

磁铁矿/磁黄铁矿复合矿物强化电修复治理 Cr(VI)污染性能 及含铬产物分析

周川野, 姬 翔, 鲁安怀, 丁竑瑞, 葛 潇, 王长秋, 李 艳

(北京大学地球与空间科学学院, 北京 100871)

摘 要: 整合还原固定材料与电修复技术, 是增强 Cr(VI)污染治理效果的有效方法。利用磁铁矿/磁黄铁矿复合材料构建矿物强化电修复的 Cr(VI)治理体系, 研究 Cr(VI)的去除效果, 比较该治理体系与电修复体系的 Cr(VI)返溶率, 并利用 Raman 光谱仪、X 射线衍射仪、环境扫描电子显微镜及能谱仪对含铬产物进行表征。结果表明: 对 Cr(VI)含量为 350 mg/kg 的污染模拟土壤, Cr(VI)去除率近 100%, 总铬(TCr)去除率可达 96%; 矿物强化电修复实验组中 Cr(VI)返溶率降低 54%以上; 铬与铁元素的分布相关性高, 铬以矿物相的形式稳定存在。实验证明, 电修复中整合矿物可以提升铬的去除率并强化铬的矿化。本工作作为长效稳定地修复 Cr(VI)污染场地提供了新思路。

关键词: 磁铁矿/磁黄铁矿复合矿物; 矿物强化作用; 电修复; 铬(VI)污染

中图分类号: P579; X53 文献标志码: A 文章编号: 0454-5648(2024)10-3122-09

网络出版时间: 2024-08-09



铬是一种重要的金属元素, 广泛应用于工业生产的各个领域, 如电镀、制革、化工、颜料、冶金、耐火材料等行业, 其废水严重威胁人类健康。铬在自然界主要以 Cr(VI)及 Cr(III) 2 种稳定价态存在。其中, Cr(VI)以络合阴离子形式存在, 氧化性强、毒性高、易致癌且在环境中易迁移。Cr(VI)已被证明通过吸入或摄入致癌, 可对人体造成慢性支气管炎、腹泻、肺气肿、头痛、肝病、肺癌及肾衰竭等危害^[1-2], 被美国环保署列为最具毒性的污染物之一, 也是我国严格控制的重金属污染物之一。而 Cr(III)毒性低, 在环境中不易迁移^[3-4]。因此, 铬污染的治理通常采取将 Cr(VI)还原为 Cr(III)的方式处理。

针对铬污染的土壤或水体, 前人主要采用了物理、化学及生物等方法。物理方法主要包括土壤置换、隔离及热处理^[5-6], 化学方法是土壤及地下水原位修复技术的常见方法, 常利用连二亚硫酸钠、多硫化钙等药剂去除污染物^[7-8]。生物修复是一种环保且具有成本效益的 Cr(VI)去除技术, 主要包括植物

修复和微生物修复^[9-10]。以上传统修复方法通常面临着不宜大范围使用、易造成二次污染及修复效果不稳定等问题。电修复技术是一种新兴的修复技术, 其原理是在污染介质两端施加电场, 主要利用电迁移驱动污染物迁移至特定位置从而去除污染物, 同时该过程还伴随一些化学反应^[11-12]。因其具有对土壤破坏小、电子来源绿色、不易造成二次污染、适用低渗透性土壤^[13]等特点, 在近年来受到人们广泛关注^[3-4, 13-14]。然而, 目前该技术也面临着修复效率不高、非目标污染物的干扰、电极的频繁更换、能耗成本较高的问题^[10, 14]。

部分矿物, 因其具有表面效应、离子交换效应、氧化还原效应及结晶效应等可用于环境修复的属性功能, 可作为铬污染治理的功能材料^[15-16]。磁黄铁矿处理 Cr(VI)浓度为 600 $\mu\text{mol/L}$ 及 3 400 $\mu\text{mol/L}$ 的电镀厂工业废水, Cr(VI)去除率在 98%以上^[17]。磁性矿物复合材料对 Cr(VI)去除能力为 45.8 mg/g, 对 Cr(VI)含量为 500 mg/kg 的污染土壤, 使用该材料修复 100 d 后, Cr(VI)浸出浓度仅为 1.95 mg/L, 远低

收稿日期: 2024-02-28。 修订日期: 2024-03-12。

基金项目: 国家重点研发计划项目(2019YFC1805900)。

第一作者: 周川野(1998—), 男, 博士研究生。

通信作者: 鲁安怀(1962—), 男, 博士, 教授。

Received date: 2024-02-28. Revised date: 2024-03-12.

First author: ZHOU Chuanye (1998—), male, Doctoral candidate.

