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ZHU Liwen, REN Chao, LI Jingtian, et al. Passivation Effect of Thiol-Modified Montmorillonite on Cadmium in Medium-Alkaline Farmland Soil in Northern China[J]. Rock and Mineral Analysis, 2024, 43(1): 124–136. DOI: [10.15898/j.ykcs.202309010147](https://doi.org/10.15898/j.ykcs.202309010147).

巯基改性蒙脱石对中国北方中碱性农田土壤镉钝化效果研究

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摘要: 农田土壤重金属污染是影响中国农产品环境质量安全的主要因素。钝化材料是修复农田重金属污染土壤的关键材料, 研究开发出高效土壤重金属钝化材料, 对于修复重金属污染农田和保障农产品食用安全非常重要。本文以蒙脱石为原材料, 将巯基团负载在其表面或层间制备巯基改性蒙脱石, 借助 X 射线衍射 (XRD)、扫描电镜 (SEM)、透射电镜 (TEM) 和傅里叶红外光谱 (FTIR) 等技术表征巯基改性蒙脱石的特性, 并开展室内土培试验, 采用二乙三胺五乙酸浸提-火焰原子吸收分光光度法分析土壤镉的有效态, 通过 Tessier 修正顺序七步提取法分析土壤镉的赋存形态。结果表明: 蒙脱石经巯基改性后不仅新增了 C-H、S-H 共价键, 而且增强了-OH 和 C=O 化学键的活性, 能与 Cd^{2+} 发生巯基及羟基配位吸附。供试土壤添加巯基改性蒙脱石后, 由于巯基配位吸附作用使土壤离子交换态镉转化为铁锰氧化物结合态, 而增强的羟基配位吸附作用使其转化为碳酸盐结合态, 结果使土壤中镉的赋存形态发生显著改变, 离子交换态大幅减少, 作物根系可吸收的土壤有效镉显著降低。添加 1%、3%、5% 巯基改性蒙脱石后, 土壤有效镉分别降低 21.92%、69.11%、82.90%; 而作为对照组添加 1%、3%、5% 蒙脱石仅分别降低 3.37%、1.80%、6.71%。蒙脱石经巯基改性后对土壤镉的钝化效果得到显著提升, 土壤有效镉的降低幅度有随巯基改性蒙脱石添加量增加而提高的趋势。巯基改性蒙脱石对中国北方中碱性农田土壤镉的钝化效果显著, 具有一定的参考应用价值。

关键词: 蒙脱石; 巯基改性蒙脱石; 钝化; 镉污染土壤; 傅里叶红外光谱 (FTIR); Tessier 修正顺序七步提取法

要点:

- (1) 蒙脱石经巯基改性后不仅新增了 C-H、S-H 共价键, 而且增强了-OH 和 C=O 化学键的活性, 能与 Cd^{2+} 发生巯基及羟基配位吸附。
- (2) 新增的巯基配位吸附作用使土壤 Cd 形态由离子交换态转化为铁锰氧化物结合态, 增强的羟基配位吸附作用使其转化为碳酸盐结合态。
- (3) 蒙脱石经巯基改性后对土壤镉的钝化效果得到显著提升, 土壤有效镉的降低幅度随添加量增加而提高。

中图分类号: P579; X53

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镉是一种剧毒重金属, 在土壤中有高迁移性、持久性和生物累积性, 对人体健康、动物和植物构成威胁^[1], 土壤镉污染形势不容乐观, 亟待解决。钝化是镉污染土壤修复的主要技术之一, 国内外已有大量研究^[2-3], 但大部分研究针对的是酸性镉污染土壤^[4-6], 中国北方和南方部分地区多为中碱性土

壤^[7-9], 其镉污染农田的钝化修复材料仍有待研究。蒙脱石是一种 2:1 型硅铝酸盐矿物^[10], 因其特殊层状结构使之比表面积较大, 对土壤重金属离子吸附能力较强, 被用于钝化修复土壤重金属污染^[11-13]。然而, 天然蒙脱石表面硅氧结构的亲水性较强、键合能力较弱, 导致其吸附过程可逆, 吸附效果有限, 钝

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化效果不稳定^[14-15],在吸附钝化土壤重金属镉应用上受到限制,因此目前研究热点集中于在使用前对其进行改性,进而增强吸附能力^[16-18]。

巯基具有很强的络合能力,黏附性能强,且巯基是一种弱碱、 Cd^{2+} 是一种弱酸,基于软硬酸碱理论,巯基与 Cd^{2+} 可形成稳定的结合态,能很好地吸附重金属离子^[19-20]。庞婷雯等^[21]对天然膨润土进行巯基化、钠化、酸化改性后,开展了 Cu^{2+} 、 Pb^{2+} 、 Zn^{2+} 吸附试验,发现巯基化改性膨润土无论在单一重金属离子的等温吸附环境下,还是在竞争吸附环境下均表现出较好的吸附能力。朱霞萍等^[22]采用溶液法对蒙脱石进行巯基改性,通过开展材料表征、动力学和热力学试验发现,改性蒙脱石对Cd的吸附容量提高了近39倍。巯基改性可使钝化材料对重金属离子的吸附能力得到大幅提升,可应用于钝化修复土壤镉污染。目前,已有研究证实了巯基改性蒙脱石对中国南方酸性镉污染土壤存在钝化效果。朱凰榕等^[23]将天然蒙脱石进行改性,制成巯基改性蒙脱石,通过盆栽和大田实验表明,巯基改性蒙脱石对南方酸性镉污染土壤(pH 5.03~5.86)有钝化修复效果,土壤Cd水溶态和离子交换态含量均有所减少,有效地抑制了小白菜对Cd的吸收。曾燕君等^[24]通过吸附解吸实验也证实材料改性处理能明显提高对Cd的饱和吸附容量,可有效地钝化南方酸性Cd污染土壤。但蒙脱石改性前后对北方中碱性Cd污染农田土壤的钝化研究鲜有报道,考虑到钝化材料对 Cd^{2+} 的吸附容量受土壤pH值影响较大^[22,25],蒙脱石改性前后对北方中碱性镉污染农田土壤的钝化效果有待进一步研究。

本文以蒙脱石为原材料,将巯基基团负载在其表面或层间制备巯基改性蒙脱石,并借助X射线衍射(XRD)、扫描电镜(SEM)、透射电镜(TEM)和傅里叶红外光谱(FTIR)表征巯基改性蒙脱石的特性,同时,开展室内培养试验研究巯基改性蒙脱石在不同添加量的情况下对中国北方中碱性农田土壤Cd的钝化效果,探究蒙脱石改性前后、不同添加量对北方中碱性农田土壤Cd钝化修复效果的影响,最后结合材料表征,分析巯基改性蒙脱石对Cd的钝化机制,以期修复北方Cd污染农田土壤提供理论依据。

1 实验部分

1.1 实验材料

1.1.1 供试土壤

供试土壤采自河南省洛阳市栾川县赤土店镇镉污染农田,按照梅花五点法采集0~20cm混合土壤

样,土壤类型为褐土,质地为粉壤土。经除杂、自然风干、研磨后保存备用。

1.1.2 钝化材料

蒙脱石(M):购自宜阳天冠膨润土有限公司,是由当地矿山开采破碎磨细制得。

巯基改性蒙脱石(GM):以天然蒙脱石矿物为原材料,经破碎、球磨后粒度达到300目后备用;按质量比例(蒙脱石粉:去离子水=1:20)混合,充分搅拌均匀后加入9.6%的无水乙醇和1.2%的3-硫丙基三乙氧基硅烷混合剂,常温搅拌6h,用去离子水充分洗净,于80℃下烘干研磨制得,干燥储存,备用。

1.2 实验方法

镉污染土壤制备:将99.95%的氯化镉(半五水合物)作为镉源配制成镉溶液,加入供试土壤中,充分混匀,并采用称重法调节土壤含水量保持在田间持水量的70%,在25±2℃的恒温培养箱中培养7天后,取出自然风干,作为镉污染的土壤用于试验,按每份100g土样装入5号自封袋中储存备用。

