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三种黏土矿物对蚕豆生长和重金属含量的影响

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摘要:以云南会泽铅锌矿周边污染农田土壤为供试土壤,施加沸石、钠基膨润土、硅藻土3种黏土矿物,开展室内种植蚕豆的盆栽试验,研究黏土矿物对蚕豆光合生理、生物量、矿质营养、重金属含量和累积量的影响。结果表明:3种黏土矿物显著增强蚕豆叶片的光合作用,增加植株的生物量,其中钠基膨润土处理的增幅最大,为21.7%。黏土矿物降低土壤速效氮、磷、钾的含量,降幅为12%~48%,改变蚕豆植株氮、磷、钾的含量,其中,硅藻土显著增加蚕豆植株磷、钾和根系氮的含量,增幅为23%~83%,钠基膨润土降低蚕豆地上部氮、磷、钾的含量。3种黏土矿物均显著降低土壤有效态铅和铜的含量,降幅为14%~28%,减少蚕豆植株的锌含量、根系铅和铜的含量;沸石还显著降低土壤有效态镉、蚕豆植株镉和地上部铅的含量。相关分析发现,土壤有效态镉与蚕豆地上部镉、有效态铜与根系铜、有效态锌与植株锌的含量呈极显著或显著正相关。研究表明黏土矿物能降低污染土壤重金属的生物有效性,减少蚕豆植株的重金属含量,改善光合作用和提高生物量。

关键词:黏土矿物;蚕豆;光合生理;矿质营养;重金属污染

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Effects of three clay minerals on the growth and heavy metal content in *Vicia faba*

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Abstract: Polluted soils from farmland around a lead-zinc mine in Huize County, Yunnan Province, were sampled and used in the present pot experiment. Three clay minerals (zeolite, sodium bentonite, and diatomite) were added to the polluted soils, which were used to grow *Vicia faba* in a greenhouse. The effects of these clay minerals on the photosynthesis, biomass, mineral nutrition, and content and accumulation of heavy metals in *Vicia faba* were investigated. The results showed the following: Photosynthesis in the leaves was enhanced significantly and biomass of *Vicia faba* increased with the three treatments; the biomass increased by 21.7% for the sodium bentonite addition. The available nitrogen (N), phosphorus (P), and potassium (K) content in the soils were reduced by 12%~48% with the clay minerals treatments. The N, P, and K content in the roots of the *Vicia faba* increased by 23%~83% with the addition of diatomite, but decreased in the shoots of the plants with the addition of sodium bentonite. The content of available lead (Pb) and copper (Cu) in the soils decreased significantly with the addition of the three clay minerals. The zinc (Zn) content in the plants and the Pb and Cu content in the roots decreased. In addition, the content of available cadmium (Cd) in the soils and in the plants, and the Pb content in the shoots of the *Vicia faba*, fell significantly with the addition of zeolite. Significant positive correlations were observed between the content of available Cd in soils and Cd content in shoots; the content of available Cu in soil and Cu content in roots; and the content of available Zn in soil and Zn content in the plants. The results indicate that clay minerals could decrease the bioavailability of heavy metals in polluted soils, reduce the heavy metal content in plants, and improve the photosynthesis and biomass of *Vicia faba*.

Keywords: clay minerals; *Vicia faba*; photosynthesis; mineral nutrition; heavy metal pollution

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近年来,由于金属矿的开采和冶炼导致矿区周边的农田土壤重金属污染严重^[1],据统计,我国农田土壤受重金属污染面积高达 $2.0\times10^7\text{ hm}^2$,占总耕地面积的 $1/5$ ^[2]。土壤中重金属不仅对土壤结构产生负面影响,导致土壤肥力下降,而且以有效态形式被作物吸收富集在体内,降低农作物的产量和品质^[3],因此对重金属污染土壤修复技术的研究已经引起了国内外的广泛关注,对重金属污染土壤进行修复,减少作物对重金属的吸收,已成为我国一项十分紧迫的任务^[4],而原位钝化修复技术^[5]是目前应用比较广泛的重金属污染土壤修复方法之一。

原位钝化修复是向污染土壤中施加活性钝化修复材料,如沸石、钠基膨润土、硅藻土等黏土矿物是常用的土壤重金属钝化剂^[6]。沸石^[7]比表面积大,吸附性能好,表面可以形成水合氧化物覆盖层出现游离负离子,通过络合作用吸附重金属离子,降低重金属有效性,提高其稳定性。钠基膨润土具有良好的离子交换性和吸附性,对重金属离子具有很好的吸附去除作用^[8-9]。硅藻土^[10]是一种多孔性硅质岩黏土矿物,比表面积大、吸附能力强,致使其对重金属的吸附能力强。以上3种钝化剂与重金属之间可以通过溶解沉淀,离子交换吸附,氧化还原和有机络合等一系列物理化学反应过程^[11],改变重金属在土壤中的存在形态,降低重金属在土壤中的生物有效性和迁移性,减少作物对重金属的吸收,减缓重金属对作物生长的毒害作用^[12]。黏土矿物资源易得、价廉,利用黏土矿物复治理重金属污染土壤修是一条值得推广的有效途径^[13]。

