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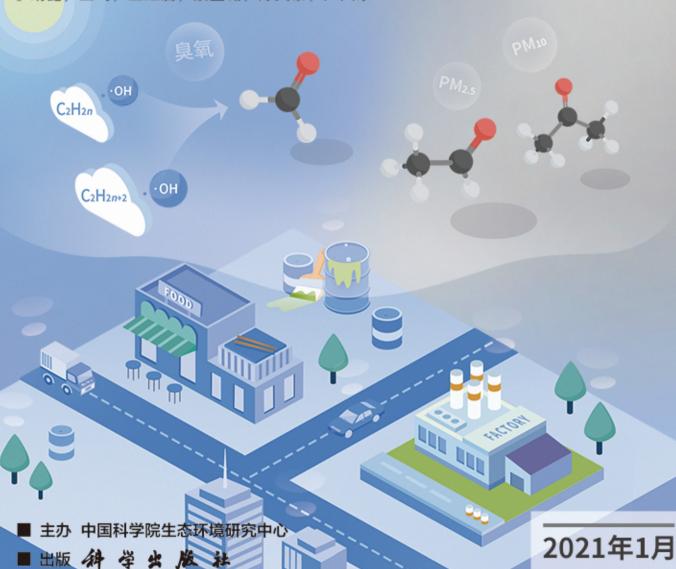
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生物炭与化肥混合对氨挥发和磷固定的影响

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摘要:为探究生物炭化肥的加合作用,利用烟沫(YM)和酒糟(JZ)这2种工业废弃物及农业废弃物玉米秸秆(JG)为原材料制成生物炭,同时将烟沫生物炭进行改性制成烟沫改性生物炭(M-YM),采用培养实验的方法,研究4种生物炭分别在不同化肥配比下,在一定时间内氨挥发和磷固定的规律,以期为生物炭的农业利用提供科学依据.结果表明:①4种生物炭与不同化肥配比下氨的累积挥发量和挥发率表现为A1>A2>A3(A1:2.25g尿素;A2:2.25g尿素+2.25g氯化钾;A3:2.25g尿素+2.25g磷酸二氢钾),尿素中添加氯化钾与磷酸二氢钾减少了氨挥发,不同生物炭在所有化肥配比下氨累积挥发量和挥发率均表现为JZ>M-YM>YM>JG;②4种生物炭在 B1、B2和 B3(B1:0.4g磷酸二氢钾;B2:0.4g磷酸二氢钾+0.3g尿素;B3:0.4g磷酸二氢钾+0.3g氯化钾)处理下磷的固定量均先增加后减小,随后在培养的第30~60d所有处理的磷固定量随时间变化不明显,4种生物炭对磷的固定率均在 B1处理时最大,在 B1、B2和 B3化肥配比下,4种生物炭对磷的固定率大小顺序均为M-YM>YM>JG>JZ。因此,在农业施肥中为降低氮肥中氨的挥发可在尿素中添加氯化钾和磷酸二氢钾,同时在磷的固定方面,可考虑增大生物炭的粒径以减弱其对磷的固定能力.

关键词:生物炭: 氨挥发: 磷固定: 化肥: 改性生物炭

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Effect of Biochar and Chemical Fertilizer Mixture on Ammonia Volatilization and Phosphorus Fixation

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Abstract: In order to explore biochar fertilizer addition, two types of industrial wastes (YM) and lees (JZ) and agricultural waste corn stover (JG) were used as the raw materials to make biochar, and the biochar was modified to make smoke-modified biochar (M-YM). The culture test method was used to study the law of ammonia volatilization and phosphorus fixation over a certain period of time with the different fertilizer ratios of the four biochars. We aimed to provide a scientific basis for the agricultural utilization of biochar. The results show that: 🛈 The cumulative volatilization and volatilization rate of ammonia of the four kinds of biochar with different fertilizer ratios were as follows; A1 > A2 > A3 (A1; 2.25 g urea; A2; 2.25 g urea + 2.25 g chlorination potassium; A3; 2.25 g urea + 2.25 g potassium dihydrogen phosphate). The addition of potassium chloride and potassium dihydrogen phosphate in urea reduced ammonia volatilization, and the cumulative ammonia volatilization and volatilization rate of different biochars under all chemical fertilizer ratios was JZ > M-YM > YM > JG; ② The amount of phosphorus by biochars fixation under the B1, B2, and B3 treatments (B1: 0.4 g potassium dihydrogen phosphate; B2: 0. 4 g potassium dihydrogen phosphate + 0. 3 g urea; B3: 0. 4 g potassium dihydrogen phosphate +0.3 g potassium chloride) all increased and then decreased. Then, the fixation amount of phosphorus not significantly changed in period from 30th to 60th day. Among four biochar, the fixation rate of phosphorus was the highest under the B1 treatment. With the ratios of B1, B2, and B3 fertilizers, the order of the fixation rate of the four biochars to phosphorus was: M-YM > YM > JC > JZ. Therefore, in order to reduce the volatilization of ammonia in nitrogen fertilizers in agricultural fertilization, potassium chloride and potassium dihydrogen phosphate can be added to urea. At the same time, in the fixation of phosphorus, increasing the particle size of biochar may weaken the phosphorous fixation ability.