室内培养试验:共设置7个处理。空白对照处理CK;添加1%、3%、5%(占供试土壤质量百分比,添加到每份100g污染土壤中)的蒙脱石粉处理M1、M3、M5;添加1%、3%、5%的巯基改性蒙脱石粉处理GM1、GM3、GM5;每个处理设置3个重复。按比例将钝化材料添加到Cd污染土壤中,于5号自封袋内充分混匀。经上述处理的土壤样品分别准确移至相应的玻璃培养皿内(模拟实验的土壤深度15mm),每隔2天用去离子水给土壤补充水分,采用称重法控制土壤含水量保持在田间持水量的70%,盖上培养皿盖,置于25±2℃的恒温培养箱内培养,与此同时用塑料勺对土壤样品进行搅拌混合,确保多次充分混合。分别在7、15、30、50、70天分5次取样,每次称取20g土样在自然状态下风干过20目筛,测定土样的pH和全Cd、有效态Cd及Cd各赋存形态含量。

1.3 测试项目与测试方法

测试项目和具体检测分析方法及依据见表1。包括:对供试土壤样品进行pH、阳离子交换量(CEC)、有机质、营养元素和Cd含量分析,对室内培养试验得到的土壤样品进行pH、全Cd、有效态Cd和Cd各赋存形态含量分析。对钝化材料进行pH、CEC、重金属全量、BET、XRD、SEM、TEM和FTIR分析。具体检测分析方法及依据见表1。所有样品检测均做两次平行实验,测定结果取平均值,平行样测量值的相对偏差小于10%。

表 1 样品的检测分析方法及依据

Table 1 Detection and analysis methods and their basis of samples.

检测项目	检测指标	检测方法	方法依据(标准方法)
土壤理化性质	pH	玻璃电极法	NY/T 1121.2—2006
	CEC	1mol/L 乙酸铵交换法	LY/T 1243—1999
	有机质	重铬酸钾氧化-外加热法	LY/T 1237—1999
土壤元素全量	N	半微量凯氏法	NY/T 53—1987
	P	碱熔法	NY/T 88—1988
	K	碱熔法	NY/T 87—1988
	Cd	王水提取-电感耦合等离子体质谱法	HJ 803—2016
土壤元素有效性	碱解氮	碱解-扩散法	LY/T 1228—2015
	有效磷	0.5mol/L 碳酸氢钠浸提法	NY/T 1121.7—2014
	速效钾	1mol/L 乙酸铵浸提-火焰光度法	LY/T 1236—1999
	有效态 Cd	二乙三胺五乙酸浸提-火焰原子吸收分光光度法	GB/T 23739—2009
	Cd 各赋存形态	Tessier 修正顺序七步提取法	DZ/T 0289—2015
钝化材料 元素全量	pH	玻璃电极法	NY/T 1121.2—2006
	CEC	1mol/L 乙酸铵交换法	NY/T 295—1995
	Cd、Pb、Cr、Cu、Ni、Zn	电感耦合等离子体质谱法	HJ 766—2015
	Hg	原子荧光光谱法	GB/T 22105.1—2008
	As	原子荧光光谱法	GB/T 22105.2—2008
钝化材料 表征分析	比表面积	气体吸附法(BET)	GB/T 19587—2017
	物相组成	多晶体 X 射线衍射(XRD)	JY/T 0587—2020
	微观形貌、微区成分和结构分析	扫描电子显微镜(SEM)	JY/T 0584—2020
	超微结构、晶体学信息	透射电子显微镜(TEM)	JY/T 0581—2020
	官能团信息	红外光谱分析法(FTIR)	GB/T 6040—2019

2 结果与讨论

2.1 供试土壤的基本性质

本研究目的是钝化材料对镉污染农田土壤镉钝化(降低其有效性)的影响,并为研发镉污染农田土壤钝化材料提供依据。为使研发的材料性能更贴近实际,实地采集了镉污染土壤,对其理化性质、营养元素和重金属 Cd 元素进行分析检测。

土壤 pH 值为 7.96,全镉含量为 1.33mg/kg,CEC 为 12.0cmol(+)/kg,有机质含量为 15.4g/kg,全氮、全磷和全钾含量分别为 0.99、1.74、21.7g/kg,碱解氮、有效磷和速效钾含量分别为 107、14.8、84.2mg/kg。

2.2 钝化材料的基本性质和材料表征

2.2.1 基本性质

蒙脱石 pH 值为 10.64,CEC 为 41.6cmol(+)/kg,重金属 Cd、Hg、As、Pb、Cr、Cu、Ni、Zn 含量为 0.07、0.04、9.60、41.9、24.1、8.00、5.53、79.9mg/kg,考虑到田间实际应用,根据《耕地污染治理效果评价准则》(NY/T 3343—2018),蒙脱石作为钝化材料投入品,满足不对耕地或地下水造成二次污染的要求。

蒙脱石的比表面积为 17.14m²/g,平均孔径

7.28nm。巯基改性蒙脱石的比表面积为 10.74m²/g,平均孔径 27.90nm。

2.2.2 X 射线衍射表征晶体结构

通过 XRD 来分析晶体结构信息变化,如图 1 所示,蒙脱石主要含有 SiO₂、KAlSi₂O₃ 等矿物,巯基改性蒙脱石与蒙脱石相比,两者 XRD 图谱基本一致,说明这种改性方法没有破坏原始矿物结构,巯基可能被负载在材料层间,也可能包裹在材料外面,进而完成改性。

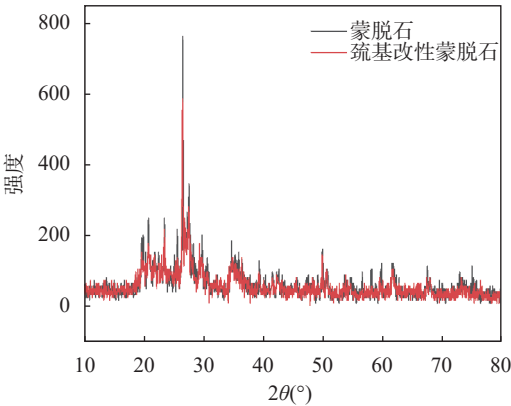


图1 蒙脱石和巯基改性蒙脱石的 X 射线衍射图谱

Fig. 1 X-ray diffraction patterns of montmorillonite and thiol-modified montmorillonite.

2.2.3 扫描电镜表征微观结构

由蒙脱石、巯基改性蒙脱石的 SEM 图像 (图 2) 可看出, 蒙脱石 (图 2 中 a, b) 为致密的片层状结构, 表面结构平坦规整, 层状结构间的通道和聚集颗粒间的空隙为重金属离子的吸附提供空间。巯基改性后的材料 (图 2 中 c, d) 表面结构卷曲、松散, 这可能是由于硅烷的黏度较大, 导致小颗粒团聚。聚集形态不规则, 颗粒间吸附空位明显增多, 表面粗糙疏松, 说明巯基在蒙脱石内部负载并不均匀, 对原蒙脱石也有表面改性的作用^[26]。

2.2.4 透射电镜表征颗粒形貌和元素分布

由图 3 可以看出, 改性前的蒙脱石 (图 3 中 a, b) 为致密的片层状结构, 内部出现小部分且少量的团聚现象, 其内部元素分布相对均匀。经过巯基改性后的蒙脱石 (图 3 中 c, d) 与未改性前相比粒度明显增大, 与 SEM 分析结果一致, 改性前蒙脱石呈片状, 改性后片状消失, 但改性前后元素并未发生改变且分布均相对均匀。

2.2.5 傅里叶红外光谱表征官能团信息

改性前后的 FTIR 图谱 (图 4) 存在明显差异, 改性前的天然蒙脱石 FTIR 图谱显示出, 3634cm^{-1} 附近是结构层内的 $-\text{OH}$ 伸缩振动峰, 3434cm^{-1} 附近是吸附的层间水形成的 $-\text{OH}$ 伸缩振动峰, 1643cm^{-1} 附近