云南省会泽县位于云南省东部,是我国铅锌的重要产地之一^[14]。会泽铅锌矿是我国铅锌矿的典型代表,矿产工业大量生产与冶炼对矿区及周边农田土壤造成不同程度的重金属污染^[15]。农田土壤与人类生产生活息息相关,具有不可替代的作用,如何有效快速地修复重金属污染农田土壤,增加农作物的产量,改善农作物品质,是一项重要任务^[16]。以往学者大多偏于研究黏土矿物对单一金属元素的影响,对多种金属元素共同影响的研究较少,但自然界中土壤不只受一种重金属污染,对受多种重金属污染的土壤进行修复治理应该得到全世界的广泛关注。本文选用会泽铅锌矿区周围田地土,研究黏土矿物对蚕豆生长、矿质营养和积累重金属(镉、铅、铜、锌)的影响。为农产品增产增收、改善品质和多种重金属污染土壤的钝化修复及修复机理提供参考。

1 材料与方法

1.1 供试材料

供试蚕豆(*Vicia faba L.*)为云豆147,所选种子大小一致且籽粒饱满。

供试土壤为山原红壤,采集自云南省曲靖市会泽铅锌矿区重金属污染农田,土壤pH为5.74,有机质含量为 $28.12\text{ g}\cdot\text{kg}^{-1}$,镉、铅、铜、锌全量分别为4.51、268.89、85.81、301.75 $\text{ mg}\cdot\text{kg}^{-1}$,碱解氮、速效磷和速效钾含量分别为 $35.04\text{ mg}\cdot\text{kg}^{-1}$ 、 $19.72\text{ mg}\cdot\text{kg}^{-1}$ 和 $125.07\text{ mg}\cdot\text{kg}^{-1}$ 。

供试黏土矿物,钠基膨润土pH为9.2,孔隙度为92%;硅藻土pH为7.1,孔隙度为91%;沸石pH为5.8,孔隙度为92%。

1.2 试验处理

将所选种子放入1%次氯酸钠(NaClO)溶液中并在超声波清洗机中处理1 min后取出,用无菌蒸馏水冲洗种子表面上残留的NaClO溶液,冲洗干净后,放入75%的乙醇溶液中并在超声波清洗机中处理3 min,然后用无菌蒸馏水漂洗至无色,放入垫有浸湿滤纸已灭菌的培养皿中,在25℃温度下恒温培养3 d,待种子萌发长成幼苗时,挑选无污染且生长一致的幼苗备用。供试土壤采回后,经自然风干,剔除杂物,捣碎研磨后过1 mm尼龙筛混匀保存,待用。

于2016年10月9日在云南农业大学实验大棚内开始试验,试验设4个处理(对照、钠基膨润土、硅藻土、沸石),每个处理4个平行,共16份盆栽,每盆添加原土3 kg。除对照外,另外3组处理在原土基础上分别加入5%的钠基膨润土、硅藻土和沸石混匀待播种。每盆播种蚕豆苗7株,实验过程中不施用化肥和农药,采用自然光照,期间根据盆栽土壤水分状况浇灌去离子水,保持土壤湿润,培育60 d后采样。

将蚕豆整株取出,抖去根部附着比较疏松的土壤,采集与根系紧密结合的根际土壤(厚度约为1 mm),自然风干捣碎研磨后装袋备用。将蚕豆植株分为地上部茎叶和地下部根系,用蒸馏水漂洗干净,晾干,于105℃杀青30 min,再经75℃烘干72 h至恒质量,碾磨粉碎备用^[15]。

1.3 测定方法

用直尺测量株高,地上部和地下部干重用电子秤称量。采用分光光度法测定叶绿素,英国PP-System公司CIRAS-1型全自动便携式光合测定系统测定^[17]光合作用参数。

分别采用碱解扩散比色法、 $0.5\text{ mol}\cdot\text{L}^{-1}$ NaHCO₃

浸提-钼锑抗比色法、 $1\text{ mol}\cdot\text{L}^{-1}\text{NH}_4\text{OAc}$ 浸提-火焰光度法测定土壤碱解氮、速效磷、速效钾的含量^[18]。

$\text{H}_2\text{SO}_4-\text{H}_2\text{O}_2$ 消煮,比色法测定植株全氮、全磷、全钾。 $\text{HNO}_3-\text{HClO}_4$ 消煮,原子吸收分光光度法测定植物镉、铅、铜、锌,称取备用的植物放入消解管中,加入10 mL浓硝酸和4 mL高氯酸,消解,用原子吸收分光光度计测定吸光值。 $0.1\text{ mol}\cdot\text{L}^{-1}\text{HCl}$ 浸提,原子分光光度法测定土壤有效态镉、铅、铜、锌,称取10.0 g备用根际土,加入50.0 mL $0.1\text{ mol}\cdot\text{L}^{-1}\text{HCl}$,振荡,过滤,用原子吸收分光光度计测定滤液吸光值^[19]。

1.4 统计分析

实验数据运用Microsoft Excel 2013进行处理,计算平均值和标准差,用IBM SPSS Statistics V 21.0数据处理软件进行统计分析,用Duncan(D)法检验各处理平均值在0.05水平的差异性,用OriginPro 9.0进行绘图。

2 结果与分析

2.1 3种黏土矿物对蚕豆植株光合生理和生长的影响

钠基膨润土显著增加蚕豆叶片叶绿素a、叶绿素b和类胡萝卜素含量,分别增加20%、21.7%和20%;硅藻土显著增加蚕豆叶片叶绿素b含量,增加13%,沸石增加蚕豆叶片叶绿素b和类胡萝卜素含量,分别增加17%和13.5%(图1)。可见,3种黏土矿物不同程度地增加蚕豆叶片光合色素的含量。

