8.47±1.46b	3.04±0.44d
BkF	7.55±1.10a	4.14±0.05c	5.41±0.58b	7.61±0.71a	5.04±0.52bc	5.86±0.20b	6.98±0.66ab
BaP	3.03±0.61a	0.19±0.03d	2.08±0.28ab	0.69±0.11c	0.63±0.05c	1.44±0.07b	0.74±0.08c
DahA	6.88±0.98a	2.95±0.29c	6.38±0.34a	6.09±1.05a	2.42±0.17c	4.69±0.49b	2.42±0.09c
IcdP	12.87±1.56a	10.43±1.35ab	11.07±0.99a	8.29±0.94b	9.18±0.94b	11.89±0.79a	7.85±0.54b

炭>污泥炭,其中施用1%和2%麦秸炭小白菜BaP含量显著降低93.73%和79.20%。

从六环芳烃来看,施用1%和2%麦秸炭小白菜DahA的含量较CK降低程度最高,分别为57.12%和64.83%。猪粪炭施用量为1%和2%时小白菜IcdP的含量分别显著降低35.59%和39.01%。

3 讨论

目前已有很多文献报道生物质炭可提高作物的产量^[24-25]和品质^[26-27]。本试验发现,在2%施用量下,小麦秸秆炭及猪粪炭均能显著提高小白菜的生物量,可能是由于生物质炭能改善土壤理化性质^[28],如降低土壤容重、增强土壤通透性、提高保水功能及养分有效性等^[29-30],且生物质炭本身可提供植物部分营养物质,从而可促进作物生长,增加作物的产量。

本研究结果显示,生物质炭可有效抑制污染土壤中小白菜对多环芳烃的吸收。Brennan等^[31]研究也发现添加玉米茬生物质炭和活性炭均能有效降低玉米根对土壤中多环芳烃的富集,Waqas等^[32]研究也表明添加污泥炭后,黄瓜中的PAHs含量显著减少。这可能是因为生物质炭具有发达的孔隙结构和巨大的比表面积,对芳香性物质有较高的亲和力^[33-34],从而可通过吸附和固定作用大幅提高PAHs在土壤体系中的固液分配系数,降低其生物可利用度,减少PAHs在植物体内的富集^[35-36]。

本研究结果表明,小白菜中PAHs含量随生物质炭施用量的增加而降低。Khan等^[37]在研究花生壳生物质炭等四种生物质炭对污染土壤中PAHs生物有效性的影响时发现,5%的施炭量比2%能更有效地降低萝卜中PAHs的含量。这可能与施用量增大可加强生物质炭对PAHs的吸附有关。Kumari等^[38]研究发现生物质炭对菲的吸附强度随用量的增加而增强,原因可能是与生物质炭和土壤矿物之间的相互作用有关。Liang等^[39]研究表明,土壤中的矿物可能会与生物质炭相互作用,遮蔽其吸附位点,因而在较高的施用量下,生物质炭可用于吸附的空位点的数目会更高,吸附作用会更强。此外,不同原料的生物质炭对小白菜吸收PAHs的影响存在差异。生物质炭对PAHs的吸附过程受多种因素的影响^[40-42],有机碳含量及表面特性是主要影响因素。有研究^[43]表明,吸附剂的有机碳含量决定了吸附剂对疏水性吸附质的吸附作用。本试验三种生物质炭中以麦秸炭有机碳含量最高,因此麦秸炭中有机碳对土壤中PAHs的吸附贡献可能要高

于猪粪炭和污泥炭。生物质炭比表面积的大小一定程度上也影响了其吸附污染物的能力^[44]。徐仁扣等^[45]研究发现4种生物质炭吸附亚甲基蓝能力的大小顺序为稻草炭>大豆秸秆炭>花生秸秆炭>稻壳炭,并且这一顺序与生物质炭表面负电荷数量和生物质炭比表面积的大小顺序基本一致。本研究中麦秸和猪粪生物质炭的比表面积远高于污泥炭,对于降低小白菜吸收PAHs起着重要的作用。此外,生物质炭表面灰分的存在可能会严重影响生物质炭的表面结构特性及吸附能力。王月瑛等^[46]研究玉米秸秆生物质炭酸洗处理去除表面灰分表明,酸洗能有效去除附着在生物质炭表面的无机盐、焦油等物质,增加生物质炭的表面吸附位点,显著提高生物质炭的吸附性能。供试生物质炭中的污泥炭灰分含量远高于麦秸炭和猪粪炭,可能也是污泥炭对小白菜吸收PAHs抑制效率较低的影响原因。

本研究还表明,生物质炭对小白菜吸收高分子量PAHs的抑制大于低分子量PAHs。Waqas等^[47]也曾报道,施加污泥炭后西红柿对高分子量PAHs累积的降低幅度比低分子量的高。低分子量PAHs一般由两个或三个苯环组成,亲脂性较低,而高分子量PAHs一般由3~6个苯环组成,油水分分配系数更高,依据相似相溶的原理,高分子量PAHs可能更容易与土壤中的生物质炭结合,从而降低其在土壤中的生物有效性^[48]。此外,Colombo等^[49]指出多种混合物同时存在时,PAH之间产生的协同或拮抗作用会促进或抑制其他组分的生物降解速率。因此,本研究的供试土壤中多种PAHs之间的复杂作用也可能是引起小白菜对不同种类PAHs吸收存在差异的原因之一。综上,土壤中PAHs组分在植物中的富集作用不仅取决于生物质炭类型,同时与PAHs以及土壤自身理化性质等诸多因素有关^[50-51]。

4 结论

三种生物质炭均可有效抑制小白菜吸收PAHs污染物(14.53%~49.41%),明显降低PAHs污染土壤利用的风险。麦秸炭、猪粪炭2%施用量处理比1%处理下抑制小白菜吸收PAHs效果更显著,三种生物质炭抑制能力的大小顺序总体表现为麦秸炭>猪粪炭>污泥炭。相对于2~3环的低分子量PAHs,生物质炭对小白菜中4~6环的高分子量PAHs普遍具有更好的降低效果。此外,2%的麦秸和猪粪炭可提高作物生物量,促进蔬菜作物生长。因此,施用生物质炭为污染

土壤中保障作物产量、降低作物 PAHs 吸收提供了有效的技术途径。

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