E-mail: ChuanyeZhou@outlook.com

Correspondent author: LU Anhuai (1962—), male, Ph.D., Professor.

E-mail: ahlul@pku.edu.cn

于美国环保署对危废 5 mg/L 的限制^[18]。纳米铁颗粒通过硅微粉负载^[19]，不易团聚，Cr(VI)的去除率相较未负载纳米铁提升 22.55%。含铁黏土矿物如绿脱石对 Cr(VI)也有较好的还原效果^[6, 20–21]。

电修复技术绿色且可用于其它方法难以修复的低渗透性土壤，但效率不足、对铬的固定能力差；具有电子供给能力的矿物材料在自然界广泛存在、成本较低、对铬的还原固定能力较强。因此本工作尝试利用矿物强化电修复系统去除污染土壤中的 Cr(VI)，并实现 Cr(VI)的长效稳定修复。本工作以天然的磁铁矿/磁黄铁矿复合矿物材料为例，结合该矿物的还原固定能力与电修复的电还原、电迁移及电吸附等属性，构建了矿物强化电修复系统的 Cr(VI)修复体系与方法，探究了矿物填充位置、电势梯度对矿-电系统的影响，使用超纯水模拟地表水或地下水的浸沥以分析该方法的修复稳定性，利用 Raman 光谱仪、X 射线衍射仪(XRD)、电感耦合等离子光谱仪(ICP–OES)、环境扫描电子显微镜(ESEM)及能谱仪(EDS)对反应前后样品进行测试分析，分析产物构成，最后讨论了矿物强化电修复作用机理。本工作成果能推动矿物强化电修复技术在 Cr(VI)污染场地的应用，实现污染的长效治理。

1 实验

1.1 原料与试剂

磁铁矿/磁黄铁矿复合矿物的原料来自山西某矿场(山西国益环保科技有限公司)，经破碎、粗磨及研磨处理后，得到粒径大小为 74 μm 的矿物颗粒。为模拟部分铬污染场地砂质土中铬的修复，选用颗粒粒度为 1~2 mm 的石英砂(铭海环保石英砂厂)制备模拟土壤。污染模拟土壤制备：将 70 mL 质量浓度为 1 000 mg/L 的 Cr(VI)溶液加入到 200 g 石英砂中混匀，得到初始含量为 350 mg/kg 的模拟土壤。上述模拟土壤共制备 35 份。Cr(VI)溶液由重铬酸钾(分析纯，北京市通广精细化工公司)配制。Cr(VI)及 TCr 测试试剂包括二苯碳酰二肼(分析纯，上海易恩化学技术有限公司)、硝酸(优级纯，北京市通广精细化工公司)、硫酸(优级纯，西陇科学股份有限公司)以及丙酮(分析纯，北京市通广精细化工公司)。

1.2 矿物强化电修复装置构建

矿物强化电动修复装置主要由圆柱形反应器[有机玻璃管，尺寸 100 mm×50 mm×3 mm (长×直径×厚)]、电极板(高纯石墨板，80 mm×50 mm×3 mm)构成，有机玻璃管顶部预留有 3 个固定取样孔(见

图 1)。在加入模拟土壤前，使用硅橡胶将电极板与有机玻璃管一侧粘结固化，将制备好的模拟土壤、复合矿物按照 10:1 的质量比例、不同的矿物填充位置(表 1)装填到反应器后，再将电极板与有机玻璃管的另一侧相粘结形成闭合实验装置。

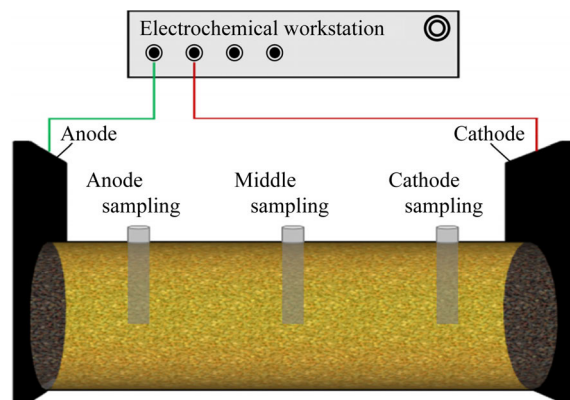


图 1 矿物强化电修复铬污染模拟土壤装置
Fig. 1 Mineral-enhanced electro-remediation device for Cr-contaminated simulated soil

表 1 各反应装置中电势差、电势梯度与矿物填充位置
Table 1 Voltage, potential gradient, and mineral filling position in each reaction system