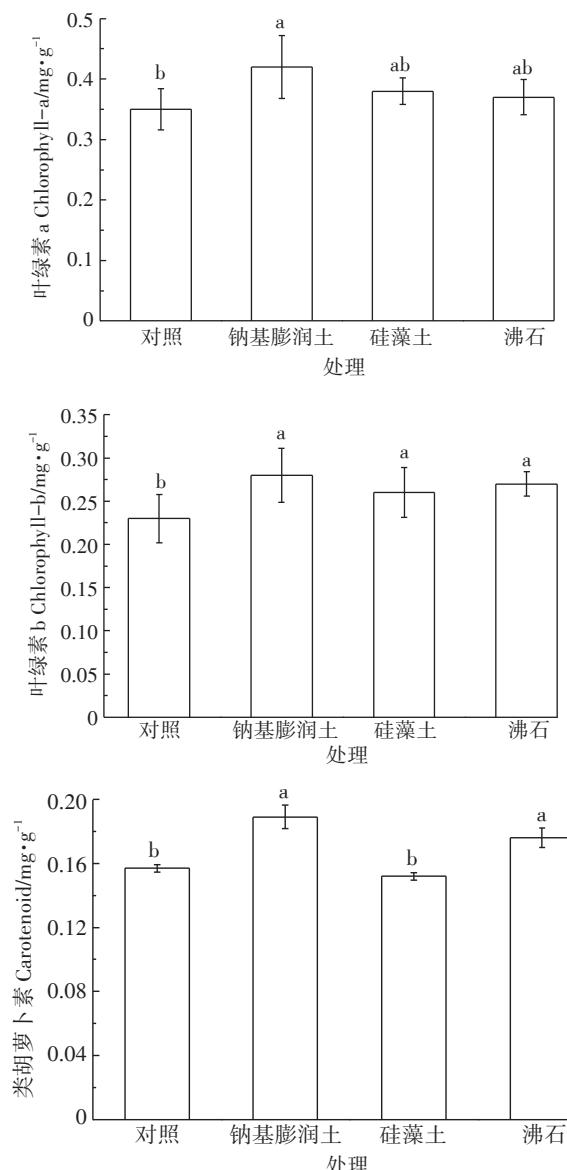
钠基膨润土和沸石显著增加蚕豆胞间 CO_2 浓度,分别增加18.2%和17.4%;3种黏土矿物都能显著增加蚕豆蒸腾速率、气孔导度、光合速率,增幅分别为22.4%~58.2%、27.3%~54.5%、28.6%~41.8%(图2)。可见重金属胁迫下,施加黏土矿物不同程度地增加蚕豆光合作用速率。

3种黏土矿物显著增加蚕豆的株高,增幅为122%~162%,以及显著增加蚕豆地上部和地下部的生物量,增幅分别为15%~60%和11%~39%(图3)。可知,施加黏土矿物显著增加蚕豆株高和生物量。

2.2 3种黏土矿物对土壤-蚕豆体系养分含量的影响

钠基膨润土、硅藻土、沸石显著降低土壤碱解氮含量,分别降低45.2%、25.8%、12.5%。硅藻土显著降低土壤速效磷含量,降低48%。钠基膨润土和硅藻土显著降低土壤速效钾含量,降幅分别为25%和12%(图4)。可知,黏土矿物降低土壤速效养分的含量,但影响效应存在差异。

硅藻土显著增加蚕豆全磷、全钾以及地下部全氮



不同小写字母表示处理间差异显著($P<0.05$)。下同
The different lowercase letters indicate significant differences among treatments ($P<0.05$). The same below

图1 不同黏土矿物对蚕豆叶片叶绿素、类胡萝卜素含量的影响

Figure 1 Effects of different clay minerals on chlorophyll and carotenoid content of *Vicia faba* leaves

含量,增幅高达83%,沸石显著增加蚕豆地下部全磷含量,增加23%,但钠基膨润土显著降低蚕豆地上部全氮、全磷、全钾含量(图5)。由此可知,施加黏土矿物能不同程度地改变蚕豆对养分的吸收。

