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Ca改性生物炭对土壤磷赋存形态影响及稳定化机制

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摘要: 针对湖库周边农田淹没后土壤磷释放风险控制的问题, 采用共热解法制备Ca改性生物炭(Ca-BC), 通过X射线光电子能谱分析(XPS)、X射线多晶粉末衍射分析(XRD)、吸附实验和模拟培养实验等, 进行Ca-BC对土壤磷赋存形态影响和稳定化机制研究. 结果表明, Ca-BC吸附磷的过程符合Langmuir($R^2 = 0.940$)和一级吸附动力学模型($R^2 = 0.961$), 表明该吸附过程为化学作用主导的单层吸附, 最大吸附量达到 $267.93 \text{ mg} \cdot \text{g}^{-1}$. 模拟培养实验表明, 当Ca-BC添加量为1%时, 土壤中较活跃性的交换态磷形态从7.42%下降至4.59%. XRD结果表明, Ca-BC吸附磷后出现 $\text{Ca}_3(\text{PO}_4)_2$ 和 $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ 吸收峰, 证明磷酸盐在生物炭表面形成较稳定的晶体沉淀. XPS分析表明, 生物炭表面羰基官能团参与磷固定过程, 提高了生物炭对磷的吸附能力. 总体来讲, Ca-BC添加量大于1%时, 对磷的释放有较好的固定能力, 具备对土壤磷释放控制的潜在应用价值.

关键词: 改性生物炭; 土壤; 新增淹没区; 磷酸盐; 赋存形态

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Effect of Ca Modified Biochar on the Chemical Speciation of Soil Phosphorus and Its Stabilization Mechanism

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Abstract: To control of phosphorus release from soil after farmland inundation around the lake and reservoir, calcium modified biochar (Ca-BC) was prepared using the coprecipitation method. Through X-ray photoelectron spectroscopy (XPS), X-ray polycrystalline powder diffraction (XRD), adsorption experiments, and simulated culture experiments, the effects of Ca-based biochar on the fraction of soil phosphorus (P) and its stabilization mechanism were studied. The results showed that the adsorption process of Ca-based modified biochar conformed to Langmuir ($R^2 = 0.940$) and the first-order adsorption kinetic model ($R^2 = 0.961$), indicating that the P adsorption was a single-layer adsorption dominated by chemical action, and the maximum adsorption capacity was $267.93 \text{ mg} \cdot \text{g}^{-1}$. The simulated culture experiment indicated that when the modified biochar was 1%, the exchangeable fraction of phosphorus in the soil decreased from 7.42% to 4.59%. The XRD results demonstrated that $\text{Ca}_3(\text{PO}_4)_2$ and hydroxyapatite absorption peaks appeared after adsorbed phosphorus on biochar, which proved that phosphate formed a relatively stable crystal precipitation. As shown in the XPS spectrum analysis, the carbonyl functional groups participated in the phosphorus fixation process, which improved the adsorption capacity of biochar for phosphorus. In general, when the concentration of Ca-based modified biochar was greater than 1%, it had a good fixation capacity for phosphorus release and had potential application value for controlling phosphorus release in soil.

Key words: modified biochar; soil; new submerged area; phosphorus; chemical speciation

生物炭是生物质在缺氧条件下通过热化学转化后获得的固体材料^[1], 被广泛用于土壤碳封存、土壤改良、有机物吸附和重金属稳定化应用^[2]. Qiu等^[3]和Zhen等^[4]将生物炭用于土壤中镉和石油烃等污染物控制, 可以降低土壤中污染物的植物可利用性. 但是, 生物炭表面以酸性官能团为主导导致带有负电荷^[5], 吸附水体中 PO_4^{3-} 等阴离子容量较小. 利用金属阳离子, 如 Ca^{2+} 、 Al^{3+} 和 Fe^{3+} 等, 与磷酸盐具有很强的亲和力, 显著提高生物炭对磷的吸附能力^[6-8]. 负载镁、钙和铁等金属元素的生物炭, 通过化学沉淀、配体交换和表面静电吸附等作用吸附磷酸盐和阴离子形态重金属, 提高了生物炭对磷酸盐等吸附容量^[9-11]. 改性后生物炭对磷酸盐等电负性物质的污染控制具有潜在的应用前景.

磷是水体富营养化限制性元素之一, 磷释放风险主要受其赋存形态含量影响^[12]. 湖泊、水库水位波动或调控常导致周边农田出现淹没现象, 淹没初期

农田土壤磷通过还原释放、解析导致向上覆水释放, 易造成水体富营养化, 土壤磷释放风险控制对湖泊水库水质安全保障十分关键^[13-15]. 王剑等^[16]研究表明丹江口水库新增淹没区土壤中全磷和速效磷含量属于中等偏丰富, 新增淹没区超过18.6%的区域存在较高的氮磷潜在释放风险. 生物炭作为常见的土壤修复材料, 能否用于淹没初期的土壤磷释放控制材料值得进一步探究.