Reaction system	Voltage/V	Potential gradient/(V·cm ⁻¹)	Mineral filling position
SM			Both sides near the electrode
SE	4	0.4	
ME	4	0.4	Random
HM	4	0.4	Middle of the device
HS	4	0.4	Both sides near the electrode
LM	2	0.2	Middle of the device
LS	2	0.2	Both sides near the electrode

SM is a separate mineral remediation system without electric field. SE is a separate electro-remediation system without mineral. ME is a mineral-enhanced electro-remediation under random distribution of mineral. HM is a mineral-enhanced electro-remediation under a 4 V voltage and mineral distribution in the middle. HS is a mineral-enhanced electro-remediation under a 4 V voltage and mineral distribution on both sides. LM is a mineral-enhanced electro-remediation under a 2 V voltage and mineral distribution in the middle. LS is a mineral-enhanced electro-remediation under a 4 V voltage and mineral distribution on both sides.

1.3 反应装置监测与采样

将反应装置与多通道电化学工作站连接(CHI1000C 型，上海辰华仪器有限公司)，对各反应装置施加不同直流电压，其电势梯度与矿物填充位置具体见表 1。在第 12、24、36、48、72、96、120、144、168 h 通过 3 个固定取样口(见图 1)取样，监测

固定点位 Cr(VI) 浓度。修复完成后, 将各装置中的污染液抽出并用超纯水水洗模拟土壤 3 次, 考察各体系对 Cr(VI) 及 TCr 的总体去除率。修复过程当中适量补充去离子水, 以弥补模拟土壤中水的电解和蒸发。

1.4 分析方法

1.4.1 矿物物相及元素分析 将所用复合矿物研磨并过 200 目筛(孔径尺寸 80 μm)后, 通过荷兰 PANalytical X-pert3 Powder 型粉末 XRD 进行测试分析。测试电压 40 kV, 电流 40 mA, X 射线源为 Cu 靶, 连续扫描模式, 扫描范围 $20^\circ\sim 80^\circ$, 扫描速率 $6^\circ/\text{min}$ 。利用 HighScore Plus 软件对矿物物相进行分析鉴定。主微量元素分析通过美国 Thermo ARL ADVANT XP+ 型 X 射线荧光光谱仪(XRF)进行。

1.4.2 Cr(VI) 及 TCr 分析 反应过程中, 通过固定取样口在规定时间内取样, 采用 GB7467—87《二苯碳酰二肼分光光度法》测定 Cr(VI) 浓度^[22], 测试仪器为美国赛默飞 EVOLUTION 220 紫外可见分光光度计(UV-Vis)。修复完成后将装置中的污染液抽出并用超纯水将模拟土壤水洗 3 次, 所得水洗液经 10000 r/min 转速离心 2 min 分离得到上清液和固体沉淀。上清液中 Cr(VI) 的测定同上; TCr 的测定采用 HJ 776—2015《水质 32 种元素的测定电感耦合等离子体发射光谱法》^[23], 测试仪器为德国 SPECTROBLUE SOP 型全谱直读 ICP-OES。

1.4.3 含铬产物矿物学分析 固体沉淀经磁性分离后得到絮状沉淀和黑色颗粒两种产物, 用搭载能谱仪的美国赛默飞 ESEM 以及英国 RENISHAW inVia Reflex 型 Raman 光谱仪进行表征分析。

1.4.4 含铬产物稳定性分析 水洗后反应装置在常温下静置 6 个月, 再次用超纯水水洗污染模拟土壤, 模拟其在特定场合中受到地表水或地下水的浸沥, 其中的有害组分浸出而进入环境的过程, 测定 Cr(VI) 及 TCr 浓度并计算含量, 考察该装置的修复稳定性。将电极板从装置上取下, 称取质量后置于 250 mL 烧杯中, 按液固比为 10:1 (L/kg) 计算出每块电极板所需浸提剂即水的体积, 加入浸提剂, 用封口膜密封后垂直固定在水平振荡装置上, 调节振荡频率为 120 次/min、振幅为 40 mm, 在室温振荡 8 h 后取出烧杯, 静置 16 h。用 0.45 μm 微孔滤膜过滤并收集浸出液, 按照上述方法测定浸出液 Cr(VI) 及 TCr 浓度并计算含量, 考察电极板吸附对于 Cr(VI) 去除的贡献量。以上浸提过程参照 HJ 557—2010《固体废物浸出毒性浸出方法水平振荡法》进行^[24]。