2.3 3种黏土矿物对土壤pH值和重金属有效态含量的影响

钠基膨润土显著升高土壤pH值,升高22%,硅藻土和沸石对土壤酸碱性没有显著性影响(图6)。

钠基膨润土和沸石显著减少土壤有效态镉的含

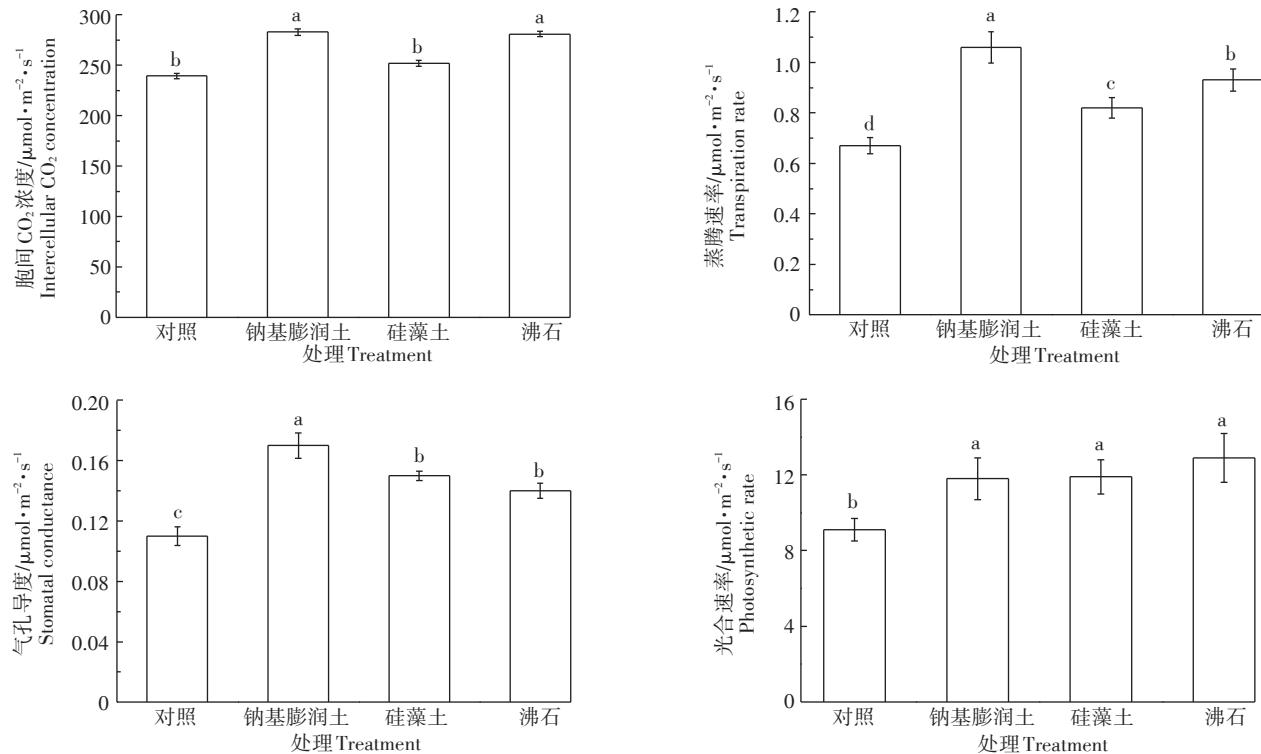


图2 不同黏土矿物对蚕豆光合指标的影响

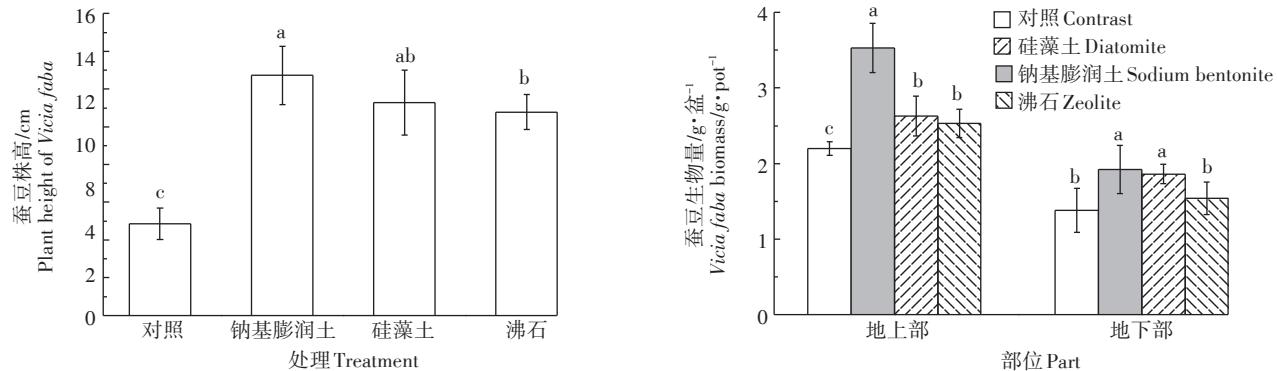
Figure 2 Effects of different clay minerals on the photosynthetic indicators of *Vicia faba*

图3 不同黏土矿物对蚕豆株高和生物量的影响

Figure 3 Effects of different clay minerals on plant height and biomass of *Vicia faba*

量,分别减少20%和12%;钠基膨润土、硅藻土和沸石显著降低土壤有效态铅和有效态铜含量,降幅分别为18%~28%和14%~23%,但3种黏土矿物对土壤有效态锌没有显著影响(图7)。可知,黏土矿物对重金属具有选择抑制性。

2.4 黏土矿物对蚕豆植株重金属含量和累积量的影响

钠基膨润土、硅藻土和沸石3种黏土矿物均显著降低蚕豆植株的锌含量,以及显著降低蚕豆地下部的铅和铜含量,降幅以沸石处理较大。此外,钠基膨润土和沸石处理显著降低蚕豆地上部的镉含量,硅藻土

和沸石显著降低蚕豆地上部的铅含量和地下部的镉含量(图8)。可见,施加黏土矿物能不同程度地降低蚕豆植株中镉、铅、铜、锌的含量。

钠基膨润土和沸石显著降低蚕豆地上部镉累积量,降幅为34%~50%,且显著降低蚕豆植株铅累积量,分别降低25%和30%。3种黏土矿物都能显著降低地下部铜累积量,降幅为10%~15%,也能显著降低蚕豆植株锌累积量,地上部和地下部降幅分别为10%~15%和10%~18%(图9)。可知施加黏土矿物不同程度地降低蚕豆对镉、铅、铜、锌的累积,其中沸石