钙对水生态环境无毒性, 而且其天然丰富且价格低廉, 是一种生态友好用于改性的金属元素^[17]. 如钙改性斜发沸石^[18]、钙修饰污泥^[19]和钙粉生物炭^[20]等可以显著改善对磷酸盐的吸附性能, 因此, 本文选择Ca改性生物炭来研究对土壤磷稳定性影响. 选取

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白洋淀水位恢复导致淹没区,以白洋淀区内农田或林地土壤为研究对象,按照不同质量比(1%、5%、10%和15%)施加Ca基改性生物炭(Ca-BC),经过室内模拟培养研究生物炭对淹没土壤磷吸附效果.利用扫描电镜(SEM)、X射线衍射(XRD)和X射线光电子能谱分析(XPS)进行改性生物炭理化表征,探明其对磷酸盐稳定化机制,以期对白洋淀新增淹没区氮磷营养盐释放提供技术支持.

1 材料与方法

1.1 Ca基改性生物炭的制备

制备生物炭的原材料采用毛竹(PP),具体制备过程如下:将原材料清洗、烘干和破碎后过100目筛,置于气氛管式炉内.通入氮气保护,设置温度为500℃热解持续时间为2 h,冷却至室温后过100目筛,获得毛竹生物炭(命名为PPBC).

Ca改性毛竹生物炭制备方法如下^[6,17]:将氧化钙和毛竹生物炭按1:15(质量比)混合,搅拌混匀、振荡和烘干.置于气氛管式炉中600℃热解2 h,随后洗涤和干燥后,获得Ca-BC.

1.2 生物炭的表征

通过场发射电子扫描显微镜-能量光谱(SEM-EDS日本日立公司,SU8010)对样品的形态结构和表面主要元素进行表征.采用X射线多晶粉末衍射仪(XRD,德国布鲁克分析仪器公司,D8 Advance)测定样品的物相结构.X射线光电子能谱仪(XPS,Thermo Scientific Escientific 250Xi,美国)分析生物炭吸附磷酸盐的表面官能团组成.

1.3 吸附动力学与吸附等温线

1.3.1 吸附动力学实验

准确称取Ca-BC(0.1±0.001)g,加入到装有40 mL磷酸盐溶液(浓度为20 mg·L⁻¹)的50 mL离心管中,然后将离心管转移到摇床,转速设定为150 r·min⁻¹,温度为25℃,振荡0.25、0.5、0.75、1、2、3、4、8、24和48 h后,测定滤液磷酸盐的浓度,每组实验重复3次.采用准一级动力学方程、Elovich动力学方程和准二级动力学方程对实验数据进行拟合^[21,22],其表达式分别如下所示.

准一级动力学方程:

$$q_t = q_e \cdot (1 - e^{-k_1 t}) \quad (1)$$

Elovich方程:

$$q_t = [\ln(a \cdot b \cdot t + 1)]/b \quad (2)$$

准二级动力学方程:

$$q_t = (k_2 \cdot q_e^2 \cdot t) / (1 + k_2 \cdot q_e \cdot t) \quad (3)$$

式中, q_e 和 q_t 分别为最大吸附量(mg·g⁻¹)和 t 时刻吸附量(mg·g⁻¹), t 为吸附时间, k_1 和 k_2 分别为准一级反应

速率常数和准二级反应速率常数, a 和 b 均为Elovich动力学参数.

1.3.2 吸附等温线实验

称取Ca-BC(0.1±0.001)g,加入到装有40 mL初始浓度为25~500 mg·L⁻¹的磷酸根溶液的50 mL离心管中,将离心管放入摇床振荡24 h,转速为150 r·min⁻¹培养温度为25℃,振荡结束后取出离心管上清液,离心和过滤后测定上清液中磷酸盐的浓度,每组实验重复3次,使用Langmuir模型和Freundlich模型对实验数据进行拟合.其表达式分别如下所示^[23].

Langmuir模型:

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

Freundlich模型:

$$q_e = K_F \cdot c_e^{1/n} \quad (5)$$

式中, q_e 为吸附饱和时生物炭的吸附量,mg·g⁻¹, $q_{\max}$ 为单分子层饱和吸附量,mg·g⁻¹, C_e 为平衡浓度,mg·L⁻¹, K_L 为Langmuir模型吸附常数,L·g⁻¹, K_F 为吸附容量,(mg·g⁻¹)·(mg·L⁻¹)^{-1/n}, n 为Freundlich吸附常数.

1.4 样品采集与分析

1.4.1 样品采集与前处理

如图1所示,基于典型代表性原则,同时考虑土地利用等环境因素,采集白洋淀区内潜在新增区农田土壤样品9个点位.将采集的样品装入自封袋密封保存,土壤样品经冷干后去除样品中砾石和动植物残体,将样品置于4℃冰箱备用.

1.4.2 土壤化学组分和磷分级分析方法

沉积物中的总磷通过在500℃灰化2 h,然后利用1 mol·L⁻¹ HCl提取,持续振荡16 h,提取液中总磷浓度采用《水质 总磷的测定 钼酸铵分光光度法》(GB/T 11893-1989)测定.土壤中总碳(TC)和总氮(TN)含量采用元素分析仪(Vario EL III, Elementar, GRE)同步测定.

土壤磷形态常见有6种:交换态磷、铁结合态磷、闭蓄态磷、自生磷、钙磷(Ca-P)和残渣态磷,为了揭示生物炭对磷形态吸附机制的差异性,采取表1所示磷分级方法进行磷形态分析^[24].模拟培养实验步骤如下:称取200 g过100目筛土壤放入烧杯中,依次加入1%、5%、10%和15%比例生物炭后,搅拌均匀,加入400 mL的超纯水,室温下连续培养72 h后进行磷形态分析.