2 结果与讨论

2.1 复合矿物元素及物相

XRF 元素含量分析显示, 磁铁矿/磁黄铁矿复合矿物中含有 Fe(63.95%, 质量分数, 下同)、O(21.72%)、S(10.23%)、Si(1.85%)、Ca(0.99%)、Na(0.41%)、Al(0.32%)、Mg(0.19%)、Mn(0.18%) 及 Ti(0.12%) 等元素, 其中 Fe、O 及 S 元素质量分数之和为 95.9%。

用 XRD 进一步研究了矿物样品的物相, 如图 2 所示。衍射峰在 $2\theta=30^\circ$, 35° 和 63° 对应于磁铁矿(220)、(311)、(440)晶面(JCPDS 01-079-0418)。衍射峰在 $2\theta=30^\circ$, 34° , 44° 对应于磁黄铁矿(100)、(101)及(102)晶面(JCPDS 01-075-0600)。同时结合元素分析结果, 推测 27° 及 29° 的特征峰为含钙钠等元素的硅酸盐杂质。经 highscore 半定量分析, 磁铁矿与磁黄铁矿质量分数分别为 70% 及 26%。

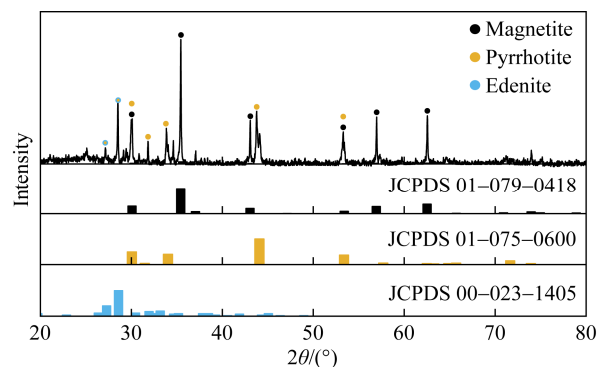


图2 磁铁矿/磁黄铁矿复合矿物 XRD 谱

Fig. 2 XRD patterns of magnetite/pyrrhotite composite mineral

2.2 复合矿物强化电修复系统效果

2.2.1 矿物材料的强化作用 在矿物单独处理下(记为 SM), 48 h 内中部及两侧监测点位的 Cr(VI) 质量浓度快速下降, Cr(VI) 初始去除速率分别为 $8.4 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ 及 $13.3 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ (见表 2)。修复完成后, 两侧监测点位中 Cr(VI) 去除率为 80.7%, 中部监测点位对应 Cr(VI) 去除率为 67.3%, 矿物材料较低的溶度积使得 Cr(VI) 去除并不彻底。

在电修复系统单独处理下(记为 SE), 前 48 h 阴阳极 Cr(VI) 初始去除速率分别为 $-0.4 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ 及 $8.0 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ 。修复完成后阳极 Cr(VI) 去除率为 43.2%, 阴极 Cr(VI) 去除率为 56.1% (见表 2)。

SM 或 SE 在单独处理 Cr(VI) 污染模拟土壤时, 都展现出了一定的效果, 但 Cr(VI) 质量浓度在降至 200 mg/L 后难以进一步降低(见图 3)。而在矿物强化

电修复体系(记为 ME)中, Cr(VI)质量浓度在修复 24 h 后降至 200 mg/L 并在第 7 d 趋近于 0, 阳阴极相对 SE 的 Cr(VI)处理率提升了 1 倍左右(见表 2)。

表 2 SM、SE 及 ME 体系下监测点位 Cr(VI)初始去除速率、去除率及相对去除率

Table 2 Initial removal rate, removal efficiency and relative removal efficiency of Cr(VI) at monitoring points under SM, SE, and ME systems

Reaction system	Initial removal rate/(mg·L ⁻¹ ·h ⁻¹)	Removal efficiency/%	Removal efficiency relative to SE/%
SM-middle	8.4	67.3	155.8
SM-both sides	13.3	80.7	143.8
SE-anode	-0.4	43.2	100.0
SE-cathode	8.0	56.1	100.0
ME-anode	18.6	99.5	230.3
ME-cathode	19.4	99.5	177.4

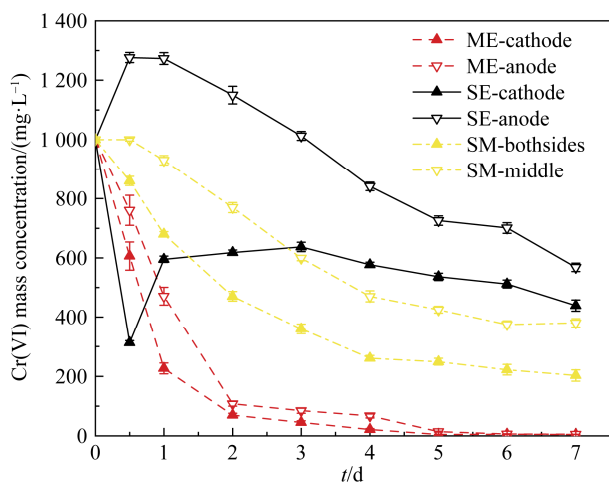


图 3 矿物修复、电修复及矿电修复下 Cr(VI) 的去除效果对比
Fig. 3 Comparison of Cr(VI) removal effect under mineral remediation, electro-remediation and mineral-enhanced electro-remediation