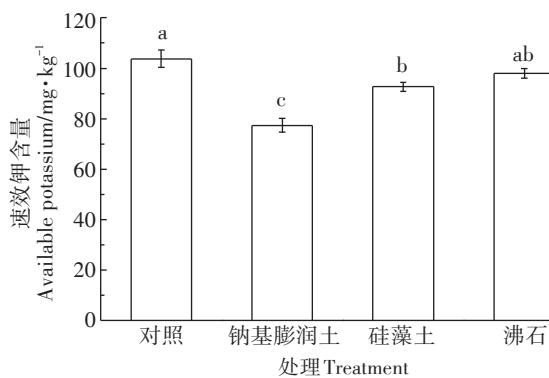
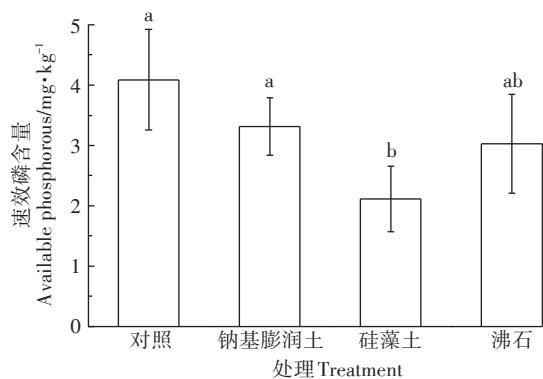
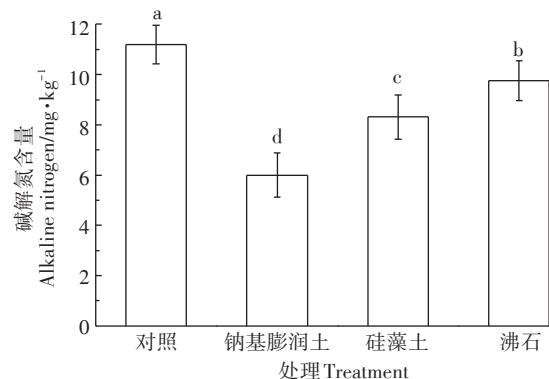


图4 不同黏土矿物对土壤速效养分含量的影响

Figure 4 Effects of different clay minerals on soil available nutrient content

的效应最大,其次是钠基膨润土。

2.5 相关分析

相关分析表明,土壤有效态镉含量与蚕豆地上部镉含量($r=0.646, P<0.01$)、有效态铜含量与蚕豆地下部铜含量($r=0.652, P<0.01$)呈极显著正相关,有效态锌含量与蚕豆地上部锌含量($r=0.614, P<0.05$)、地下部锌含量($r=0.608, P<0.05$)均呈显著正相关。

3 讨论

3.1 重金属污染胁迫下黏土矿物对植物生长的影响

叶绿素和类胡萝卜素是作物进行光合作用的重

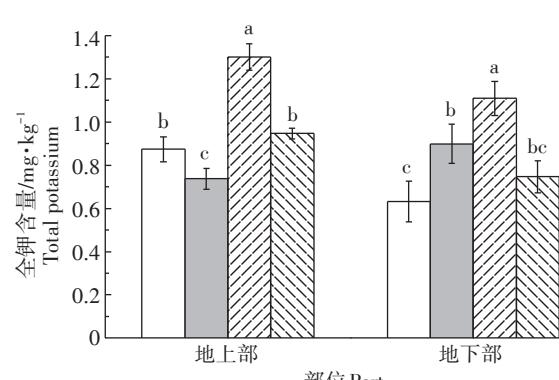
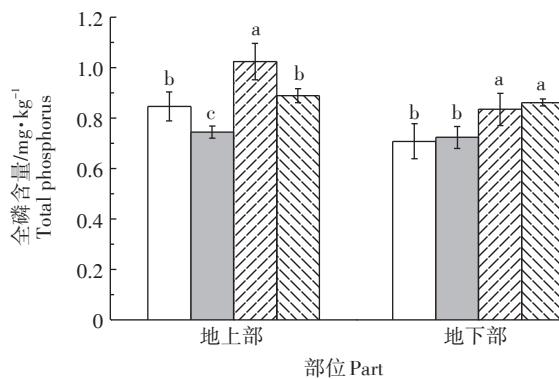
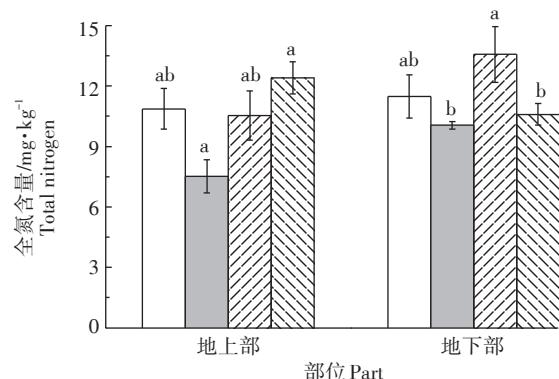


图5 不同黏土矿物对蚕豆植株养分含量的影响

Figure 5 Effects of different clay minerals on nutrient content of *Vicia faba* plants