1.5 数据处理与分析

数据分析处理采用Excel 2018软件,采用Origin Pro 2017进行实验数据绘图,拟合吸附动力学和吸附等温线.样品采集点位图利用ArcMap 10.8绘制.生物炭的XPS图谱分峰采用XPS Peak 4.1分析.

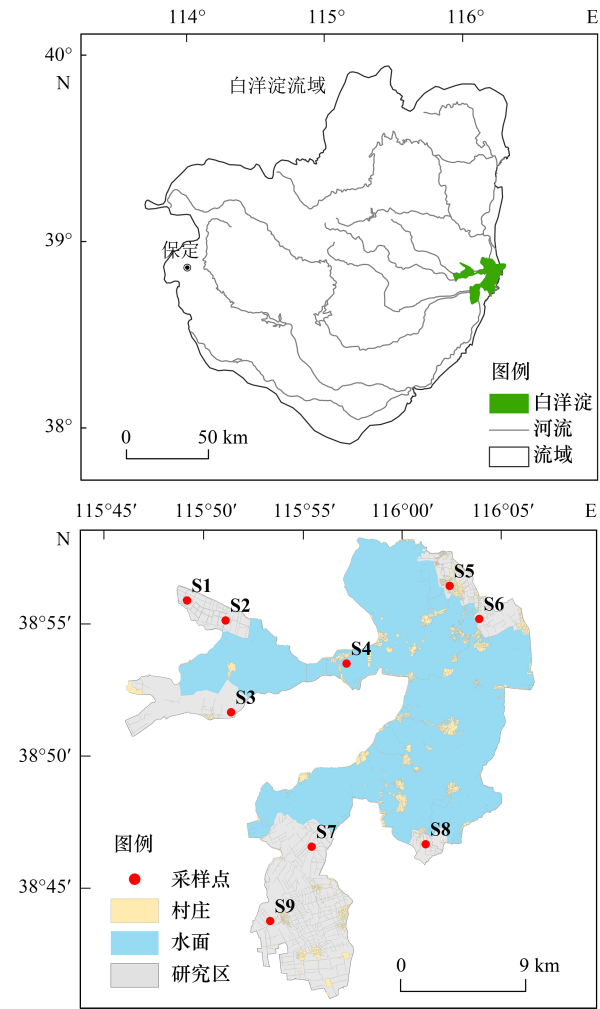


图1 白洋淀土壤样品采集样点分布示意
Fig. 1 Distribution map of soil sample collection in Baiyangdian Lake

2 结果与讨论

2.1 吸附动力学与吸附等温线

2.1.1 吸附动力学过程

Ca-BC 的磷吸附动力学特征曲线如图 2(a), 4 h

内为快速吸附阶段, 吸附量达到 138.90 mg·g⁻¹, 随着反应时间超过 8 h, 生物炭的表面吸附位点逐渐被占据, 逐渐达到吸附平衡值. Ca-BC 表面较多的结合位点和磷酸盐浓度差导致的传质推动力是吸附的主要动力^[25]. 快速吸附阶段, Ca-BC 表面有较多吸附位点和较大磷酸根浓度差所产生的传质驱动力, 导致磷酸盐快速附着在其生物炭表面; 而吸附平衡阶段, 随着有效结合位点和磷酸盐浓度差的减小导致吸附速率趋于缓慢.

采用准一级动力学、Elovich 方程和准二级动力学进行拟合, 拟合吸附动力学参数结果如表 2 所示. 准一级动力学模型($R^2 = 0.961$)呈现较好的拟合结果, 表明 Ca 质子化后的 CaOH⁺ 与磷酸盐之间的静电吸附, 以及生物炭表面的范德华力对于磷酸盐的吸附起到关键作用^[26]. 除此之外, 准二级动力学模型($R^2 = 0.934$)也呈现较好的拟合效果, 说明 Ca-BC 对磷的吸附中化学吸附也起到一定作用^[27], 包括 Ca-BC 和磷之间的交换或共享电子并可能形成共价键或新化合物^[23,28].

2.1.2 吸附等温线过程

如图 2(b) 所示, Ca-BC 吸附磷的吸附过程呈现先快速增加然后趋于平衡特征. 磷吸附平衡浓度小于 65.09 mg·L⁻¹, 磷吸附量呈快速增加趋势, 由 7.94 mg·g⁻¹ 增加到 67.45 mg·g⁻¹. 当平衡液中磷浓度超 95.90 mg·L⁻¹ 时, 吸附量从 122.05 mg·g⁻¹ 缓慢增加到 143.50 mg·g⁻¹, 最后吸附趋于稳定, 达到吸附平衡.