修复完成后将装置中的污染液抽出并水洗模拟土壤 3 次, 测定污染液、水洗液的 TCr 以及 Cr(VI) 浓度并计算相应含量(见表 3), 结果表明, 矿物强化电修复体系下, TCr 去除率相对电修复体系提升 2 倍。

表 3 SM、SE 及 ME 体系下 Cr(VI) 及 TCr 残留量与总体去除率

Table 3 Residue and overall removal efficiency of Cr(VI) and TCr in SM, SE and ME systems

Reaction system	Cr(VI) residue/mg	TCr residue/mg	Cr(VI) overall removal efficiency/%	TCr overall removal efficiency/%
SM	18.7	22.9	73.3	67.3
SE	34.9	47.9	50.1	31.6
ME	0.36	4.67	99.5	93.3

2.2.2 矿物填充方式及电势梯度对 Cr(VI) 去除的影响 不同矿物填充位置及电势梯度作用下, 各实验组均表现出良好的 Cr(VI) 治理效果(见表 4)。在电势梯度为 0.4 V/cm、矿物中部填充实验组(HM)中, 修复完成后阴阳两侧监测点位 Cr(VI) 浓度分别降至 0 mg/L 及 7.7 mg/L, 装置 Cr(VI) 总体去除率近 100%。在电势梯度为 0.4 V/cm、矿物两极填充实验组(HS)中, Cr(VI) 浓度在前 48 h 急速下降, 阳阴极 Cr(VI) 初始去除速率为 20.4 mg·L⁻¹·h⁻¹ 及 20.8 mg·L⁻¹·h⁻¹, 阴极 Cr(VI) 质量浓度降至 0 mg/L。修复完成后阴阳极监测点 Cr(VI) 质量浓度均降至 0 mg/L。

表 4 HM、HS、LM 及 LS 矿-电体系下监测点位 Cr(VI) 初始去除速率、去除率及相对去除率

Table 4 Initial removal rate, removal efficiency and relative removal efficiency of Cr(VI) at monitoring points in HM, HS, LM and LS systems

Reaction system	Initial removal rate/(mg·L ⁻¹ ·h ⁻¹)	Removal efficiency/%	Removal efficiency relative to SE/%
HM-anode	12.1	99.2	229.6
HM-cathode	14.2	100.0	178.3
HS-anode	20.4	100.0	231.5
HS-cathode	20.8	100.0	178.3
LM-anode	9.1	98.3	227.5
LM-cathode	11.1	99.6	177.5
LS-anode	11.3	100.0	231.5
LS-cathode	12.7	100.0	178.3

电势梯度为 0.2 V/cm、矿物中部填充实验组(LM)对 Cr(VI) 去除率在 98% 以上。电势梯度为 0.2 V/cm、矿物两极填充实验组(LS)中, 阴阳两极 Cr(VI) 浓度在第 6 d 趋近于 0, Cr(VI) 去除率 100%。

修复完成后将各装置中的污染液抽出并水洗污染土壤 3 次, 测定水洗液浓度并计算各装置中 Cr(VI) 及 TCr 含量。如表 5 所示, 电势梯度较高的 HM、HS 2 组实验体系对 TCr 的去除效果好于电势梯度

表 5 HM、HS、LM 及 LS 体系下 Cr(VI) 及 TCr 残留量与总体去除率

Table 5 Residue and overall removal efficiency of Cr(VI) and TCr in HM, HS, LM and LS systems

Reaction system	Cr(VI) residue/mg	TCr residue/mg	Cr(VI) overall removal efficiency/%	TCr overall removal efficiency/%
HM	0.0	3.2	100.0	95.4
HS	0.0	3.0	100.0	95.7
LM	0.1	11.9	99.8	82.9
LS	0.0	11.1	100.0	84.2