要色素因子,光合作用是作物生长发育的基础^[20],胞间CO₂浓度、蒸腾速率和气孔导度是影响净光合速率的重要因素,在光合作用过程中需要它们的协同作用,才能使作物的光合作用顺利进行^[21-22]。本次实验研究结果得出,重金属胁迫下施用黏土矿物(钠基膨润土、硅藻土、沸石)显著增加蚕豆叶绿素和类胡萝卜素含量,提高胞间CO₂浓度、蒸腾速率、气孔导度和光合速率。因为黏土矿物通过矿物表面的吸附、离子交换固定重金属,降低重金属向作物体内的迁移,减少

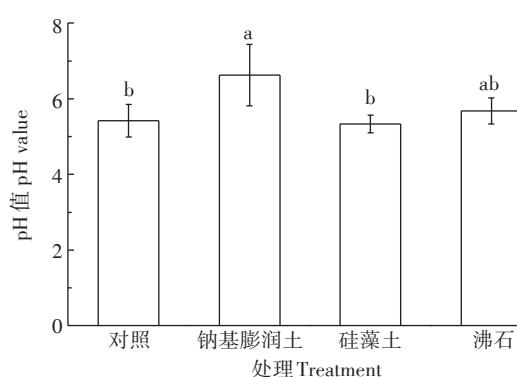


图6 不同黏土矿物对土壤pH值的影响

Figure 6 Effects of different clay minerals on soil pH value

作物体内重金属的含量,减弱叶绿体基质的毒害,增加作物的光合作用^[23]。研究表明在重金属的胁迫下,严重伤害叶片中的叶绿体和线粒体,而叶绿体和线粒体是植物光合作用和呼吸作用的重要场所^[24],叶绿体基质受到破坏会抑制作物叶片中叶绿素和类胡萝卜素的合成,导致作物光合速率降低^[25],施用钝化剂(黏土矿物)会降低这种毒害作用,促进作物的光合作用。作物光合作用增加,产生大量能量提供给根系,用于对土壤中养分(氮、磷、钾)的吸收,土壤中养分的含量

减少,提高作物养分(氮、磷、钾)累积量,促进作物的生物量和产量^[26]。对一些作物的研究发现:硅藻土可促进雀稗对氮磷钾的吸收,沸石和膨润土可提高玉米和小白菜植株中氮磷钾的含量^[27-29]。土壤中施加膨润土对油菜生长影响的研究表明,施加膨润土显著提高油菜的叶绿素含量和生物量^[30],与本实验得出的重金属胁迫下,施加黏土矿物蚕豆养分(全氮、全磷、全钾)累积量增加,提高蚕豆的生物量和产量的结果相一致。

3.2 重金属污染胁迫下黏土矿物对土壤-作物体系重金属迁移的影响

重金属在土壤中以不同化学形态存在^[31],如:有效态(水溶态、交换态),缓溶态(Fe/Mn氧化物结合态、有机结合态)和无效态(残渣态),仅金属有效态能被植物吸收并累积在体内。如何降低土壤重金属的生物有效性是重金属污染土壤修复需要解决的根本问题。本实验分析得出,在重金属污染胁迫下施用黏土矿物(钠基膨润土、硅藻土、沸石)对土壤中的重金属(镉、铅、铜)有显著钝化作用,但对锌钝化效果不显著。钠基膨润土、沸石和硅藻土主要成分中富含大量的不稳定活性基团,通过离子交换吸附-配合-共沉淀作用,促使土壤中的重金属由交换态向残渣态转

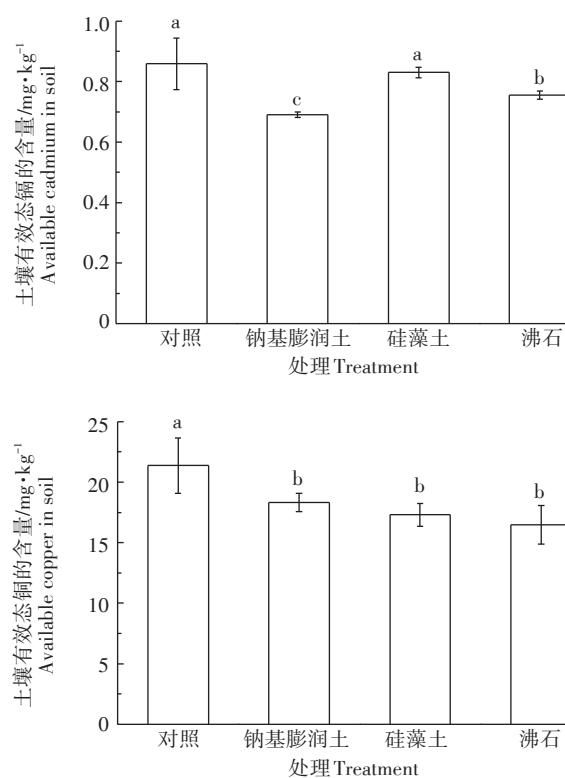
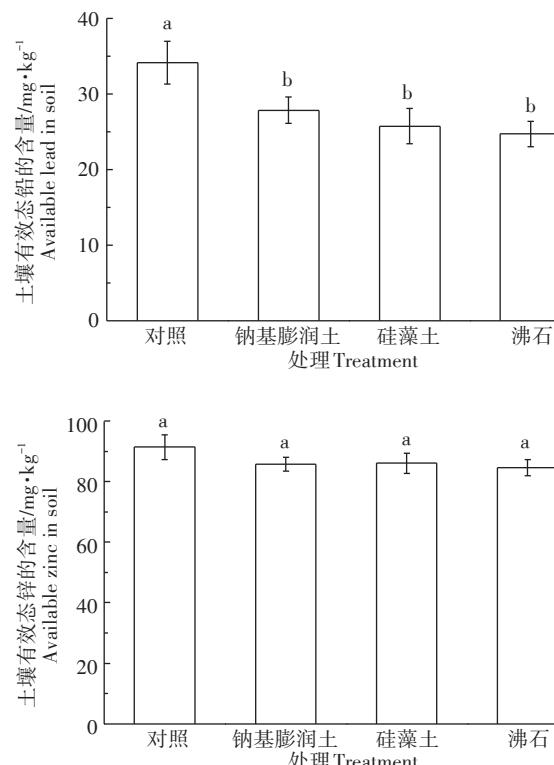