Key words: biochar; ammonia volatilization; phosphorus fixation; chemical fertilizer; modified biochar

氮是全球生态系统的重要元素,也是许多有机、无机物的组成部分^[1].磷仅次于氮,是初级生产中第二重要的元素^[2].氮和磷元素是细胞组成的必需物质,是农作物生长必需的养分.近年来,随着人口数量逐年增加,全球对水稻小麦等主要粮食作物的需求量进一步扩大,由于粮食作物产量小、质量低等情况的出现,农业生产中施用化肥已经成为解决此类问题的重要途径,其中氮肥与磷肥是农业生产中常用的基础肥料.但随着氮肥和磷肥施用量的增加

以及人类不合理的施用方法,不仅降低了肥料利用率,还造成了环境破坏,这种不对等的产投比在严重破坏自然界氮磷流动系统内部代谢与循环的同

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时^[3],还会导致土壤酸化^[4]、水体富营养化^[5~7]和产生温室气体^[8]等一系列问题.因此寻找一种既具备良好的养分特性又能减轻氮磷对环境造成不良影响的物质是当前迫在眉睫要解决的问题之一.

生物质炭通常是用工农业废弃物、动植物组织等生物质在无氧或者部分缺氧及相对低温(<700℃)的条件下裂解炭化形成的炭材料,其表面含有丰富的含氧官能团和多孔结构^[9],可为土壤微生物的栖息和生长提高良好的环境条件^[10].近些年人们发现生物炭的结构特性可通过一些物理和化学方法来进行改性^[11,12],改性后的生物炭具有比原本生物炭更强的吸附能力^[13]、更大的阳离子交换量和更高的pH^[14].有研究表明,添加小麦秸秆生物炭可改善红壤的理化性质,在修复重金属对红壤性水稻土污染的同时可改善土壤肥力状况^[15].李娇等^[16]的研究发现,与常规施肥相比,生物炭不仅能提高作物产量和系统净初级生产力,还能增加土壤的固碳量.

目前国内对生物炭的研究大部分集中在以农业废弃物为原材料的生物炭与化肥复合制得的生物炭基肥进行还田时对作物生长的影响,而我国工业生产上所产生的废弃物数量也相当庞大,对工农业废弃物制成的生物炭与化肥混合时对氨挥发和磷固定影响的研究较少. 因此,本研究利用烟沫和酒糟这两种工业废弃物以及玉米秸秆为原材料制成生物炭,同时将烟沫生物炭进行改性处理,来分析4种生物炭与化肥混合后在一定时间内氨挥发和磷固定的规律,以期为工业废弃物的可持续利用和提高化肥中N、P元素的利用率提供一定的实验依据和理论指导.

1 材料与方法

1.1 供试材料

以贵州省贵阳市周边的酒厂、烟厂及农场收集的酒糟、烟沫和玉米秸秆为研究对象,对3种原料进行清理和干燥,粉碎后放置在无氧密闭容器中,在马弗炉内加热到450℃热解,研磨热解产物,用超纯水清洗若干次,烘干,即得到生物炭成品.酒糟、烟沫和玉米秸秆热解制成的生物炭分别记为JZ、YM和JG.取上述制备好的烟沫生物炭按4:1的比例加入硅钙镁肥(pH8.5~10.5,SiO₂25%,CaO40%),放入马弗炉内混合烧制,即得烟沫改性生物炭,记为M-YM.供试化肥分别为尿素(含氮46.0%)、氯化钾(含钾60.0%)和磷酸二氢钾(含磷52%、含钾34%).

1.2 实验设计

1.2.1 生物炭与化肥混合后对氨的挥发实验 称取过 0.25 mm 筛的 YM、M-YM、JZ 和 JG 这 4 种生物炭各 15 g 于 500 mL 广口瓶中,分别与 3 种 不同化肥添加水平(A1: 2.25 g 尿素; A2: 2.25 g 尿素 +2.25 g 氯化钾; A3:2.25 g 尿素 +2.25 g 磷 酸二氢钾)充分混匀平铺于广口瓶底部,用喷洒的 方式向混合物中加入去离子水,保证混合物含水量 为 150 g·kg^{-1[17]},同时设置空白对照(即不加生物 炭和化肥),所有样品在培养前均置于25℃的恒温 箱中预培养一夜.次日在培养瓶内的混合物表面垫 一块尼龙布,将盛有 10 mL 2% 硼酸-指示剂混合液 的塑料瓶放在广口瓶内作为 N 的吸收杯,将培养瓶 用保鲜膜封住加盖密封好并置于(28 ±1)℃的恒温 箱中培养,在培养的第5、10、15、20、30、45 和60 d 时取出吸收杯,同时放入同样规格盛有 10 mL 2% 硼酸-指示剂混合液的吸收杯于培养瓶中加盖密封 继续培养. 将替换下来的吸收杯用标准 HCI 滴定, 使硼酸-指示剂混合液至淡紫色,记录标准酸用量, 根据标准酸的用量计算混合物中 N 的挥发量. 每个 处理设置3个重复,在整个培养期间定期采用称重 法补充混合样品水分.