较低的实验体系(LM、LS), 同样的矿物填充位置下, 高电势组比低电势组的 TCr 总体去除率提升 10%以上。

2.3 修复稳定性

修复 7 d 后, 各组实验断电, 装置在室温静置 6 个月, 期间监测点位 Cr(VI)浓度未见上升, 说明该体系中 Cr(VI)不易溶出, 修复稳定性较好。为进一步模拟环境中地表水或地下水对修复后土壤的浸沥, 同时考察电极板吸附对 Cr(VI)去除的贡献量, 以水为浸提剂提取污染土壤和电极板中的 Cr(VI)。经测试分析, 各实验组污染土壤中 Cr(VI)残留量接近于 0, 各电极板除电修复实验组 SE 中阴极和阳极板各有 4.9、14.2 mg 残留, 其余电极板 Cr(VI)返溶

量近乎于 0 (见表 6)。该结果说明, 电修复体系 SE 中有大量 Cr(VI)返溶, Cr(VI)赋存形式并不稳定。而矿物强化电修复治理 Cr(VI)污染体系中, Cr(VI)返溶率低, Cr(VI)赋存状态较为稳定, 展现了该方法治理 Cr(VI)时的长期稳定性。

2.4 产物分析

针对矿-电实验体系, 借助磁性特征从模拟土壤水洗液分离得到一种可肉眼观察到的絮状产物和一种磁性颗粒产物, 利用搭载能谱仪的 ESEM 和 Raman 光谱仪对产物进行分析。SEM 照片(见图 4a)显示, 絮状产物表面不均匀地分布着亚微米球状颗粒, 球状颗粒的铬含量在 4%~5%间(见图 4b), 针状物质(见图 4c)主要为 CaSO₄。

表 6 电极板与模拟土壤的 Cr(VI)返溶量与返溶率*

Table 6 Redissolved amount and redissolved ratio of electrode plates and simulated soil*

Reaction system	Removal amount before leaching/mg	Redissolved amount of soil/mg	Redissolved amount of electrodes/mg	Total redissolved amount/mg	Redissolved ratio/%
SE	35.10	0.04	19.06	19.10	54.42
HM	70.00	0.01	0.15	0.16	0.23
HS	70.00	0.01	0.00	0.01	0.01
LM	69.86	0.01	0.35	0.36	0.52
LS	70.00	0.01	0.31	0.32	0.46

*The redissolved ratio was calculated by the ratio of total redissolved amount to removal amount before leaching.