是 $\text{C}=\text{O}$ 伸缩振动峰, 1424cm^{-1} 附近是 $\text{C}-\text{O}$ 反对称伸缩振动峰, 1037cm^{-1} 附近是 $\text{Si}-\text{O}-\text{Si}$ 反对称伸缩振动峰, 796cm^{-1} 附近是 $\text{Si}-\text{O}-\text{Si}$ 对称伸缩振动峰。巯基改性蒙脱石在上述位置均出现特征吸收峰, 且在 3419cm^{-1} 附近的 $-\text{OH}$ 伸缩振动峰和 1640cm^{-1} 附近的 $\text{C}=\text{O}$ 伸缩振动峰强度均明显增强, 表明负载巯基后没有改变蒙脱石固有的官能团, 但增强了 $-\text{OH}$ 和 $\text{C}=\text{O}$ 化学键的活性。另外, 在 $2000 \sim 3000\text{cm}^{-1}$ 还增加了两个吸收峰, 2932cm^{-1} 附近是饱和 $\text{C}-\text{H}$ 对称伸缩振动, 2027cm^{-1} 附近是 $\text{S}-\text{H}$ 伸缩振动。

根据 SEM、TEM 分析及 BET 结果, 改性后蒙脱石粒度增大, 平均孔径由 7.28nm 增加至 27.90nm , 层间距减小, 比表面积由 $17.14\text{m}^2/\text{g}$ 减少至 $10.74\text{m}^2/\text{g}$, 而巯基位于另一端, 也可以有效地嫁接于蒙脱石表面或层间, 巯基在蒙脱石上成功实现负载, 形成了稳定的巯基改性蒙脱石。结合 FTIR 分析图谱, 发现改性后的蒙脱石不仅新增了 $\text{C}-\text{H}$ 、 $\text{S}-\text{H}$ 共价键, 而且增强了 $-\text{OH}$ 和 $\text{C}=\text{O}$ 化学键的活性。

2.3 钝化材料对土壤 pH 的影响

土壤重金属钝化修复是通过施加钝化材料与土壤重金属发生吸附、离子交换、络合、沉淀、固胶体、氧化还原等作用来降低土壤重金属的活性^[27-28], 其

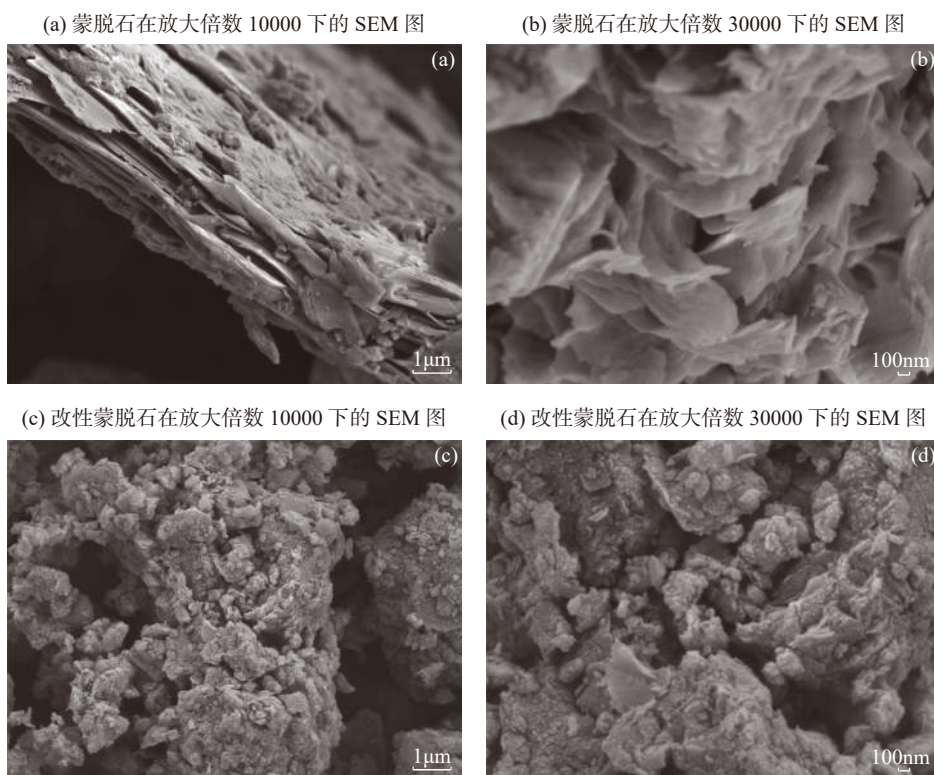


图2 蒙脱石和巯基改性蒙脱石的 SEM 图像

Fig. 2 Scanning electron microscopy images of montmorillonite and thiol-modified montmorillonite.

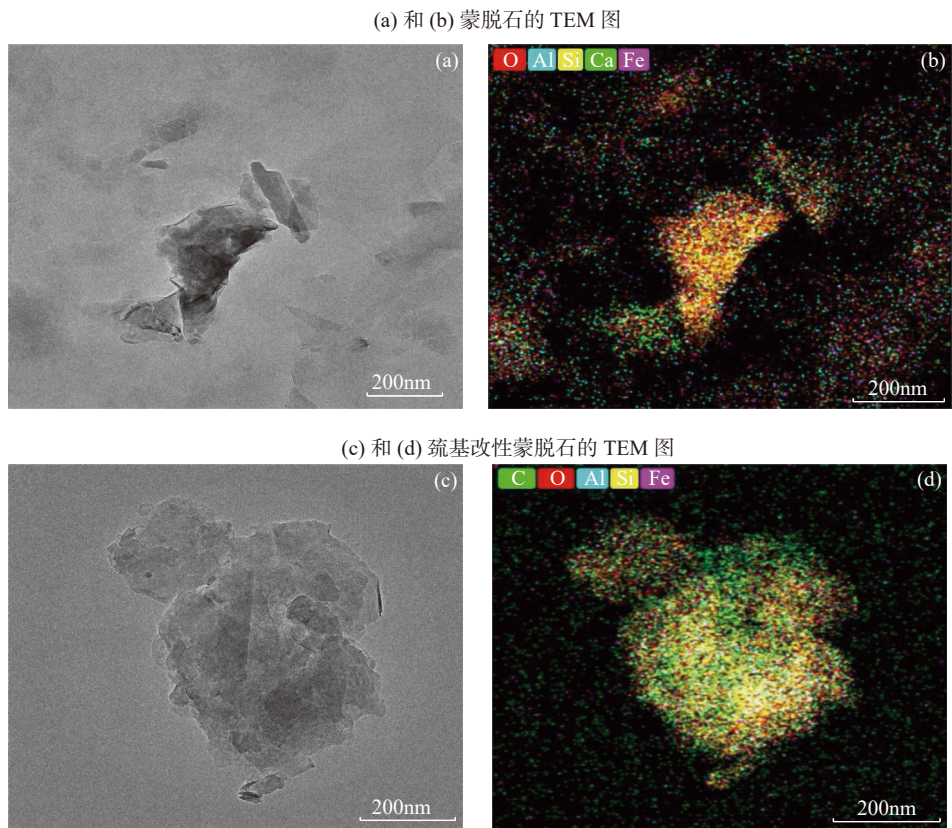


图3 蒙脱石和巯基改性蒙脱石的 TEM 图

Fig. 3 TEM images of montmorillonite and thiol-modified montmorillonite.