1.2.2 生物炭与化肥混合后对磷的固定实验

称取过 0.25 mm 筛的 YM、M-YM、JZ 和 JG 4 种生物炭各 2 g(每种生物炭需称取 42 份),加入 100 mL 离心管中,分别与 3 种不同化肥添加水平 (B1: 0.4 g 磷酸二氢钾、B2: 0.4 g 磷酸二氢钾 + 0.3 g 泵化 明)充分混匀,用喷洒的方式向混合物中加入去离子水,保证混合物含水量为 150 g·kg^{-1[17]},同样设置空白对照,用保鲜膜封口置于 25℃的恒温箱中培养,在培养的第 5、10、15、20、30、45 和 60 d 时分别取出相应混合样品的离心管,直接测定其有效磷含量.每个处理设置 2 个重复,在整个培养期间定期采用称重法补充混合样品水分.

1.3 测定方法

1.3.1 生物炭性质的测定

采用常规分析方法测定生物炭基本理化性质^[18]. 其中测定 pH 时称取烘干过筛后的生物炭于离心管中,按炭土比为 1: 20 的比例加入去离子水,置于振荡器中恒温振荡 90 min,再用离心管离心 5 min,用 pH 计测定上清液的 pH,重复 3 次;含水量采用烘干法;全氮采用 H_2SO_4 - H_2O_2 消煮、靛酚蓝比色法; 全磷采用 H_2SO_4 - H_2O_2 消煮、钒钼黄比色法; 颗粒粒径采用筛分法; 灰分含量测定时将生物炭放在马弗炉中,调节温度为 760° 、保持 6 h,对剩余物质进行称量,其质量即为生物炭的灰分含量.

1.3.2 混合样品的测定

氨的挥发量采用 2% 硼酸-指示剂混合液的吸

收、标准盐酸滴定法;有效磷采用碳酸氢钠浸提-钼 锑抗比色法测定.

1.4 数据处理

①氨挥发累积排放量为每次测得的氨挥发量之和;②氨的挥发速率[mg·(kg·d)⁻¹]=氨挥发量/培养时间;③氨的挥发率=挥发的氨量/样品中加入的氮量×100%;④磷的固定量=样品加入磷量-测定有效磷量;⑤磷的固定率=(样品加入磷量-测定有效磷量)/样品加入磷×100%.

采用 Excel 2010 和 IBM SPSS 21.0 软件对数据进行处理,不同处理之间的多重比较采用 LSD 最小显著差数法(P < 0.05),所有图表采用 Excel 2010及 Origin 8.5 绘制.

2 结果与分析

2.1 生物炭的基本性质与粒径分布

2.1.1 生物炭的基本性质

4 种生物炭的基本性质如表 1, 4 种生物炭均呈碱性,烟沫改性后提高了生物炭的 pH 值, 4 种生物炭 pH 大小顺序为: JZ > M-YM > YM > JG. 4 种生物炭中全氮及全磷的含量最高的均为 JZ,比最低的 JG 分别高了 24.66 g·kg⁻¹和 15.33

g·kg⁻¹. 烟沫改性后降低了生物炭的全氮含量、提高了全磷含量. 灰分是衡量生物炭中矿物质的一个重要指标, 4 种生物炭灰分含量(质量分数)在 25. 44%~37. 91%之间, 灰分含量大小顺序为: M-YM > YM > JZ > JG. 另外, 烟沫改性后提高了生物炭的含水量, 在自然条件下, YM 与 M-YM 含水量均高于 JZ 与 JG.

2.1.2 不同生物炭粒径分布特征

图 1 表示 4 种生物炭在 5 种不同粒径范围下的分布情况. 从中可知, 4 种生物炭所占质量分数最多的粒径均集中在 0.125 ~ 0.25 mm 范围内,其中大于 2 mm 的粒径在所有粒径中所占质量分数最小,YM、M-YM 和 JZ 的粒径所占质量分数均在10%以内,而 JG 较多,所占质量分数为 13.75%; 4 种生物炭在 > 2 mm 和 1 ~ 2 mm 粒径范围内所占质量分数的大小顺序均为: JG > JZ > YM > M-YM,在 0.25 ~ 1 mm 粒径范围内时表现为 JZ > JG > YM > M-YM,而从 0.125 ~ 0.25 mm 和 < 0.125 mm 开始,YM 与 M-YM 的粒径所占质量分数显著增加,此时大小顺序为: M-YM > YM > JZ > JG,说明 4 种生物炭中 YM 与 M-YM 的总体粒径更小,即 YM 和 M-YM 的比表面比 JZ 和 JG 大.