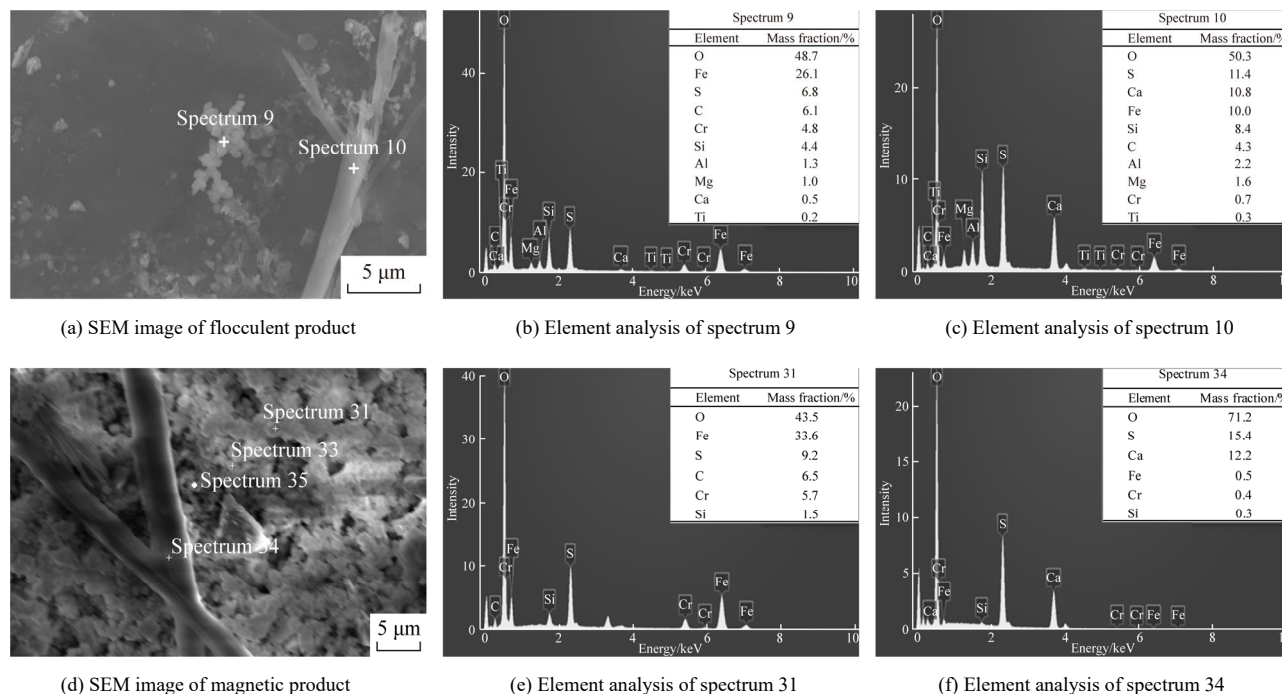


图 4 含铬产物 SEM 照片及元素分析

Fig. 4 SEM images and element analysis of Cr-containing products

EDS 面扫结果(见图 5)则说明, 铬的分布主要集中在球状颗粒上。同时, 铁与氧元素在此区域也更

为富集。利用 Python 对 Fe、Cr 及 O 元素的面扫图谱进行灰度化和二值化处理, 计算框选区域的图片

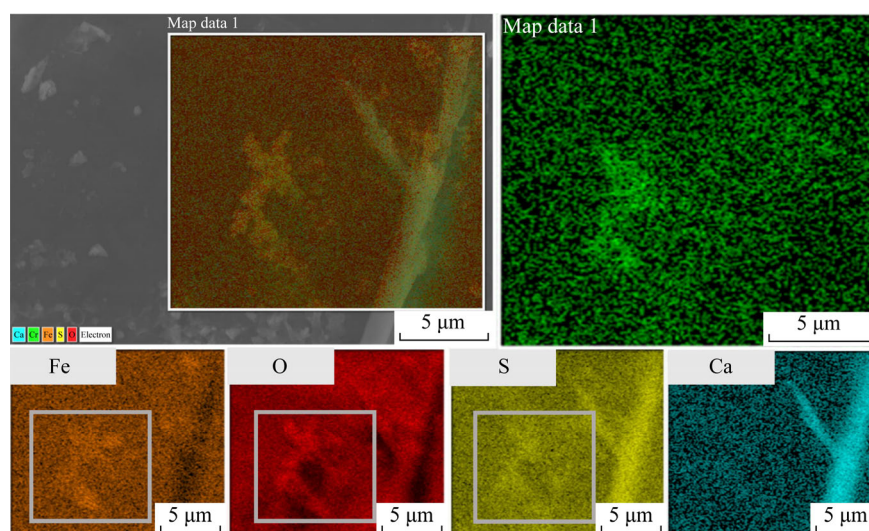


图 5 絮状产物 EDS 面扫描照片
Fig. 5 EDS mapping of flocculent product

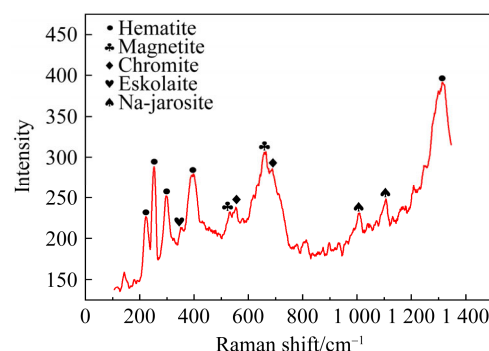
相似度。结果表明, 铬与铁、氧元素的分布具有高度相关性。根据以上结果, 推测球状颗粒是铁与铬的共沉淀氧化物或是氢氧化物^[25], 也可能是铬在铁氧化物上吸附或同晶替代 Fe(III) 形成^[26]。

与之相比, 磁性颗粒产物表面分布着更为密集的球状颗粒(见图 4d), 铬的质量占比在 4%~6% 之间(见图 4e)。同时, 产物中有一些硫酸钙的针状结晶(见图 4f), 说明矿物中的 S^{2-} 参与到了铬的还原。

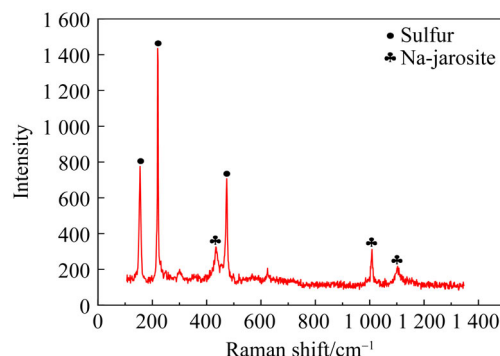
为进一步明晰可能的含铬产物, 利用 Raman 光谱仪和 XRD 对絮状物和磁性颗粒进行测试分析, 结果表明, 产物中存在着赤铁矿、绿铬矿、钠铁矾、硫酸钙及硫单质等产物(见图 6), Raman 结果显示, 223、253、298 cm^{-1} 对应赤铁矿; 350、553 cm^{-1} 分别对应绿铬矿^[27]的 E_g 、 A_{1g} ; 687、553 cm^{-1} 的主峰和 645 cm^{-1} 的肩峰对应铬铁矿^[28]; 664、532 cm^{-1} 对应磁铁矿^[29](图 6a); 221、434、1 008 cm^{-1} 和 1 103 cm^{-1} 对应钠铁矾^[29](图 6b)的 Raman 特征峰。此外, 发现了石膏、硫单质(见图 6b 和图 6c)等产物。以上含铁铬的产物因较差的结晶度, 较小的颗粒尺寸对峰强及峰位造成了一定影响。