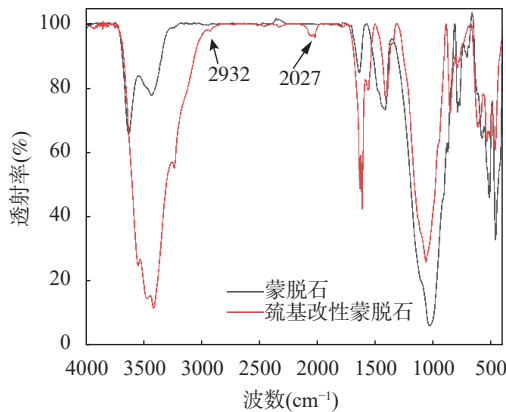


图4 蒙脱石和巯基改性蒙脱石的红外光谱图

Fig. 4 Infrared spectra of montmorillonite and thiol-modified montmorillonite.

中碱性物质,如硅酸钠、石灰、碳酸盐类等,钝化机理是通过提高土壤的酸碱度,增加其吸附重金属离子的能力,促进重金属在土壤中的沉淀反应,减少其迁移性^[29];黏土矿物,如蒙脱石、海泡石、高岭土等,因其特殊的晶体结构,具有较大的孔容和比表面积,

层间离子可交换^[12],能与重金属发生吸附、离子交换、共沉淀和配位反应^[13],进而降低土壤中重金属离子浓度与活性。针对中国北方广泛分布的中碱性土壤^[8],考虑到钝化材料的施加会影响土壤 pH,过高的 pH 易导致土壤板结、保水保肥能力降低^[9],故针对其重金属污染问题,不适合施加 pH 调节型碱性钝化材料,环境友好且有一定钝化效果的黏土矿物或改性黏土矿物更适用于北方中碱性农田土壤。在本研究中,添加不同剂量的蒙脱石、改性蒙脱石后,土壤 pH 分别提高了 0.12~0.78、0.30~0.85,提升幅度不大(表 2)。这可能是由于蒙脱石自身呈碱性且含有羟基等基团^[30],使土壤 pH 值升高。与蒙脱石相比,巯基改性蒙脱石对土壤 pH 也有轻微升高,可能是由于改性材料是 3-巯丙基三乙氧基硅烷,它的酸度系数 (pK_a) 比较高,可达到 10.39,因此巯基改性蒙脱石加入土壤后确实可在一定程度上提升土壤的 pH 值,但影响不大。

2.4 钝化材料对土壤中镉的钝化效果

2.4.1 钝化材料对土壤有效态镉含量的影响

重金属元素的有效态含量是影响其在土壤的生物有效性和移动性的主要因素,影响重金属被植物

表 2 不同钝化处理对土壤 pH 值的影响 (70 天)

Table 2 Effects of different passivation treatments on soil pH (70d).

钝化剂处理	处理代号	土壤 pH
空白对照	CK	8.22±0.05 ^c
1% 蒙脱石	M1	8.34±0.03 ^d
3% 蒙脱石	M3	8.66±0.03 ^b
5% 蒙脱石	M5	9.00±0.03 ^a
1% 巯基改性蒙脱石	GM1	8.52±0.07 ^c
3% 巯基改性蒙脱石	GM3	8.72±0.03 ^b
5% 巯基改性蒙脱石	GM5	9.07±0.05 ^a

注: 不同小写字母 a、b、c、d 表示各处理间差异显著 ($p < 0.05$)。

吸收累积程度,能很好地表征其污染特征以及对植物毒害程度^[31-32]。蒙脱石、改性蒙脱石在 1%、3%、5% 添加量下土壤有效态 Cd 含量的变化见图 5。两者均能降低土壤有效态 Cd 含量,但改性蒙脱石对有效态 Cd 含量的降低效果显著优于蒙脱石。

蒙脱石本身具备一定的离子交换性及吸附性,对土壤有效态 Cd 含量的降低幅度仅为 1.80% ~ 6.71%,效果不显著 ($p < 0.05$),这与化党领等^[33]、任露陆等^[34]的研究结果一致。Gupta 等^[35]研究表明,有效态 Cd 含量的降低主要是由于蒙脱石自身的负电荷对 Cd^{2+} 的静电吸附作用,其次是由于蒙脱石表面或层间的 $-\text{OH}$ 、 OH_2^+ 等基团与 Cd^{2+} 、 CdOH^+ 发生的离子交换行为,而且其 $-\text{OH}$ 官能团能与 Cd 发生配位吸附,形成 $\text{Cd}(\text{OH})_2$ 沉淀。改性后制得的巯基改性蒙脱石在吸附土壤有效态 Cd 时表现出高效性能,对土壤有效态 Cd 含量的降低幅度达到

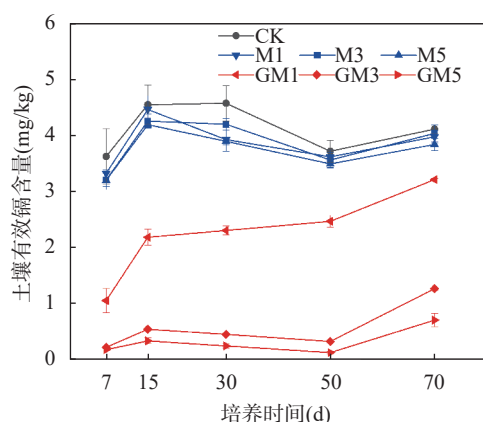


图5 钝化材料 1%、3%、5% 添加量下土壤有效态镉含量的变化

Fig. 5 Changes of soil available cadmium content under 1%, 3% and 5% addition of passivation materials.

21.92% ~ 82.90%, 效果显著。添加改性蒙脱石 70 天后,土壤有效态 Cd 含量略有提升,而且改性蒙脱石与蒙脱石均出现同样的趋势,该变化可能与培养过程中土壤性质的变化有关,并不是改性蒙脱石特有。不同添加量的钝化材料对有效态 Cd 的降低效果也有所差别,其中,蒙脱石的不同添加量对土壤镉的钝化效果差异不大,1%、3%、5% 的添加量对土壤有效态 Cd 分别降低了 3.37%、1.80%、6.71%。改性蒙脱石 1%、3%、5% 的添加量对土壤有效态 Cd 分别降低了 21.92%、69.11%、82.90%。由此可见,改性蒙脱石对土壤镉的钝化效果显著,钝化效果与添加量成正比,施用 5% 改性蒙脱石对土壤镉的钝化效果最好,土壤有效态 Cd 含量降低幅度高达 82.90%。

卿艳红等^[12]研究发现,巯基改性的蒙脱石既具备蒙脱石自身的尺寸稳定性、吸附性和阻隔性,又具有硅烷分子多种功能基团的反应活性。结合材料表征结果,XRD 分析结果显示改性后蒙脱石的结构并未发生改变,对有效镉仍具备静电吸附、离子交换吸附、羟基配位吸附能力。FTIR 分析结果显示,改性后蒙脱石对土壤中有有效态 Cd 含量的大幅降低主要来源于两方面:一方面是由于改性后新增了 C-H、S-H 共价键,能与 Cd^{2+} 发生巯基配位吸附作用,其作用力明显强于静电吸附、离子交换吸附和羟基配位吸附作用力,这与以往^[24,36]的研究结果一致;另一方面是由于改性后增强了 $-\text{OH}$ 和 $\text{C}=\text{O}$ 化学键的活性,增强了蒙脱石原有的羟基配位吸附作用,反应示意图见图 6。

2.4.2 钝化材料对土壤镉赋存形态的影响

本研究钝化修复 Cd 污染土壤的主要原理是基于对土壤 Cd 赋存形态的转化,故分析改性前后的蒙脱石对土壤 Cd 赋存形态的影响。考虑到待测土壤样品的 pH 值为 7.91 ~ 9.26,偏碱性,采用 Tessier 修正顺序七步提取法对重金属活性态进行提取^[37]。原状土的 Cd 以离子交换态和碳酸盐结合态为主要赋存形态,蒙脱石改性前后均对土壤 Cd 赋存形态有所影响,培养 70 天后土壤镉的赋存形态变化如图 7 所示。

添加蒙脱石对土壤 Cd 赋存形态的影响不大,变化幅度小于 5%。培养 70 天后(图 7a),水溶态、强有机结合态和硅酸盐残余态 Cd 含量基本无变化,其他形态 Cd 含量发生一定程度的变化,离子交换态 Cd 所占比例降低 1.17% ~ 4.87%,碳酸盐结合态、腐植酸结合态、铁锰氧化物结合态 Cd 所占比例分别升高 0.97% ~ 3.53%、0.74% ~ 1.06%、0.19% ~ 0.51%。

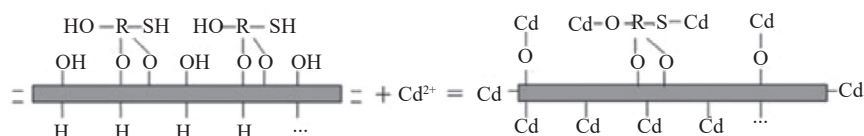


图6 巯基改性蒙脱石与镉的反应示意图

Fig. 6 Reaction diagram of mercapto thiol-modified montmorillonite with Cd.