吸附等温线拟合结果如表 3 所示, Langmuir 吸附模型(R^2 为 0.940)能够更好地描述 Ca-BC 对磷酸盐的吸附过程, 磷酸盐的最大吸附容量($q_{\max}$) 达到 267.93 mg·g⁻¹. 吸附等温线拟合结果表明, Ca-BC 对磷酸盐吸附机制多以同质单层吸附为主, 主要依靠化学键力在表面形成紧密结构, 通过孔道进行内扩

表1 土壤磷形态分级测定方法
Table 1 Method for determination of phosphorus fractions in soil

形态	提取方法
交换态磷	称取 0.3 g 沉积物, 加入 30 mL 1 mol·L ⁻¹ MgCl ₂ 振荡 2 h 后, 5 000 r·min ⁻¹ 离心 20 min, 获得上清液, 重复清洗 2 次合并上清液, 测定上清液磷浓度
铁结合态磷	30 mL 0.5 mol·L ⁻¹ NH ₄ F 加入到上步残渣态里振荡 1 h, 离心获得上清液, 其余步骤同交换态磷
闭蓄态磷	24 mL 0.3 mol·L ⁻¹ 柠檬酸钠、1 mol·L ⁻¹ NaHCO ₃ 和 0.675 g Na ₂ S ₂ O ₄ 配成的混合提取剂 (pH 7.6) 加入到上步残渣态, 搅拌 15 min 后加入 6 mL 0.5 mol·L ⁻¹ 的 NaOH, 离心获得上清液, 其余步骤同上
自生磷	30 mL 1 mol·L ⁻¹ NaAc-HAc (pH 为 4) 缓冲液加入到上步残渣态, 振荡 6 h, 离心得上清液, 采用 30 mL 1 mol·L ⁻¹ MgCl ₂ 提取, 然后用 30 mL 去离子水提取一次, 合并后过滤, 测定上清液中磷浓度
Ca-P	30 mL 1 mol·L ⁻¹ HCl 加入到上步残渣态里振荡 16 h, 离心获得上清液, 其余步骤同交换态磷
有机磷	上步残渣转移到瓷坩锅中烘干, 550 °C 灼烧 2 h, 冷却后加入 30 mL 1 mol·L ⁻¹ HCl 振荡 16 h, 过滤上清液, 测定上清液中磷浓度

表2 生物炭吸附磷酸根的吸附动力拟合参数
Table 2 Fitting results of adsorption kinetics parameters for PO₄²⁻ adsorption on biochar

生物炭	准一级动力学方程			准二级动力学方程			Elovich 模型		
	$q_e/\text{mg}\cdot\text{g}^{-1}$	k_1/h^{-1}	R^2	$q_e/\text{mg}\cdot\text{g}^{-1}$	$k_2/\text{g}\cdot(\text{mg}\cdot\text{h})^{-1}$	R^2	a	b	R^2
Ca-BC	141.74	0.67	0.961	160.57	4.80×10^{-3}	0.934	238.09	0.03	0.843

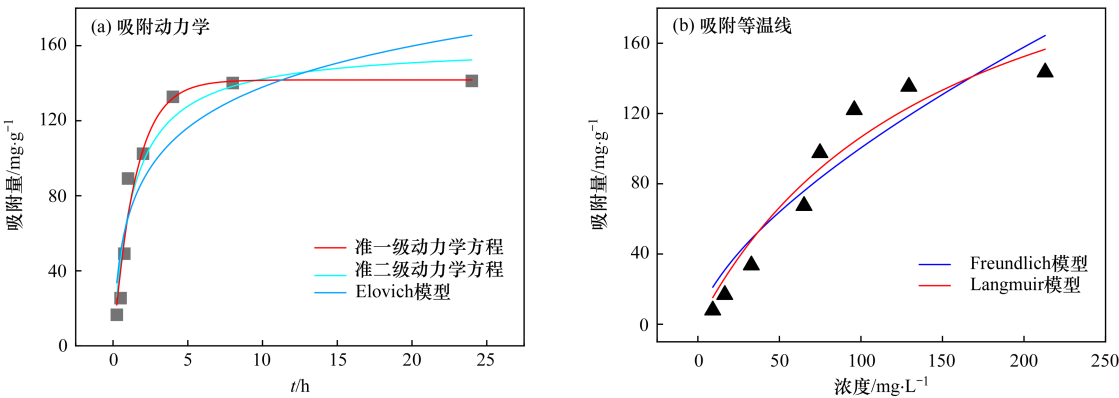


图2 Ca基改性生物炭吸附磷酸根的吸附动力学和吸附等温线拟合
Fig. 2 Adsorption kinetics and adsorption isotherm for PO_4^{2-} of Ca-based modified biochar

表3 生物炭吸附磷酸根的吸附等温线拟合参数

Table 3 Fitting results of adsorption isotherm parameters for PO_4^{2-} adsorption on biochar

生物炭	Langmuir 吸附模型			Freundlich 吸附模型		
	$q_{\text{max}}/\text{mg}\cdot\text{g}^{-1}$	$K_{\text{L}}/\text{L}\cdot\text{g}^{-1}$	R^2	$K_{\text{F}}/(\text{mg}\cdot\text{g}^{-1})\cdot(\text{mg}\cdot\text{L}^{-1})^{-1/n}$	n	R^2
Ca-BC	267.93	6.60×10^{-3}	0.940	4.99	1.54	0.894

散从而促进传质过程^[23,26]. 与已有研究对比,Ca-BC 吸附磷酸盐的容量好于其它元素改性的生物炭材料^[29,30].