图7 不同黏土矿物对土壤重金属有效态含量的影响

Figure 7 Effects of different clay minerals on soil heavy metals content



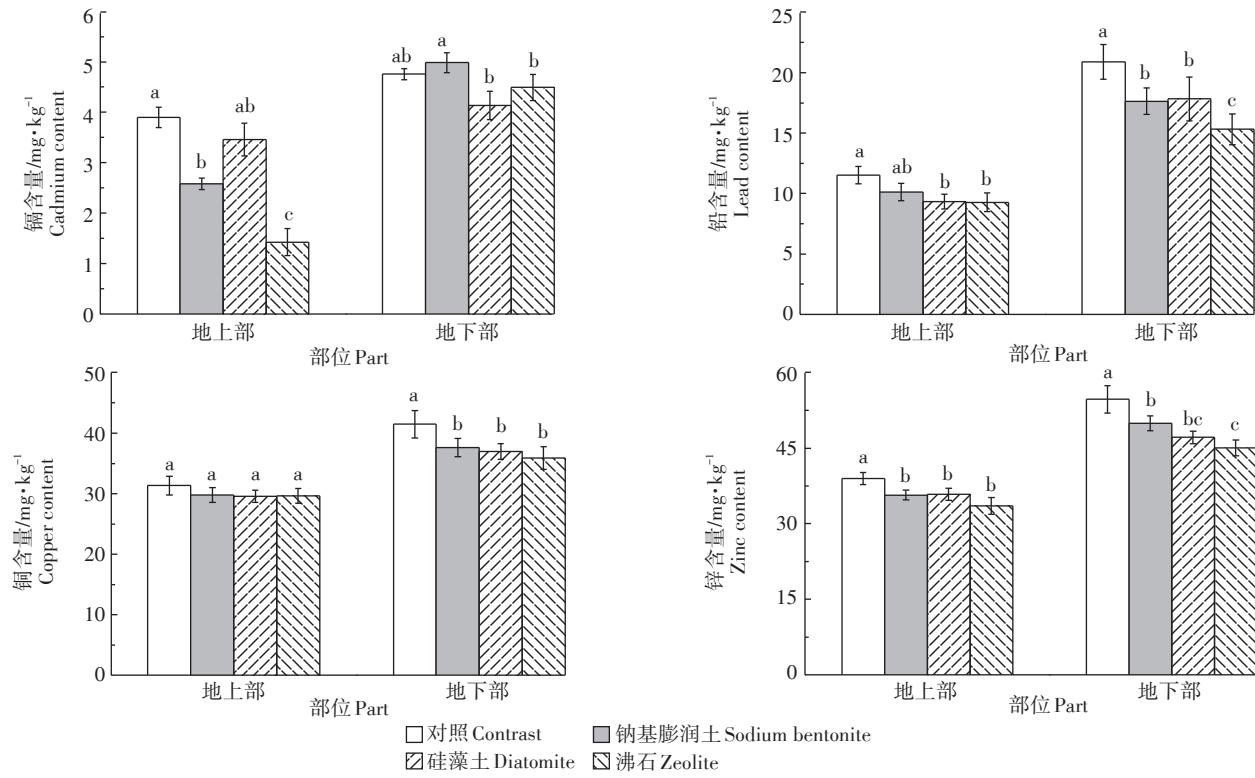


图8 不同黏土矿物对蚕豆植株重金属含量的影响

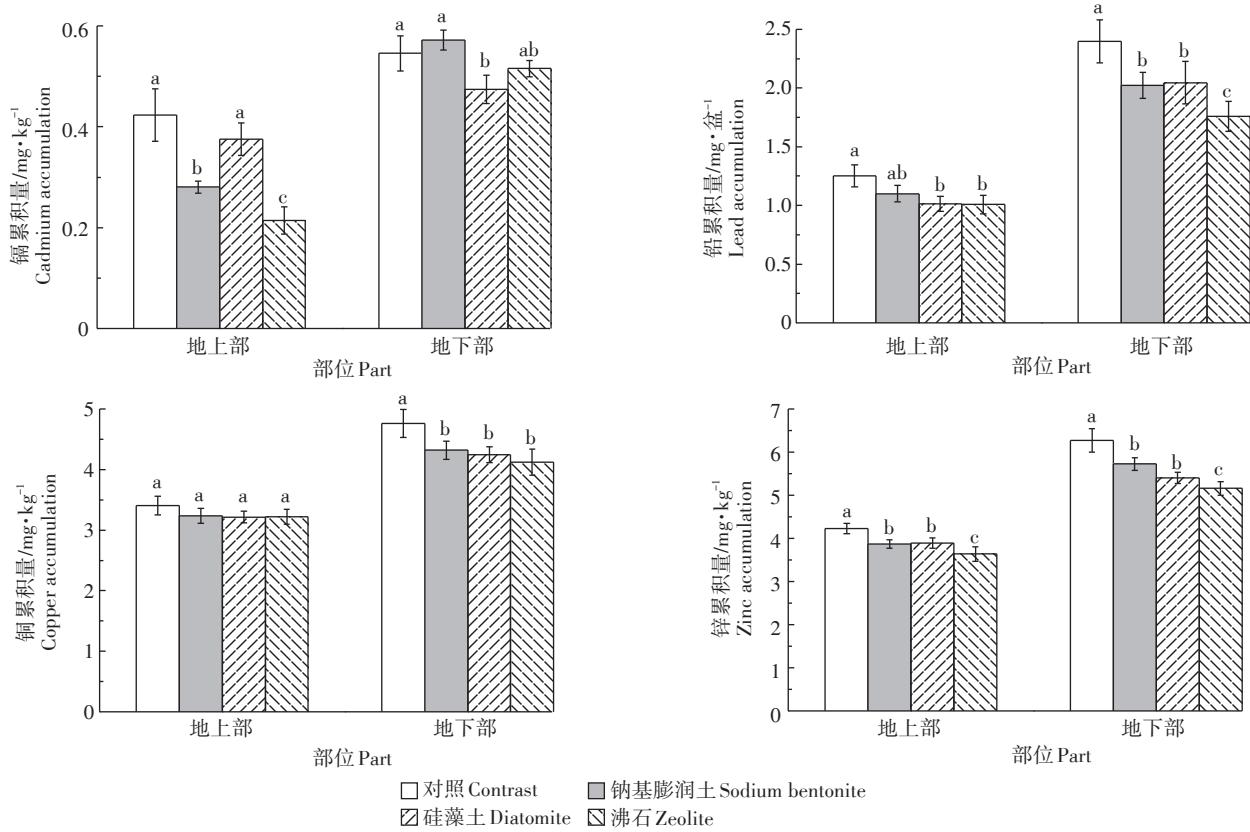
Figure 8 Effects of different clay minerals on heavy metal content in *Vicia faba* plants

图9 不同黏土矿物对蚕豆植株重金属累积量的影响

Figure 9 Effects of different clay minerals on heavy metal accumulation in *Vicia faba* plants

变,从而降低重金属(镉、铅、铜)的生物有效性与迁移性。有学者研究表明^[32]施加海泡石、磷酸盐可显著增加水稻生物量,降低镉、铅有效态含量。Usman等^[33]在重金属污染土壤(锌、镉、铜、镍)中施加黏土矿物(钠基膨润土、钙基膨润土和沸石),得出施加黏土矿物可显著降低土壤有效态锌、镉、铜、镍的含量。

不同黏土矿物对不同重金属的吸附能力有差异,由于黏土矿物之间存在理化性质的差异^[34],钠基膨润土^[8]结构中存在不稳定的Na⁺,易与其他阳离子发生离子交换;硅藻土^[10]自身带负电荷且表面有大量不同种类的硅羟基光能团;沸石^[7]主要成分是四面体网状结构铝硅酸盐,多孔性具有极强的离子交换能力。本试验得出,对土壤中铅、铜的吸附效果为,沸石>硅藻土>膨润土;钠基膨润土对镉的吸附作用最显著。