添加蒙脱石后土壤 Cd 主要由离子交换态转化为碳酸盐结合态, 仍以这两种赋存形态为主。

添加改性蒙脱石 70 天后, 土壤 Cd 赋存形态发生显著改变 (图 7a), 与空白对照组相比, 水溶态 Cd 含量略有提升, 但仍保持在低位稳定状态, 离子交换态 Cd 所占比例大幅降低 (12.76% ~ 40.84%), 碳酸盐结合态、腐植酸结合态、铁锰氧化物结合态 Cd 所占比例分别提高了 2.86% ~ 8.45%、2.76% ~ 9.34%、6.67% ~ 34.75%, 而强有机结合态、硅酸盐残余态

Cd 含量略有下降。添加巯基改性蒙脱石后, 主要促使土壤 Cd 形态从离子交换态转化为铁锰氧化物结合态。不同添加量的改性蒙脱石对土壤 Cd 赋存形态的影响分别见图 7 中 b、c 和 d), 随着改性蒙脱石添加量的增加, 离子交换态 Cd 含量大幅降低, 铁锰氧化物结合态 Cd 含量大幅增加, 碳酸盐结合态 Cd 含量也有提升, 其他形态 (水溶态、腐植酸结合态、强有机结合态、硅酸盐残余态) Cd 含量变化不大, 这

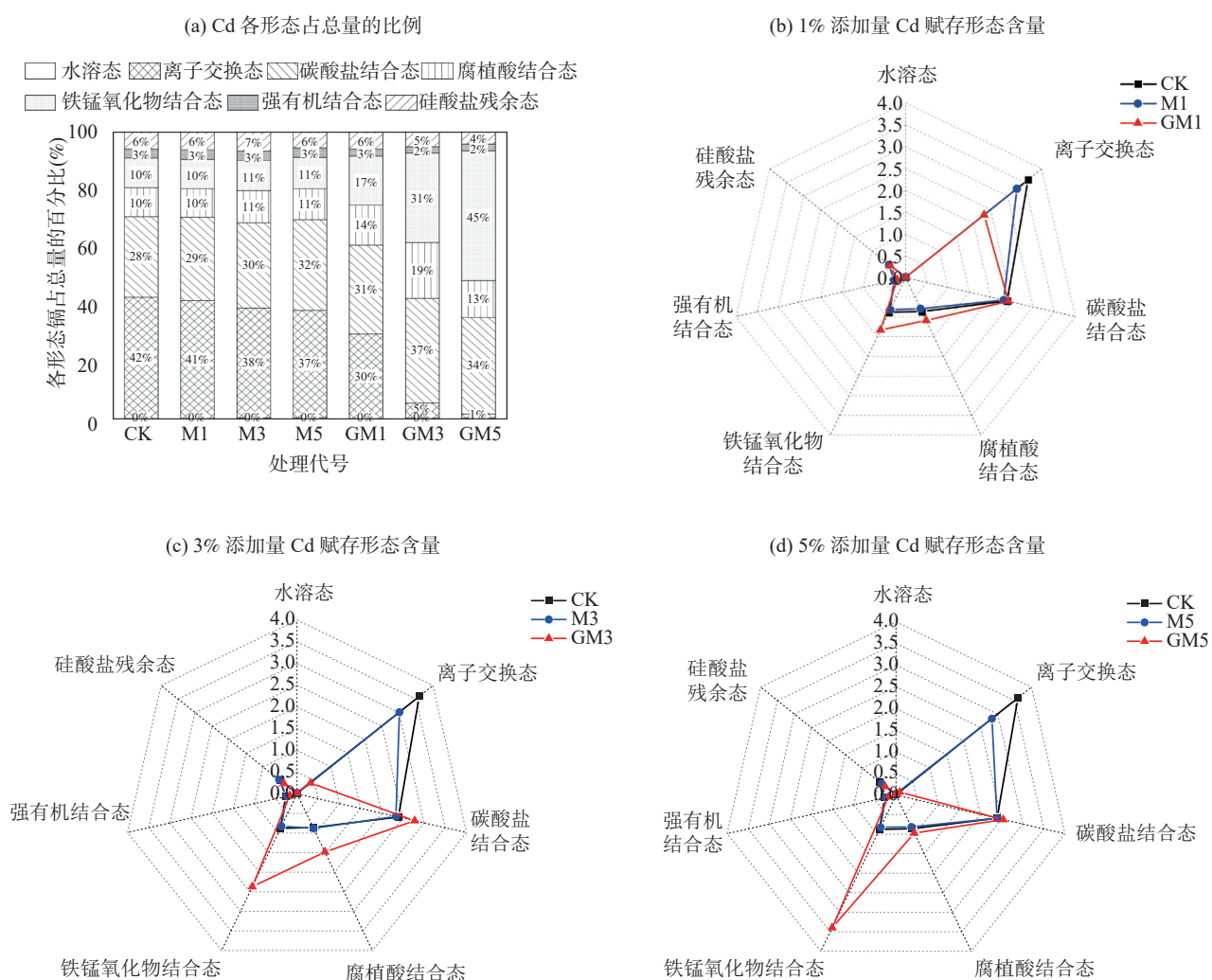


图7 添加钝化材料培养 70 天后土壤镉赋存形态变化

Fig. 7 The change of cadmium speciation in soil after 70 days of incubation with passivation materials.

可能是由于土壤添加改性蒙脱石后并没有改变土壤有机质含量和性质^[38], 因此, 其他形态发生变化过程中, 没有影响强有机结合态 Cd 含量。通过对比改性前后的蒙脱石对土壤 Cd 赋存形态的影响差异, 对于改性蒙脱石而言, 巯基的增加可与土壤 Cd 发生巯基配位吸附^[39], 促使离子交换态转变为铁锰氧化物结合态, 另外羟基的活性增强可与土壤 Cd 发生羟基配位吸附, 促使离子交换态转化为碳酸盐结合态, 两者均可使土壤 Cd 的活性降低。

3 结论

用 3-巯丙基三乙氧基硅烷对天然蒙脱石进行改性后能够实现巯基在蒙脱石上成功负载, 形成稳定

的巯基改性蒙脱石。改性后的蒙脱石不仅新增了 C-H、S-H 共价键, 而且增强了 -OH 和 C=O 化学键的活性, 并通过与 Cd^{2+} 发生巯基及羟基的配位吸附作用, 提高蒙脱石对土壤镉的吸附能力。当施加 5% 巯基改性蒙脱石时, 土壤有效镉的降低幅度可在对照组 6.71% 的基础上, 提高到 82.90%。

施加巯基改性蒙脱石后, 土壤 Cd 赋存形态发生显著改变, 离子交换态大幅减少, 新增的巯基配位吸附作用使其转化为铁锰氧化物结合态, 增强的羟基配位吸附作用使其转化为碳酸盐结合态。巯基改性蒙脱石对中国北方镉污染农田土壤的钝化效果显著, 可作为北方镉污染农田土壤安全利用的钝化材料。

Passivation Effect of Thiol-Modified Montmorillonite on Cadmium in Medium-Alkaline Farmland Soil in Northern China

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HIGHLIGHTS

- (1) The thiol-modified montmorillonite not only added C-H and S-H covalent bonds, but also enhanced the activity of -OH and C=O chemical bonds, and could adsorb Cd^{2+} with thiol and hydroxyl groups.
- (2) The newly added thiol coordination adsorption made the form of Cd in soil change from ion exchange state to iron-manganese oxide binding state, and the enhanced hydroxyl coordination adsorption made it change into carbonate binding state.
- (3) The passivation effect of montmorillonite on soil cadmium was significantly improved after thiol modification, and the decrease of available cadmium in soil increased with the increase of addition amount.