2.2 改性生物炭对磷吸附效果的影响

选取白洋淀潜在淹没区的9个样点土壤样品进行Ca-BC对磷稳定性影响研究.S1~S9样品总碳、总

磷和总氮含量为451.74~1 779.27、1 633.25~4 317.01和1 633.25~4 317.01 $\text{mg}\cdot\text{kg}^{-1}$. 白洋淀土壤中总磷以Ca-P为主,形态所占比例均值为32.02%. 土壤中交换态磷含量占比5.60%~10.74%,该部分磷受环境变化影响易释放到水体,对白洋淀水质安全造成潜在风险^[31,32].

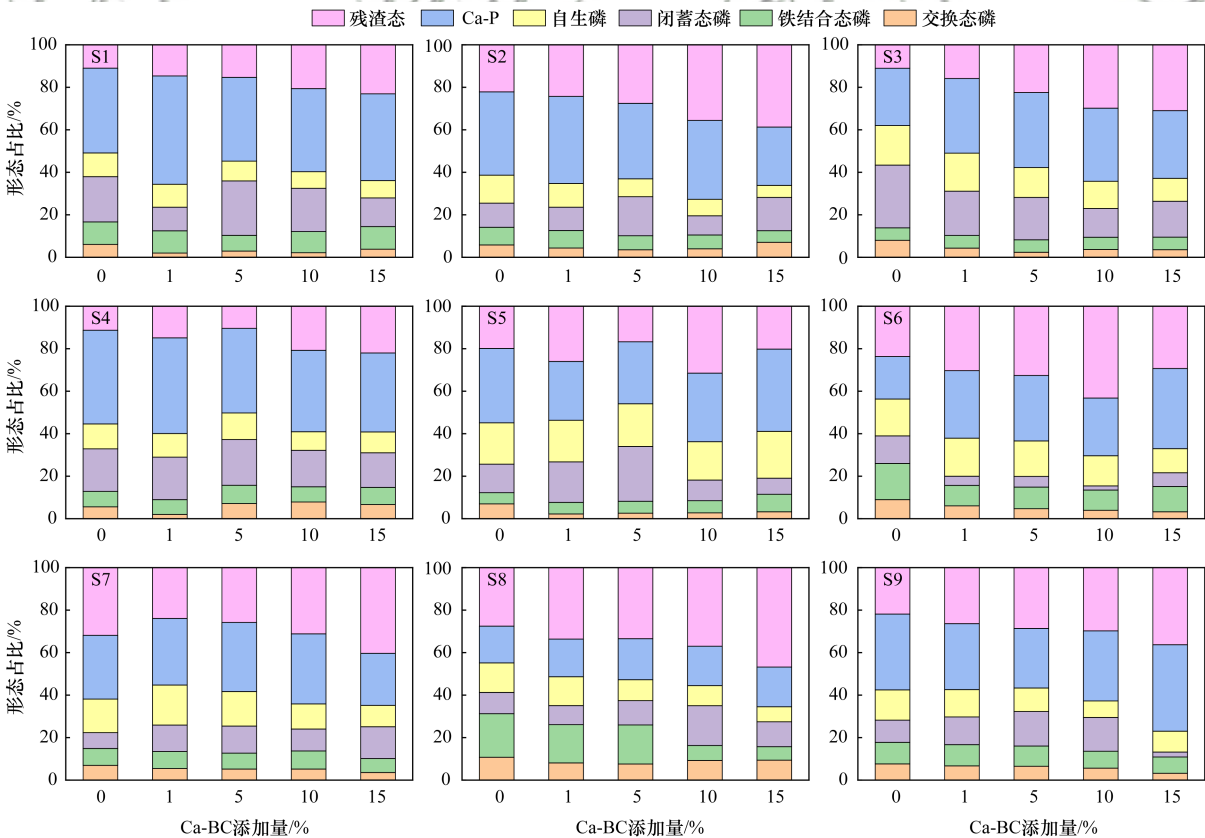


图3 不同Ca改性生物炭添加量(0~15%)对土壤磷含量的影响
Fig. 3 Effects of different content of Ca-based modified biochar additions (0-15%) on phosphorus fraction in soil