表 1 4 种生物炭的基本性质

C 30 11 0	Table I	Basic physical and chemica	d properties of four type	s of biochar	49	
生物炭种类	pН	全氮/g·kg ⁻¹	全磷/g·kg-1	灰分/%	含水量/%	
YM	9. 89	10. 22	6. 73	33. 78	2. 74	
M-YM	10. 47	7. 26	8. 74	37. 91	3. 01	
JZ	10.86	28. 51	18. 38	29. 65	1.08	
IG	9. 77	3, 85	3, 05	25, 44	1. 25	

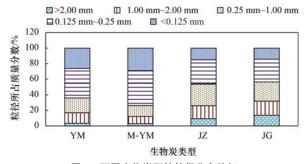


图 1 不同生物炭颗粒粒径分布特征

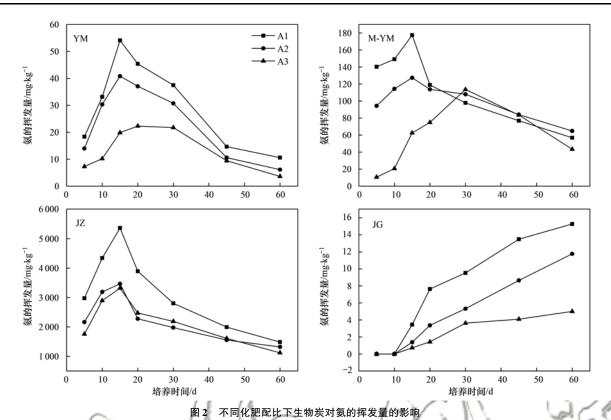
Fig. 1 Distribution characteristics of the particle size of different biochar particles

2.2 不同生物炭与化肥混合对氨挥发的影响

2.2.1 不同生物炭与化肥混合对氨的挥发量的影响

4 种生物炭在不同化肥配比下各培养时间段内 氨的挥发量如图 2 所示,从中可以看出:YM、M-YM 和 JZ 在 A1、A2 和 A3 处理下,整个培养时间内氨 的挥发量均呈现先增大后减小的趋势,而 JG 的 3 个 处理下则呈缓慢上升的趋势. 在培养 15~30 d 时间

范围内,YM、M-YM、JZ 这 3 种生物炭在 3 种水平 下氨的挥发量达到最大值,这是因为在该时间段内 尿素不断被水解为 NH₄ ,而随着 NH₄ 浓度的增加, 促进了 NH₄ 向 NH₃ 的转化,从而导致该时间段内 氨的挥发量急剧增加,且 JZ 在 A1 处理下,在培养的 第15 d 时氨的挥发量最大, 达5 366. 72 mg·kg⁻¹. JG 生物炭在前 10 d 均未出现氨的挥发,从第 10 d 开始各处理均出现少量的氨挥发,但远远低于其余 3 种生物炭处理. 在整个培养时间内,JG 氨挥发量 随着培养时间的增加而增加,且在第60 d 时出现最 大值. 在整个培养时间内, 4 种生物炭在不同化肥 配比下的氨挥发量大小均为:JZ > M-YM > YM > JG, 这与生物炭 pH 大小关系一致,可见 pH 在生物炭对 氨挥发方面的影响之大. 另外, YM 和 JG 在各培养 阶段内3种化肥配比下氨挥发量的总体规律为 A1 > A2 > A3, 说明在 YM 和 JG 混合物中添加磷酸二 氢钾对氨的挥发抑制作用在整个培养过程中都比氯

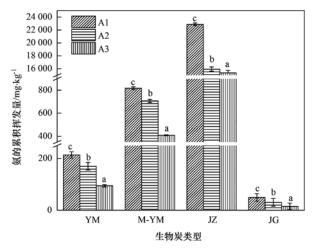


Effect of biochar on ammonia volatilization with different fertilizer addition ratios

化钾强;在 JZ 混合物中添加磷酸二氢钾和氯化钾对氨的挥发抑制作用差异不大; M-YM 混合物中则在培养前 30 d内,添加磷酸二氢钾对氨的挥发抑制作用强于氯化钾,而在培养的后 30 d内,在尿素中添加这两种肥料对氨挥发的抑制作用差异不大.

2.2.2 不同生物炭与化肥混合对氨的累积挥发量的影响

培养结束时 4 种生物炭在 A1、A2 和 A3 处理下氨的累积挥发量如图 3 所示. YM、M-YM、JZ 和 JG 在不同化肥配比下氨的累积挥发量差异显著(P



不同小写字母表示不同化肥配比差异显著(P<0.05)

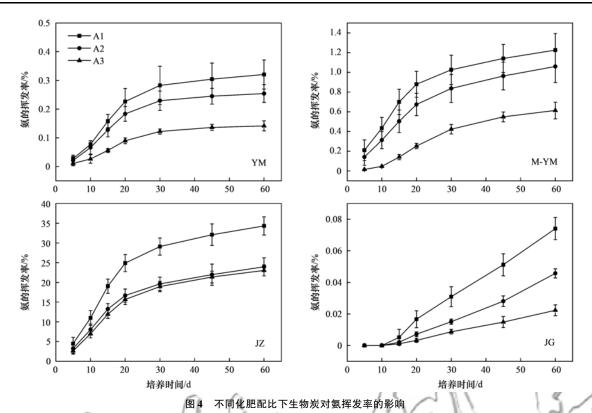
图 3 不同化肥配比下生物炭对氨的累积挥发量的影响

Fig. 3 Effect of biochar on cumulative ammonia volatilization with different fertilizer addition ratios