ABSTRACT: Passivation material is a key material for repairing heavy metal contaminated soil in farmland. To study and develop efficient soil heavy metal passivator, thiol-modified montmorillonite was studied. Montmorillonite was used as the raw material, and the thiol group was loaded on the surface or interlayer of montmorillonite to prepare thiol-modified montmorillonite. The characteristics of thiol-modified montmorillonite were characterized by XRD, SEM, TEM and FTIR, and the indoor soil culture test was carried out. The thiol-modified montmorillonite not only added C-H and S-H covalent bonds, but also enhanced the activity of -OH and C=O chemical bonds, and could adsorb with Cd^{2+} by thiol and hydroxyl coordination. As a result, the occurrence form of Cd in the soil was significantly changed, the ion exchange state was greatly reduced, and the available Cd in the soil absorbed by the crop roots was significantly reduced. After adding 1%, 3% and 5% thiol-modified montmorillonite, the available Cd in soil decreased by 21.92%, 69.11% and 82.90%, respectively. The passivation effect of montmorillonite on soil Cd was significantly improved after thiol modification, and the decrease of

available Cd in soil tended to increase with the increase of thiol-modified montmorillonite. The BRIEF REPORT is available for this paper at <http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202309010147>.

KEY WORDS: montmorillonite; thiol-modified montmorillonite; passivation; cadmium contaminated soil; Fourier transform infrared spectroscopy (FTIR); Tessier modified sequential seven-step extraction method

BRIEF REPORT

Significance: Heavy metal pollution in farmland soil is the main factor affecting the environmental quality and safety of agricultural products in China. Passivation material is a key material for repairing heavy metal contaminated soil in farmland. Research and development of efficient soil heavy metal passivation materials is very important for repairing heavy metal contaminated farmland and ensuring the food safety of agricultural products. Passivation is one of the main technologies for the remediation of Cd-contaminated soil. There have been a lot of studies at home and abroad^[2-3], but most of the studies are aimed at acidic Cd-contaminated soil^[4-6]. Most of the northern and southern parts of China are alkaline soil^[7-9], and the passivation remediation materials for Cd-contaminated farmland still need to be studied.

The passivation effect of montmorillonite before and after modification on the alkaline Cd contaminated farmland soil in northern China needs to be further studied. Montmorillonite is a 2 : 1 type aluminosilicate mineral^[10]. Due to its special layered structure, it has a large specific surface area and strong adsorption capacity for heavy metal ions in soil, and has been used to passivate and repair heavy metal pollution in soil^[11-13]. However, due to the strong hydrophilicity and weak bonding ability of the silicon-oxygen structure on the surface of natural montmorillonite, the adsorption process is reversible, the adsorption effect is limited, and the passivation effect is unstable^[14-15], which is limited in the application of adsorption and passivation of soil heavy metal Cd. Therefore, the current research focuses on the modification of natural montmorillonite before use, thereby enhancing the adsorption capacity^[16-18]. The thiol group has a strong complexing ability, strong adhesion, and is a weak base. Cd²⁺ is a weak acid, based on the theory of soft and hard acid-base, thiol group and Cd²⁺ can form a stable binding state, and can be a good adsorption of heavy metal ions^[19-20]. At present, studies have confirmed that thiol-modified montmorillonite has a passivation effect on acidic Cd-contaminated soil in the south. However, considering that the adsorption capacity of passivation materials for Cd²⁺ is greatly affected by soil pH^[22,25], and the passivation of montmorillonite before and after modification on alkaline Cd-contaminated farmland, soil in the north is rarely reported. Therefore, this study was carried out to analyze the changes in material characterization before and after montmorillonite modification, the passivation effect of montmorillonite before and after modification, and different amounts of montmorillonite on Cd in alkaline farmland in the north.

Methods: Montmorillonite was used as the raw material, and the thiol group was loaded on the surface or interlayer of montmorillonite to prepare thiol-modified montmorillonite. The characteristics of thiol-modified montmorillonite were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). At the same time, indoor soil experiments were carried out to study the passivation effect of thiol-modified montmorillonite on Cd in northern alkaline farmland soil with different addition amounts, and explore the effects of montmorillonite modification and different addition amounts on the passivation and repair effect of Cd in northern alkaline farmland soil. Finally, combined with material characterization, the passivation mechanism of thiol-modified montmorillonite on Cd was analyzed in order to provide a theoretical basis for the remediation of Cd-contaminated farmland soil in northern China.

A total of 7 treatments were set up. Blank control treatment CK; montmorillonite powder treatments M1, M3 and M5 were added with 1%, 3% and 5% (percentage of soil quality, added to 100g contaminated soil per share). GM1, GM3 and GM5 were treated with 1%, 3% and 5% thiol-modified montmorillonite powder. Each treatment

was set up with 3 replicates. The passivation material was added to the Cd-contaminated soil in proportion and fully mixed in the No.5 self-sealing bag. The soil samples treated above were accurately moved to the corresponding glass culture dish (the soil depth of the simulation experiment was 15mm), and the soil was replenished with deionized water every 2 days. The soil moisture content was controlled by the weighing method to maintain 70% of the field water holding capacity, and the culture dish was covered and placed in a constant temperature incubator at $25\pm 2^{\circ}\text{C}$. At the same time, the soil samples were stirred and mixed with a plastic spoon to ensure multiple full mixing. Samples were taken 5 times at 7, 15, 30, 50 and 70 days, and 20g soil samples were weighed and dried in natural state through 20 mesh sieves. The pH, total Cd content, available Cd content and Cd content of each form were determined. The specific detection and analysis methods and basis are shown in Table 1.

Data and Results: The crystal structure, microstructure, particle morphology and functional group information were analyzed by material characterization techniques. The change of crystal structure was analyzed by XRD. The XRD patterns of montmorillonite and thiol-modified montmorillonite (Fig.1) were basically the same, indicating that this modification method did not destroy the original mineral structure. The thiol group may be loaded between the layers of the material, or it may be wrapped outside the material to complete the modification. According to the results of SEM (Fig.2), TEM (Fig.3) and BET, the particle size of montmorillonite increased after modification, the surface structure changed from flat and regular to curly and loose, and the interlayer spacing decreased. The thiol group had been effectively grafted onto the surface or interlayer of montmorillonite, forming a stable thiol-modified montmorillonite. Combined with FTIR analysis (Fig.4), it was found that the modified montmorillonite not only added C-H and S-H covalent bonds, but also enhanced the activity of -OH and C=O chemical bonds.