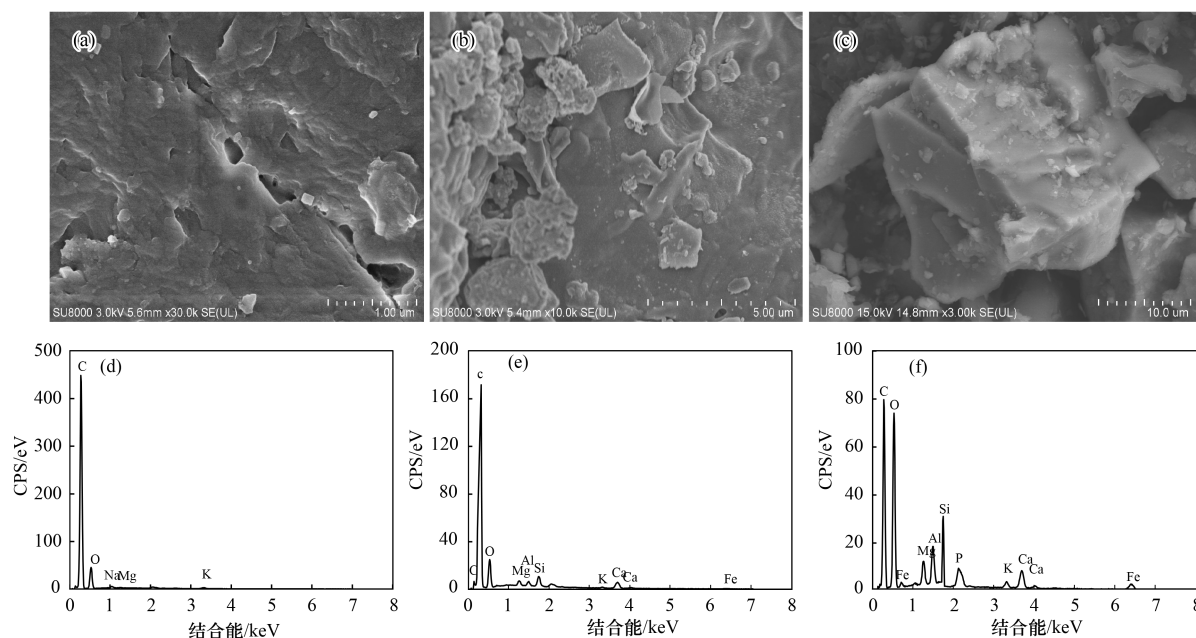
模拟培养实验添加1%~15%的Ca-BC后土壤中磷形态变化如图3所示. 当Ca-BC的添加量为1%时,土壤中较活跃性的交换态磷形态占比从空白组的7.42%下降至4.59%. 而Ca-BC的添加量为1%、5%、10%和15%时,稳定态磷(Ca-P和残渣态磷)占比由空白对照组的52.05%分别提升至57.95%、55.87%、63.59%和65.02%. 当Ca-BC的添加量为5%时,土壤的磷赋存形态由较活跃的交换态磷(占比从7.42%下降至4.73%)变为较稳定的残渣态磷(占比从20.03%提升至23.66%). 总的来看,添加1%的Ca-BC可有效降低交换态磷形态, Ca-P和残渣态磷构成的稳定态磷呈上升

趋势.

2.3 Ca基生物炭表征和吸附机制研究

2.3.1 SEM-EDS能谱分析

毛竹生物炭、Ca-BC的SEM-EDS的图谱如图4所示,生物炭主要由C、O、K和Na组成,改性后生物炭表面增加了Ca、Si和Fe等元素. 吸附磷酸盐后,由图4可见,EDS图谱中出现了较明显的P元素的峰,表明P被吸附在BC表面上. Ca-BC表面呈不规则颗粒状,生物炭表面凹凸不平,热解过程中CO₂的生成使生物炭内部有丰富的喉道和孔隙,这种特征有利于增加吸附位点;吸附后吸附剂表面出现大量絮状沉淀物,导致活性位点消失^[33-35].



(a)和(d)毛竹生物炭,(b)和(e) Ca基改性生物炭吸附前,(c)和(f)Ca基改性生物炭吸附磷酸盐后

图4 电子扫描电镜及能谱分析

Fig. 4 SEM and EDS spectral image analysis of the materials

2.3.2 XRD分析

从图5可以看出,Ca-BC加入前后XRD图谱特征峰出现明显变化. 改性后2 θ 共出现多个特征峰:在30°、40°和45°位点附近出现了CaO和CaCO₃强特征衍射峰;25°位点出现CaSO₄的微弱特征峰. 高温热解有利于形成更多的SiO₂和CaCO₃矿物灰分,灰分对生物炭固定重金属等污染物起到关键作用^[36]. 已有研究表明,生物炭对磷吸附主要通过表面的Al、Fe和Ca等与磷共沉淀作用^[37].

改性生物炭吸附磷酸盐后的XRD图谱(图5)表明,吸附磷后30°位点出现了较强的Ca₃(PO₄)₂吸收峰,40°~50°位点之间出现了较弱的羟基磷灰石(HAP)吸收峰,说明Ca-BC对磷酸根发生了明显的吸附作用,转化路径主要为CaO和PO₄³⁻结合后发生结

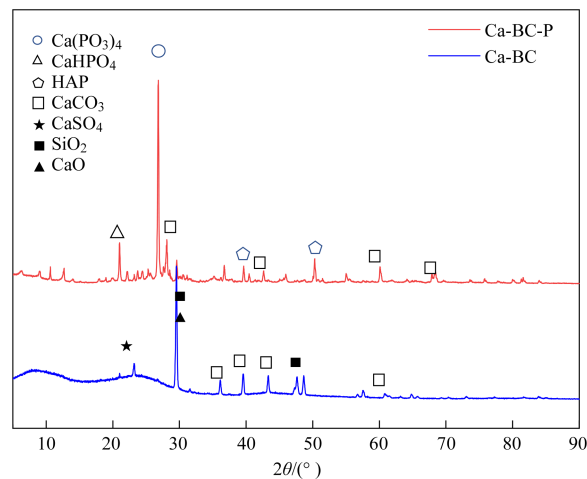
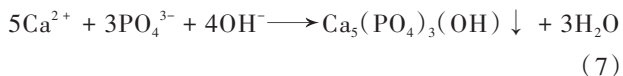
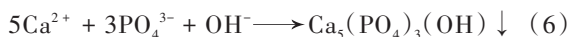


图5 生物炭吸附磷酸盐前后的XRD分析

Fig. 5 XRD analysis of pre-sorption Ca-based biochar and post-sorption for phosphate

晶反应,具体反应过程如式(6)和式(7),生成了稳定性高的HAP^[38,39].