<0.05),且均表现为:A1 > A2 > A3,说明添加氯化钾与磷酸二氢钾降低了尿素中氨的挥发,且添加磷酸二氢钾的抑制作用更强,这是因为磷酸二氢钾在该过程中被水解,水解使得其产生 H⁺,从而使得环境的 pH 降低,进而抑制尿素水解产生的铵盐向氨气转化;但氯化钾并不能改变环境的 pH,因此也不能很好地抑制 NH₄⁺ 向 NH₃ 的转化,即会有较高的氨挥发量.4 种生物炭在所有 A1、A2 和 A3 处理下氨的累积挥发量均表现为:JZ > M-YM > YM > JG,其中 JZ 在 A3 水平下氨的累积量分别是 YM、M-YM和 JG 处理的 162.6、37.5 和1 031.3倍,这是因为 JZ 的 pH 高于其他 3 种生物炭,而 pH 又是决定氨挥发的主要因素之一,随着 pH 的增加,环境中铵态氮的比例升高,使得氨挥发的潜力增大[19].

2.2.3 不同生物炭与化肥混合对氨的挥发率的影响

4 种生物炭处理在 A1、A2 和 A3 处理下对氨的挥发率的影响如图 4 所示. 4 种生物炭在 3 种化肥配比下每个对应的培养阶段内,不同生物炭处理氨的挥发率大小顺序均为: JZ > M-YM > YM > JG. 当培养第 60 d 时,氨的挥发率最大和最小分别是 JZ、JG处理. 从各生物炭氨的挥发率的最大值也可以得出,在 A1、A2 和 A3 处理下,4 种生物炭处理氨的挥发率的大小均表现为: A1 > A2 > A3, YM、M-YM、JZ和 JG的 A3 处理氨的挥发率分别比 A1 处理氨的挥发率减少了 0.179%、0.612%、11.261%和 0.052%、



ig. 4 Effect of biochar on ammonia volatilization ratio with different fertilizer addition ratios

说明磷酸二氢钾能减少生物炭与尿素混合物中的氨的挥发率,这是因为磷酸二氢钾水解使得环境变为酸性,而酸性条件有利于NH⁺₄-N的固定,减少NH₃的挥发^[20]. 在YM、M-YM和JZ处理中,3种化肥水平下氨的挥发率均先快速增大后缓慢增大;JG处理从培养第10d开始到培养结束氨的挥发率随时间呈线性增加的趋势.

2.2.4 不同生物炭与化肥混合下氨挥发动力学模型 在相同培养温度下,除 JG 外,YM、M-YM 和 JZ 在不同化肥配比下氨的挥发累积量的趋势基本一致,说明不同生物炭对氨的累积挥发量有影响,将所有处理中氨的累积挥发量与培养时间用 Elovich(y = a + blnt)与 Bangham(y = At^{1/B})动力学方程进行拟合,拟合结果如图 5 和表 2 所示. 方程中,y 表示氨

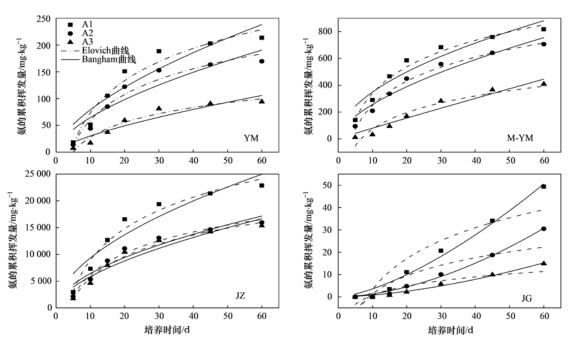


图 5 氨的累积挥发量与时间的拟合曲线

Fig. 5 Fitting curve of cumulative ammonia volatilization and ammonia volatilization time

的累积挥发量, t 表示培养时间; 其中在 Elovich 方程中, 参数 a 表示第 1 d 氨的挥发量, 参数 b 为斜率, 可用来表征不同处理的 NH, 挥发速率; 在该方程中, 4 种生物炭在不同处理间均表现出差异性, 且 a 和 b 两个参数的大小与累积氨挥发量的变化趋势一致,除 JZ 外,其余 3 种生物炭在 A3 水平下 a 的绝对值和 b 值均远低于 A1 和 A2 水平, 可见这 3 种生物炭在 A3 水平下氨挥发容量和强度均小于 A1和 A2 水平, 说明在 YM、M-YM和 JG 中添加磷酸二

氢钾更有效抑制了氮的损失. 同时根据拟合参数可知, YM、M-YM和JZ的 Elovich 方程相关系数(R^2)在 $0.932 \sim 0.986$ 之间,均达到了极显著水平,而Bangham 方程相关系数(R^2)在 $0.839 \sim 0.932$ 之间,远低于 Elovich 方程,说明 Elovich 方程能更好地拟合 YM、M-YM和JZ中氨累积挥发量的规律. JG的Bangham 方程相关系数(R^2)分别为 0.981、0.993和 0.984,高于 Elovich 方程相关系数(0.805、0.734和 0.761),说明 JG 用 Bangham 方程拟合程度更好.