The passivation effect of thiol-modified montmorillonite on Cd in soil was significant. After the addition of thiol-modified montmorillonite to the test soil, the ion-exchanged Cd in the soil was converted into an iron-manganese oxide-bound state due to the thiol coordination adsorption, and the enhanced hydroxyl coordination adsorption converted it into a carbonate-bound state. As a result, the occurrence form of Cd in the soil was significantly changed, the ion exchange state was greatly reduced, and the available Cd in the soil absorbed by the crop roots was significantly reduced. After adding 1%, 3% and 5% thiol-modified montmorillonite, the available Cd in soil decreased by 21.92%, 69.11% and 82.90%, respectively (Fig.5). As the control group, the addition of 1%, 3%, and 5% montmorillonite only decreased by 3.37%, 1.80%, and 6.71%, respectively. The passivation effect of montmorillonite on soil Cd was significantly improved after thiol modification, and the decrease of available Cd in soil tended to increase with the increase of thiol-modified montmorillonite. When 5% thiol-modified montmorillonite was applied, the decrease of available Cd in soil could be increased to 82.90% on the basis of 6.71% in the control group. The passivation effect of thiol-modified montmorillonite on Cd-contaminated farmland soil in northern China is significant, and it can be used as a passivation material for safe utilization of Cd-contaminated farmland soil in Northern China.

参考文献

- [1] 綦崢, 齐越, 杨红, 等. 土壤重金属镉污染现状、危害及治理措施[J]. *食品安全质量检测学报*, 2020, 11(7): 2286–2294.
- Qi Z, Qi Y, Yang H, et al. Status, harm and treatment measures of heavy metal cadmium pollution in soil[J]. *Journal of Food Safety and Quality*, 2020, 11(7): 2286–2294.
- [2] Liu L W, Li W, Song W P, et al. Remediation techniques for heavy metal-contaminated soils: Principles and applicability[J]. *Science of the Total Environment*, 2018, 633: 206–219.
- [3] Lin H, Wang Z W, Liu C J, et al. Technologies for removing heavy metal from contaminated soils on farmland: A review[J]. *Chemosphere*, 2022, 305: 135457.
- [4] Gong S T, Wang H, Lou F, et al. Calcareous materials effectively reduce the accumulation of Cd in potatoes in acidic cadmium-contaminated farmland soils in mining areas[J]. *International Journal of Environmental*

- Research and Public Health, 2022, 19(18): 11736.
- [5] Li Y P, Li X, Kang X R, et al. Effects of a novel Cd passivation approach on soil Cd availability, plant uptake, and microbial activity in weakly alkaline soils[J]. *Ecotoxicology and Environmental Safety*, 2023, 253: 114631.
- [6] 宿俊杰, 刘永兵, 王鹤立, 等. 面向碱性农地镉污染土壤钝化的凹凸棒改性特征及效果研究[J]. *岩矿测试*, 2022, 41(6): 1029–1039.
- Su J J, Liu Y B, Wang H L, et al. Characteristics and effects of modified attapulgite for stabilization of cadmium contaminated alkaline soils[J]. *Rock and Mineral Analysis*, 2022, 41(6): 1029–1039.
- [7] 张力浩, 白姣杰, 田瑞云, 等. 中国北方碱性农田土壤镉污染修复: 现状与挑战[J/OL]. *土壤学报*, 2024. DOI: [10.11766/trxb202209110503](https://doi.org/10.11766/trxb202209110503).
- Zhang L H, Bai J J, Tian R Y, et al. Cadmium remediation strategies in alkaline arable soils in Northern China: Current status and challenges[J/OL]. *Acta Pedologica Sinica*, 2024. DOI: [10.11766/trxb202209110503](https://doi.org/10.11766/trxb202209110503).
- [8] 韩天富, 柳开楼, 黄晶, 等. 近30年中国主要农田土壤pH时空演变及其驱动因素[J]. *植物营养与肥料学报*, 2020, 26(12): 2137–2149.
- Han T F, Liu K L, Huang J, et al. Spatio-temporal evolution of soil pH and its driving factors in the main Chinese farmland during past 30 years[J]. *Journal of Plant Nutrition and Fertilizers*, 2020, 26(12): 2137–2149.
- [9] 解晓露, 袁鑫, 朱晓龙, 等. 中碱性镉污染农田原位钝化修复材料研究进展[J]. *土壤通报*, 2018, 49(5): 1254–1260.
- Xie X L, Yuan C, Zhu X L, et al. In-situ passivation remediation material in cadmium contaminated alkaline agricultural soil: A review[J]. *Chinese Journal of Soil Science*, 2018, 49(5): 1254–1260.
- [10] Anjos V E d, Rohwedder J R, Cadore S, et al. Montmorillonite and vermiculite as solid phases for the preconcentration of trace elements in natural waters: Adsorption and desorption studies of As, Ba, Cu, Cd, Co, Cr, Mn, Ni, Pb, Sr, V, and Zn[J]. *Applied Clay Science*, 2014, 99: 289–296.
- [11] Du J, Wang Q H, Chen J. Understanding Cd²⁺ adsorption mechanism on montmorillonite surfaces by combining DFT and MD[J]. *Processes*, 2022, 10(7): 1381.
- [12] 卿艳红, 苏小丽, 王钺博, 等. 蒙脱石黏土矿物环境材料构建的研究进展[J]. *材料导报*, 2020, 34(10): 19018–19026.
- Qing Y H, Su X L, Wang Y B, et al. Research progress in construction of montmorillonite environmental mineral materials[J]. *Materials Reports*, 2020, 34(10): 19018–19026.
- [13] 朱维, 刘代欢, 陈建清, 等. 黏土矿物在土壤重金属污染中的应用研究进展[J]. *土壤通报*, 2018, 49(2): 499–504.
- Zhu W, Liu D H, Chen J Q, et al. Research progress on the application of clay minerals in the remediation of cadmium polluted farmland[J]. *Chinese Journal of Soil Science*, 2018, 49(2): 499–504.
- [14] 任超, 朱利文, 李竞天, 等. 不同钝化剂对弱酸性镉污染土壤的钝化效果[J]. *生态与农村环境学报*, 2022, 38(3): 383–390.
- Ren C, Zhu L W, Li J T, et al. Study on the passivation effect of different treatments on weakly acidic cadmium polluted soil[J]. *Journal of Ecology and Rural Environment*, 2022, 38(3): 383–390.
- [15] 任超, 李竞天, 朱利文, 等. 不同钝化剂对碱性镉污染土壤钝化效果研究[J]. *环境科学与技术*, 2021, 44(3): 71–78.
- Ren C, Li J T, Zhu L W, et al. Study on the passivation effect of different passivators on alkaline cadmium contaminated soil[J]. *Environmental Science & Technology*, 2021, 44(3): 71–78.
- [16] Jiang M, Wang K, Li G, et al. Stabilization of arsenic, antimony, and lead in contaminated soil with montmorillonite modified by ferrihydrite: Efficiency and mechanism[J]. *Chemical Engineering Journal*, 2023, 457: 141182.
- [17] Meng Z Y, Li J, Zou Y X, et al. Advanced montmorillonite modification by using corrosive microorganisms as an alternative filler to reinforce natural rubber[J]. *Applied Clay Science*, 2022, 225: 106534.
- [18] Song C H, Zhao Y, Pan D L, et al. Heavy metals passivation driven by the interaction of organic fractions and functional bacteria during biochar/montmorillonite-amended composting[J]. *Bioresource Technology*, 2021, 329: 124923.
- [19] 李正龙, 周咏春, 李海波, 等. 巯基改性生物炭对镉污染土壤的稳定化效果[J]. *环境工程*, 2022, 40(9): 143–149.
- Li Z L, Zhou Y C, Li H B, et al. Stabilization of cadmium-contaminated soil by sulfhydryl modified biochar[J]. *Environmental Engineering*, 2022, 40(9): 143–149.
- [20] 王亚玲, 李述贤, 杨合. 有机改性蒙脱石负载巯基修复汞污染土壤[J]. *环境工程学报*, 2018, 12(12): 3433–3439.