有学者研究膨润土与硅藻土对重金属污染底泥的稳定性发现,高浓度污染胁迫下硅藻土比膨润土对铜抑制效果更显著^[35]。康宏宇等研究黏土矿物对重金属钝化作用中发现,硅藻土对土壤中铜、铅钝化效果仅次于沸石^[36]。因此针对不同重金属污染土壤可选用不同黏土矿物进行原位钝化修复,但黏土矿物长期存留在土壤中对土壤有何影响或者发生何种变化还有待深入研究。

3.3 重金属污染胁迫下黏土矿物对作物重金属吸收的影响

土壤中重金属随着作物根系对养分的吸收迁移到体内,对作物的新陈代谢、生长发育产生影响。降低重金属的生物有效性是控制作物对重金属吸收的关键性因素^[37]。有学者研究表明施用海泡石显著降低菠菜地上部、地下部镉含量;蛭石显著降低莴苣、菠菜体内重金属含量^[38-41]。硅藻土、沸石等处理显著降低玉米籽粒对镉、铅的吸收量和累积量,镉含量降低高达89%、铅含量降低46%^[42]。本试验得出,重金属胁迫下,施加黏土矿物不同程度降低蚕豆中镉、铅、铜和锌的含量,其中钠基膨润土和沸石显著降低蚕豆地上部有效态镉含量,分别降低33.8%和63.4%。黏土矿物具有大量的活性官能团,与活性低的重金属能发生离子交换,将重金属固定在土壤中,降低重金属的生物有效性^[43]。

4 结论

重金属污染胁迫下施加黏土矿物能促进蚕豆叶片光合作用,改变蚕豆对土壤养分(氮、磷、钾)的吸收,提高生物量;降低重金属在土壤中的有效态含量,

减少蚕豆对重金属的吸收;3种黏土矿物显著抑制铅和铜在土壤中的生物有效态,但对土壤有效态锌没有显著影响;钠基膨润土对镉的钝化效果最显著。因此针对不同重金属污染土壤可施用不同种类的黏土矿物,为快速有效治理修复重金属污染土壤提供理论依据。

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