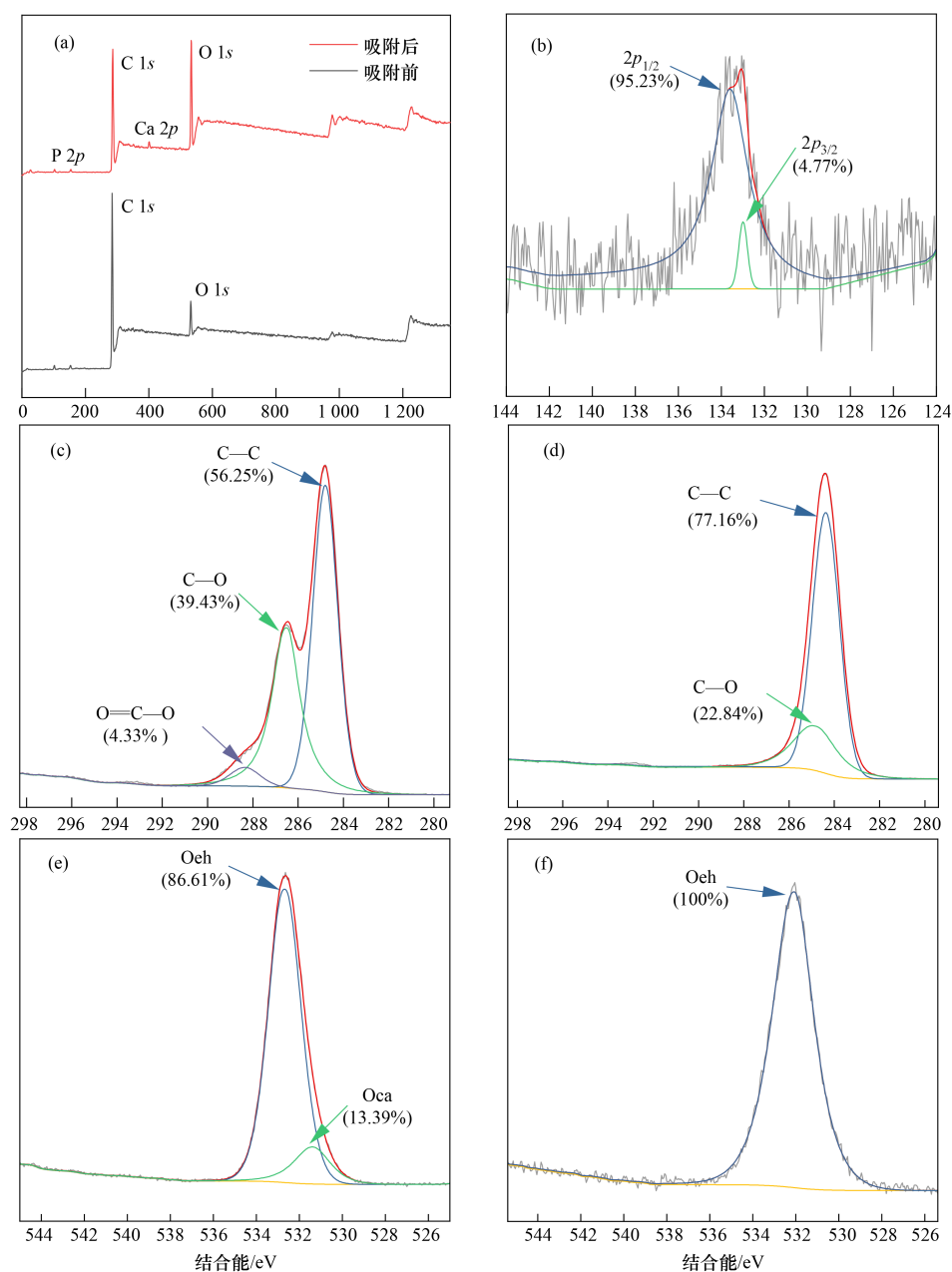


2.3.3 XPS分析

Ca-BC吸附磷酸盐前后进行XPS分析来探究官能团组成和变化,图6(a)是吸附前后的XPS全谱图,吸附磷后在134 eV出现P 2p峰,表明改性生物炭成功吸附磷酸盐.如图6(b)所示,高分辨率P 2p光谱可以区分峰为两个位于133.8 eV和132.8 eV重叠峰,分别归因于磷酸根的P 2p_{1/2}和P 2p_{3/2}. XPS光谱结果表

明Ca-BC和磷酸盐(例如H₂PO₄⁻和HPO₄²⁻ PO₄³⁻)形成较强的O—P键,其是通过配体交换或单配位和双配位的表面络合物形成^[40,41].