表 2 氨的累积挥发量与时间的拟合曲线参数

Table 2 Fitting	curve parameters of	cumulative	ammonia	volatilization	and	ammonia	volatilization	time
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生物炭类型	化肥配比		Elovich 方程			Bangham 方	程
生初灰矢堡	化加油比	a	b	R^2	A	В	R^2
	A1	- 125. 94	86. 67	0. 95	19. 25	1. 63	0. 85
YM	A2	- 99. 15	69. 11	0.950	16. 15	1.66	0. 84
	A3	-63.90	39. 95	0.95	6. 10	1.44	0. 87
	A1	-319.36	285. 85	0.98	105. 64	1. 93	0.90
M-YM	A2	- 348. 73	259. 85	0.99	63. 53	1.65	0, 93
	A3	- 340. 23	178. 93	0. 93	8. 60	1. 04	0. 93
	A1	- 10 572. 39	8 471. 98	0. 97	2 644. 63	1. 82	0.87
JZ	A2	-7 039. 06	5 755. 70	0.98	1 826. 58	1. 83	0.90
	A3	-7 698. 17	5 781. 61	0.98	1 531. 09	1. 72	0.90
	Al	-42.75	19. 98	0.81	0.12	0. 68	0. 98
JG	A2	-25.64	11.71	0.73	0.02	0. 57	0. 99
(0 /	A3	- 12. 94	5.93	0.76	0.02	0.61	0. 98

- 2.3 不同生物炭与化肥混合对磷固定的影响
- **2.3.1** 不同生物炭与化肥混合对磷的固定量的动态变化

4 种生物炭在 B1、B2 和 B3 处理下各培养时间

段内磷的固定量的动态变化如图 6 所示,从中可以看出,4 种生物炭在不同的化肥配比下,磷的固定量均在第 10 d 时达到最大值,随后随培养时间的增加磷的固定量急剧减小,除 YM 的 B1 处理外,其余

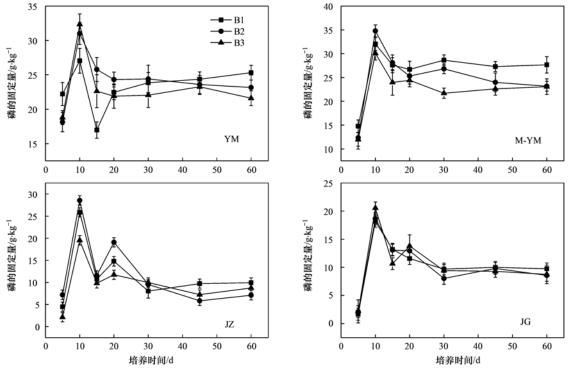


图 6 不同化肥配比下生物炭对磷的固定量的影响

Fig. 6 Effect of biochar on phosphorus fixation with different fertilizer addition ratios

处理均在第 15 d 时出现最低值,当培养时间从第 15 ~ 20 d 时,磷的固定量急剧上升,随后逐渐趋于平缓. 4 种生物炭中,M-YM 对磷的固定量最大,JG 最小,且在整个培养时间内,M-YM 在 B1、B2 和 B3 处理下磷固定量最大值分别是最小值的 2.17、2.82 和 2.51 倍,JG 在 B1、B2 和 B3 处理下磷固定量最大值分别是最小值的 10.84、8.79 和 9.42 倍.

2.3.2 不同生物炭与化肥混合对磷的固定率的影响 不同生物炭与化肥混合对磷的固定率的影响如 表 3 所示. 在所有生物炭中,磷的固定率在 16.48% ~61.22%之间.YM 和 M-YM 在 B1、B2 和 B3 处理 下磷的固定率大小顺序均为:B1 > B2 > B3, JZ 和 JG 在 B1、B2 和 B3 处理下磷的固定率大小顺序则均 为:B1 > B3 > B2; 通过显著性分析可知, YM 中 B1 处理与 B3 处理差异显著(P<0.05), 而 B2 处理与 两者之间差异均不显著(P<0.05), M-YM 处理 B1 处理与其余两种处理间差异显著(P<0.05),但B2 与 B3 两种处理间无显著差异, JZ 与 JG 的所有处理 间差异均不显著(P<0.05). 这表明氯化钾的添加 会降低磷肥与 YM 的混合物中磷的固定率,而尿素 对混合物无影响; 氯化钾与尿素的加入均会降低磷 肥与 M-YM 混合物中磷的固定率,但两者之间的效 果无显著差异; 而氯化钾与尿素的添加对 JZ 和 JG 两种生物炭与磷肥的混合物在磷固定中无较大影 响. 在 B1、B2 和 B3 处理下, 4 种生物炭对磷的固 定率大小顺序均为: M-YM > YM > JG > JZ,且3种化 肥配比下 M-YM 比 JZ 固定率分别高出 40.91%、 37.70%和30.33%.