- Wang Y L, Li S X, Yang H. Mercury contaminated soils remediation by using organic modified montmorillonite with sulfhydryl group loading[J]. *Chinese Journal of Environmental Engineering*, 2018, 12(12): 3433–3439.
- [21] 庞婷雯, 杨志军, 黄逸聪, 等. 巯基化、钠化和酸化膨润土对 Cu^{2+} 、 Pb^{2+} 和 Zn^{2+} 的吸附性能研究[J]. *光谱学与光谱分析*, 2018, 38(4): 1203–1208.
- Pang T W, Yang Z J, Huang Y C, et al. Adsorption properties of thiol-modified, sodium-modified and acidified bentonite for Cu^{2+} , Pb^{2+} and Zn^{2+} [J]. *Spectroscopy and Spectral Analysis*, 2018, 38(4): 1203–1208.
- [22] 朱霞萍, 刘慧, 谭俊, 等. 巯基改性蒙脱石对 $\text{Cd}(\text{II})$ 的吸附机理研究[J]. *岩矿测试*, 2013, 32(4): 613–620.
- Zhu X P, Liu H, Tan J, et al. Mechanism study of cadmium(II) adsorption on thiol-modified montmorillonite[J]. *Rock and Mineral Analysis*, 2013, 32(4): 613–620.
- [23] 朱凰榕, 赵秋香, 倪卫东, 等. 巯基-蒙脱石复合材料对不同程度 Cd 污染农田土壤修复研究[J]. *生态环境学报*, 2018, 27(1): 174–181.
- Zhu H R, Zhao Q X, Ni W D, et al. Immobilization of cadmium by thiol-functionalized montmorillonite in soils contaminated by cadmium in various degrees[J]. *Ecology and Environmental Sciences*, 2018, 27(1): 174–181.
- [24] 曾燕君, 周志军, 赵秋香. 蒙脱石-OR-SH 复合体材料对土壤镉的钝化及机制[J]. *环境科学*, 2015, 36(6): 2314–2319.
- Zeng Y J, Zhou Z J, Zhao Q X. Mechanism study of the smectite-OR-SH compound for reducing cadmium uptake by plants in contaminated soils[J]. *Environmental Science*, 2015, 36(6): 2314–2319.
- [25] Marković J, Jović M, Smičiklas I, et al. Cadmium retention and distribution in contaminated soil: Effects and interactions of soil properties, contamination level, aging time and in situ immobilization agents[J]. *Ecotoxicology and Environmental Safety*, 2019, 174: 305–314.
- [26] 代亚平, 吴平霄. 3-氨丙基三乙氧基硅烷改性蒙脱石的表征及其对 $\text{Sr}(\text{II})$ 的吸附研究[J]. *环境科学学报*, 2012, 32(10): 2402–2407.
- Dai Y P, Wu P X. Characterization of APTES-modified montmorillonite and adsorption of $\text{Sr}(\text{II})$ [J]. *Acta Scientiae Circumstantiae*, 2012, 32(10): 2402–2407.
- [27] 刘雪梅, 屈凌霄. 土壤重金属污染钝化修复技术研究进展[J]. *应用化工*, 2022, 51(6): 1799–1803.
- Liu X M, Qu L X. Research progress of passivation remediation technology for soil heavy metal pollution[J]. *Applied Chemical Industry*, 2022, 51(6): 1799–1803.
- [28] 王泓博, 苟文贤, 吴玉清, 等. 重金属污染土壤修复研究进展: 原理与技术[J]. *生态学杂志*, 2021, 40(8): 2277–2288.
- Wang H B, Gou W X, Wu Y Q, et al. Progress in remediation technologies of heavy metals contaminated soil: Principles and technologies[J]. *Chinese Journal of Ecology*, 2021, 40(8): 2277–2288.
- [29] 周春海, 张振强, 黄志红, 等. 不同钝化剂对酸性土壤中重金属的钝化修复研究进展[J]. *中国农学通报*, 2020, 36(33): 71–79.
- Zhou C H, Zhang Z Q, Huang Z H, et al. Passivation and remediation of heavy metals in acid soil with different passivators: A research progress[J]. *Chinese Agricultural Science Bulletin*, 2020, 36(33): 71–79.
- [30] 陶玲, 仝云龙, 杨万辉, 等. 碱改性凹凸棒石对土壤中镉化学形态及环境风险的影响[J]. *岩矿测试*, 2022, 41(1): 109–119.
- Tao L, Tong Y L, Yang W H, et al. Chemical speciation and environmental risk of Cd in soil stabilized with alkali-modified attapulgite[J]. *Rock and Mineral Analysis*, 2022, 41(1): 109–119.
- [31] 付成, 雷泞菲, 裴向军, 等. 巯基改性凹凸棒石黏土对土壤有效态镉及油菜吸收镉的影响[J]. *岩石矿物学杂志*, 2022, 41(5): 941–949.
- Fu C, Lei N F, Pei X J, et al. Effects of sulfhydryl-modified attapulgite on available cadmium in soil and cadmium absorption by rape[J]. *Acta Petrologica et Mineralogica*, 2022, 41(5): 941–949.
- [32] 段海芹, 秦秦, 吕卫光, 等. 有机肥长期施用对设施土壤全镉和有效态镉含量的影响[J]. *土壤学报*, 2021, 58(6): 1486–1495.
- Duan H Q, Qin Q, Lyu W G, et al. Effects of long-term application of organic manure on contents of total and available cadmium in greenhouse soil[J]. *Acta Pedologica Sinica*, 2021, 58(6): 1486–1495.
- [33] 化党领, 朱利楠, 赵永芹, 等. 膨润土、褐煤及其混合添加对铅、镉复合污染土壤重金属形态的影响[J]. *土壤通报*, 2020, 51(1): 201–206.
- Hua D L, Zhu L N, Zhao Y Q, et al. Fractions of heavy metals in Cd/Pb contaminated soil amended with bentonite and lignite[J]. *Chinese Journal of Soil Science*, 2020, 51(1): 201–206.
- [34] 任露陆, 蔡宗平, 王固宁, 等. 不同钝化机制矿物对土壤重金属的钝化效果及微生物响应[J]. *农业环境科学学报*, 2021, 40(7): 1470–1480.

- Ren L L, Cai Z P, Wang G N, et al. Effects of minerals with different immobilization mechanisms on heavy metals availability and soil microbial response[J]. *Journal of Agro-Environment Science*, 2021, 40(7): 1470–1480.
- [35] Gupta S S, Bhattacharyya K G. Adsorption of heavy metals on kaolinite and montmorillonite: A review[J]. *Physical Chemistry Chemical Physics*, 2012, 14(19): 6698–6723.
- [36] 刘慧, 朱霞萍, 韩梅, 等. 巯基改性蒙脱石对 Cd^{2+} 的吸附及酸雨解吸[J]. *非金属矿*, 2013, 36(3): 69–72. DOI: CNKI:SUN:FJSK.0.2013-03-024.
- Liu H, Zhu X P, Han M, et al. Cd^{2+} adsorption on thiol-modified montmorillonite and desorption by acid rain[J]. *Non-Metallic Mines*, 2013, 36(3): 69–72. DOI: CNKI:SUN:FJSK.0.2013-03-024.
- [37] 刘丹丹, 缪德仁, 刘菲. 不同提取方法对土壤中活性部分重金属提取能力的对比研究[J]. *安徽农业科学*, 2009, 37(35): 17613–17615.
- Liu D D, Miu D R, Liu F. Comparison study on the extraction ability of some heavy metals in active parts of soils by different extraction methods[J]. *Journal of Anhui Agricultural Sciences*, 2009, 37(35): 17613–17615.
- [38] 安艳, 朱霞萍, 孟兴锐, 等. 巯基膨润土钝化修复镉污染水稻土的研究[J]. *土壤通报*, 2021, 52(4): 934–939.
- An Y, Zhu X P, Meng X R, et al. Passivation remediation of Cd contaminated paddy soils by mercapto bentonite[J]. *Chinese Journal of Soil Science*, 2021, 52(4): 934–939.
- [39] 孟兴锐. 巯基膨润土对水稻土中镉形态转化的影响研究[D]. 成都: 成都理工大学, 2019.
- Meng X R. Effect of sulfhydryl-modified bentonite on transformation of cadmium in rice soil[D]. Chengdu: Chengdu University of Technology, 2019.