如图6(c)所示,C 1s谱图显示吸附前可以分为3个峰,结合能为284.4、286.1和288.0 eV,这些峰分别来自Ca-BC表面的C—C、C—O和O=C—O等官能团.当生物炭吸附磷酸盐后,光谱显示O=C—O峰消失,而C—O不仅转向较低的值(285.7 eV),而且积分面积比略有下降(39.43%~22.84%).O 1s图谱也表明生物炭吸附后官能团O=C—O积分面积从13.29%下降至检出限以下[图6(b)和6(f)].综合O 1s和C 1s谱图分析,羧基



(a)生物炭吸附磷酸盐前后全谱图;(b)生物炭吸附磷酸盐后P谱图;(c)和(d)分别为生物炭和吸附磷酸盐后的O1s图;(e)和(f)生物炭吸附前、吸附后的C1s图;Oeh(醚或羟基)和Oca(羧酸、酸酐或内酯)

图6 生物炭吸附磷酸盐前后的XPS光谱特征

Fig. 6 XPS characterization of Ca-based modified biochar before and after phosphate adsorption

表面官能团内层表面络合过程在吸附磷酸根的过程中起关键作用^[41]。

2.3.4 生物炭对磷稳定性机制分析

Ca 改性能有效提高生物炭对磷的吸附容量, 改变生物炭表面的离子存在形态, 为磷酸盐吸附提供更多的吸附位点, 从而提高对磷酸盐的吸附能力。图 7 为磷酸盐在 Ca-BC 上主要的吸附稳定机制。首先, 生物炭去除磷的过程主要是由于磷酸盐离子和钙掺杂生物炭之间涉及共享电子的化学键合或化学吸附^[42,43]。Ca-BC 中有大量 CaO、CaCO₃ 和 CaSO₄ 等, 钙盐和磷结合形成稳定的 Ca₃(PO₄)₂、CaHPO₄ 和羟基磷灰石 [Ca₅(PO₄)₃(OH)], 反应过程优先生成磷酸二钙、磷酸三钙和磷酸八钙等前体物后转化为 HAP, 导致 Ca-BC 表面钙磷沉淀, 从水体中取出溶解

性磷酸盐。根据生物炭吸附磷前后的 XRD 和 SEM 分析(图 4 和图 5), Ca-BC 表面的 Ca、Fe 和 Mg 等离子及其水和化合物等与水体中的磷形成难溶性化合物, 从而增加了水体和沉积物中的磷向稳态转化^[44~46]。其次, 已有类似研究表明, Mg/Al 改性水稻生物炭的质子化表面羟基基团通过形成 O—P 键, 在内球表面通过络合作用固定磷酸盐^[41], XPS 分析结果(图 6)证明了 Ca-BC 与磷反应后的 O—P 键的形成。改性生物炭表面的 Ca²⁺ 和 Mg²⁺ 以配位键的形式和磷酸根形成杂环结构, 螯合效应的稳定性较络合作用更强, 促进土壤中较活跃的磷酸盐向稳态转化^[47]。Ca-BC 表面的 CaOH⁺ 能和含磷的阴离子 (H₂PO₄⁻、HPO₄²⁻ 和 PO₄³⁻) 产生静电吸附作用使得磷酸盐稳定化^[23]。

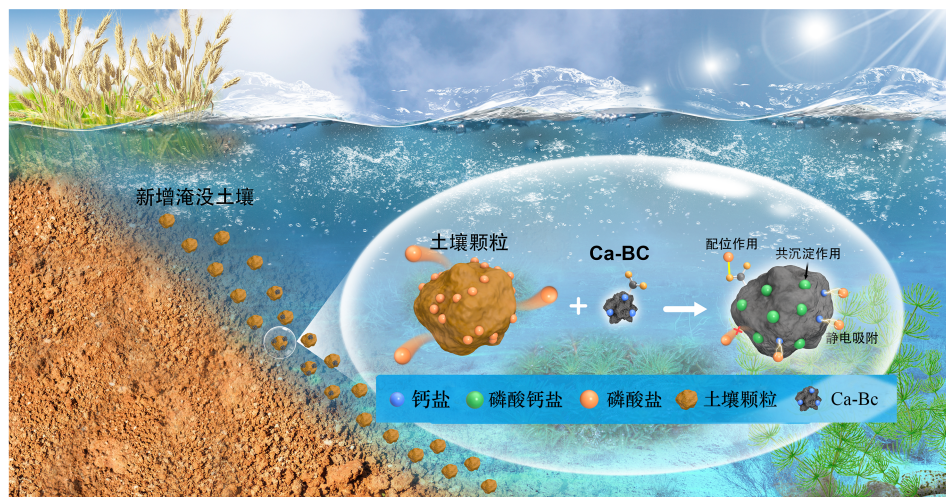


图 7 Ca 改性生物炭对新淹没土壤中磷组分的稳定机制

Fig. 7 Stability mechanism of Ca-based modified biochar to phosphorus fraction in new submerged area

3 结论

(1) 本研究采用共热解方法制备 Ca 改性生物炭作为土壤磷稳定剂, Ca-BC 对磷吸附过程符合一级动力学模型和 Langmuir 模型, 该吸附过程主要是以单层吸附为主, 依靠化学键作用。改性生物炭 Ca-BC 具有用于控制新增淹没区土壤磷释放污染的潜力。

(2) Ca-BC 在生物炭表面形成 CaO、CaCO₃ 和 CaSO₄ 等物质, 磷的稳定化主要通过 Ca-P 共沉淀、配位作用和静电吸附等作用, 有助于提升生物炭对土壤磷形态的稳定性, 当 Ca-BC 添加量达到 1% 时, 交换态磷逐渐向残渣态磷和 Ca-P 形态转变, 降低了土壤磷的释放风险。

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