表 3 不同化肥配比下生物炭对磷的固定率的影响¹⁾/%
Table 3 Effect of biochar on the fixed ratio of phosphorus with different fertilizer addition ratios/%

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化肥配比	生物炭种类					
PLALIE IL	YM	M-YM	JZ	JG		
B1	53. 86b	61. 22b	20. 31a	21. 57a		
B2	52. 14ab	54. 18a	16. 48a	19. 34a		
В3	49. 02a	49. 35a	19. 02a	20. 13a		

1)不同小写字母表生物炭的不同处理间的差异性显著(P<0.05)

3 讨论

3.1 不同生物炭与化肥混合对氨的挥发量与累积 挥发量的影响

尿素分解受外界水分、pH 以及微生物的影响较大^[21],在本研究中,YM、M-YM 和 JZ 在不同化肥配比下,在培养前期氨的挥发量剧增,这主要是由于此阶段尿素与混合物中的水分接触,促使尿素发生水解反应,产生氨气,同时有一部分原因是由于生物炭呈碱性,而碱性环境会使尿素中的氮向氨气转化,对氨的挥发有促进作用,这也与 Schomberg 等^[22]的研

究结果类似. 在此 3 种生物炭的培养后期,氨的挥发率逐渐减小,出现这种现象的原因可能是由于在前期尿素水解过程中会生成一些酸性物质(如氨基甲酸铵),使培养环境的 pH 减小,同时由于此时培养环境趋于稳定,生物炭内的官能团逐渐活跃,对尿素中氮的吸收固持量增加,减少了氨的挥发. 成功等人[^{23]}利用静态暗箱-气相色谱原位研究小麦-玉米轮作系统条件下添加不同量生物炭对土壤碳氮排放、作物产量的影响,发现添加生物炭的处理使得整个小麦-玉米轮作农田土壤系统中氮素的吸附显著增加了 27.6%~38.7%,这也与本研究的结果类似.

JG 与其余 3 种生物炭结果不同,在前 10 d 内均无法测出氨的挥发,且培养后期氨的挥发量也远远低于其余 3 种生物炭,这与以往理论研究有较大的差别,笔者推测可能是由于 JG 中大颗粒粒径较多,自身的浸润性较强,而较强的浸润性会紧紧包裹住外界添加的水分,使水分无法与尿素等肥料接触,导致无氨气的挥发,且由于添加水量不多,与水分结合的生物炭只有少数,所以虽然生物炭呈碱性,但无液体作为其中介质,pH 对尿素的作用缓慢,这也是后期 JG 中氨挥发量低的主要原因.

本研究结果显示, 4 种生物炭在不同化肥配比 下氨的累积挥发量差异显著(P<0.05)且均表现 为:A1 > A2 > A3,这表示尿素中添加氯化钾与磷酸 二氢钾均降低氨的累积挥发量,且在 YM、M-YM 和 JG 中添加磷酸二氢钾对氨挥发的抑制作用强于氯 化钾,而在 JZ 混合物中添加这两者对氨挥发的抑制 作用差异不大.有研究认为,钾离子与氯离子能与尿 素分子通过相互作用形成离子-分子缔合物,这也是 导致混合物中氨的挥发量减少的原因之一[24]. 尿素 处理土壤且加入磷酸二氢钾后氨的挥发量最低,这 很有可能是由于磷酸二氢钾水解呈酸性,酸性环境 会使铵根离子持留在样品中,氨气的挥发减少.在本 研究中将4种生物炭氨的累积挥发量进行对比,发 现在所有化肥配比水平上生物炭的大小顺序均为: JZ > M-YM > YM > JG, 这与 4 种生物炭的 pH 大小 关系一致,其中 JZ 在 A1 水平下氨的挥发比同期其 他 3 种生物炭 A1 水平下都强,这是因为 JZ 的 pH (10.86) 高于其他 3 种生物炭, 在相同NH₄ -N水平 下,pH 每升高一个单位, 氨挥发量增加 10 倍[25]. 同 时,由于改性后的生物炭具有比原本生物炭更大的 阳离子交换量和更高的 pH[14], 使得 M-YM 具有比 YM 更高的 pH,导致当生物炭与化肥混合后,M-YM 与化肥混合后的氨挥发量、累积挥发量和挥发率均 高于 YM. 因此在实际应用中, 当与化肥混合时, 应 尽量选取未改性生物炭,这样可降低氨的挥发率,进

而增大肥料利用率.

另外还与生物炭的自身官能团、孔隙结构等有极大的关系. 易从圣等^[26]的研究认为,不同原材料对生物炭与化肥混合后对氮的缓释性能影响较大,在稻壳炭、油茶壳炭制成的两种生物炭中,稻壳炭的效果更好,这可能是因为稻壳炭比油茶壳炭孔隙结构更发达,表面积更大,对尿素的吸附和负载能力更强. 因此为减少氮肥中氨的挥发,在生物炭与氮肥混合时,应尽量选择 JG 和 YM,因为这两种生物炭在提高工农业废弃物利用率的同时又可明显降低氨的挥发,且在这两种混合物中添加磷酸二氢钾对氨挥发具有更强的抑制作用,从而大大减少氮的损失,提高氮利用率;而 JZ 由于与氮肥混合后具有较大的氨挥发量,因此在实际应用中不宜在氮肥中添加.

3.2 不同生物炭与化肥混合对磷固定量的动态变化及磷固定率的影响

由于磷肥的快速性,将生物炭与磷肥混合后施 入土壤,利用生物炭对养分的固持作用使磷素缓慢 释放到环境中,延长磷肥的有效性,在本研究中,4 种生物炭在整个培养时间内均对磷有一定的固定作 用,但每个阶段内的固定量有所差别. 在前5 d 内, 磷的固定量极低,而在培养第10 d时,磷的固定量 最大,这可能是在前期时混合物中的磷素主要以游 离态存在,混合物中的生物炭及水分无较大的作用. 在5~10 d期间,磷的固定量急剧上升,此时混合物 中的水分在蒸气压的推动下与磷酸二氢钾混合,形 成饱和溶液[27],由于生物炭的原因混合物环境呈碱 性,而从前人研究成果可知生物炭在 pH 为 9 左右 时对磷的吸附最好[28],所以在此阶段生物炭将饱和 溶液中的磷快速固定. 在 10~15 d 期间,磷的固定 量逐渐下降,这可能是由于磷溶解的原因,有研究认 为磷的固定机制是不断溶解-沉淀的结果[29]. 在第 30~60d时,磷的固定量差别不大,此时生物炭由于 自身的吸持特性及混合物中的环境已达到一个相对 稳定的系统,磷的固定量在一个较小的范围内波动, 此阶段下也可以推断生物炭在实际应用中的最大固 定量.

M-YM 生物炭对磷的固定率最高,且 4 种生物炭对磷固定量的大小顺序与生物炭粒径 < 0.125 mm 所占质量分数的大小顺序一致,即 M-YM > YM > JZ > JG,其中在 M-YM 混合物中添加尿素和氯化钾均会降低对磷的固定,但二者之间降低效果无显著差异; YM 混合物中添加氯化钾会降低对磷的固定,但尿素对其无影响; 而在 JZ 和 JG 混合物中添加氯化钾和尿素对磷的固定均无较大影响. 另外,可以推断出生物炭对磷的固定率可能与生物炭自身的

粒径大小有关, 孟庆瑞等[30]的研究表明生物炭巨大 的比表面积和多孔结构, 以及丰富的官能团为其吸 附磷提供了载体结构基础. 宋小宝等[31] 通过一步共 沉淀法制备的2-La-MHTC具有更大的比表面,同时 其对磷的固定作用更强,具有高效的除磷能力,最 大吸附量可达 100. 25 mg·g-1. 这些与本研究结果类 似,当生物炭中粒径较小时,生物炭与化肥的接触比 表面积更大,作用点位更多,而磷固定过程的实质是 与生物炭发生物理或化学反应的过程,接触面积越 大,反应越充分,因此小粒径的生物炭相较于大粒径 的生物炭对磷的固定作用更强.同时,生物炭改性提 高了生物炭本身的比表面积,使得其与化肥的接触 面积更大, 化肥中的磷酸根更易被改性生物炭吸附, 从而导致改性生物炭在一定程度上降低了磷的生物 有效性. 因此当生物炭与磷肥混合时, 为降低生物炭 对磷的固定,宜选择 JC 和 JZ,且在这两种生物炭与 磷肥混合物中无需添加氯化钾或尿素,以免造成化 肥资源的浪费;另外,若可供添加的生物炭中只有 M-YM 可选择,为了减少其对磷的固定,可在 M-YM 与磷肥的混合物中添加尿素或氯化钾,也可通过增 大 M-YM 的粒径来提高磷的生物有效性.

4 结论

- (1)4种生物炭在 A1、A2 和 A3 处理下氨的挥发量、累积挥发量和挥发率均表现为: JZ > M-YM > YM > JG; 尿素中添加氯化钾与磷酸二氢钾可在一定程度上抑制氨挥发; Elovich 方程能更好地拟合YM、M-YM 和 JZ 的所有处理中氨的累积挥发量与培养时间的变化趋势,而 JG 用 Bangham 方程拟合程度更好.
- (2)在 B1、B2 和 B3 化肥配比下, 4 种生物炭对磷的固定率的大小顺序均为: M-YM > YM > JG > JZ; 所有处理下磷的固定量均先增加后减小, 随后逐渐稳定, 且在培养的第 10 d 达到最大值.
- (3)当生物炭与氮磷肥混合时,考虑到生物炭会同时导致氨挥发和磷固定而使得氮磷元素的生物有效性降低,在实际应用中,若在氮磷肥中添加 M-YM,则不需添加氯化钾、添加 JG 时与 M-YM 一样但需适当多施磷肥、添加 YM 时则需加入适量氯化钾以及适当增加磷肥用量,这样可在减少氨挥发和磷固定的同时又最大限度地减少化肥的投入,但因 JZ 不能同时提高氮磷的利用率而使得其不可与氮磷肥混合施用.

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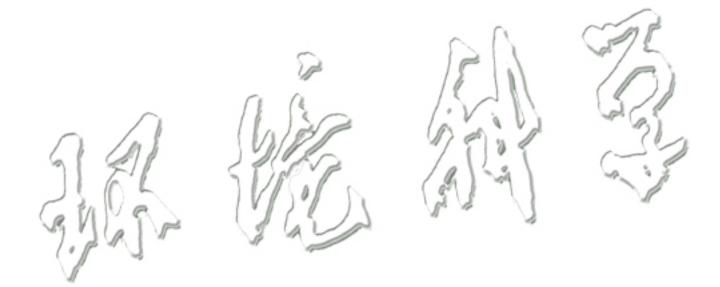
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