磁性颗粒经 Highscore 分析为磁铁矿(见图 7), 并含有无定形硫酸铁杂质。与反应前的矿物材料相比, 其对应磁黄铁矿的特征峰 $2\theta=34^\circ$ 、 44° 未出现, 说明矿物材料中的磁黄铁矿在 Cr(VI) 的还原过程中起到了电子供体的关键作用, 结合本节上述的 Raman 分析, 磁黄铁矿在与 Cr(VI) 反应后转变成系列铁的氧化物氢氧化物, 同时促进了硫单质及硫酸盐的生成。

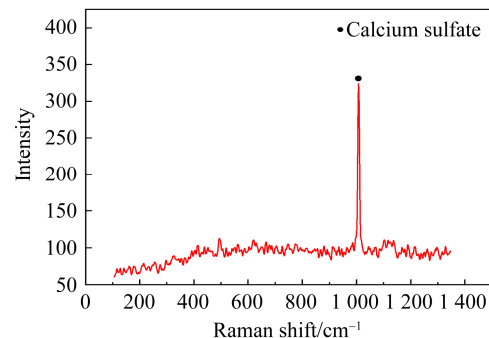
根据 2.2~2.4 节结果, 推测电-矿物协同作用下, 模拟土壤中 Cr(VI) 的去除机理包括磁铁矿/磁黄铁



(a) Raman spectra of Fe_2O_3 , Fe_3O_4 , FeCr_2O_4 , and Cr_2O_3



(b) Raman spectra of S and Na-jarosite



(c) Raman spectra of CaSO_4

图 6 絮状产物 Raman 分析

Fig. 6 Raman analysis of flocculent products

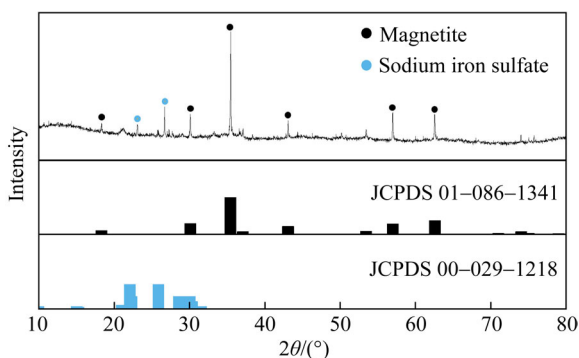
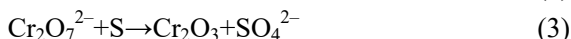
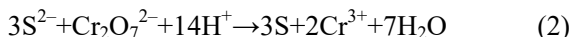
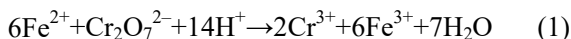


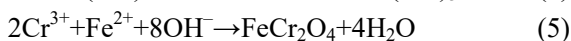
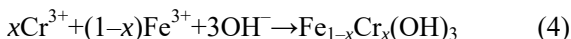
图7 磁性产物 XRD 谱

Fig. 7 XRD patterns of magnetic product

矿复合矿物和电极阴极对 Cr(VI)的还原、Cr(III)的沉淀及电极板的吸附等，过程中形成了绿铬矿、钠铁矾及类铬铁矿等产物。复合矿物与 Cr(VI)的反应方程式：



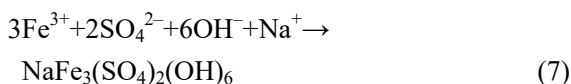
Cr(III)可与 Fe(III)共沉淀形成 $\text{Fe}_{1-x}\text{Cr}_x(\text{OH})_3$ ，同时也可能有类铬铁矿的生成：



在阴极偏碱性环境，被还原后的 Cr(III)可形成绿铬矿：



此外 Cr(VI)可从阴极上得到电子，矿物释放的 Fe(II)也可在迁往阴极后将 Cr(VI)还原。同时， SO_4^{2-} 及 Fe^{3+} 的存在，促进了钠铁矾等矿物的生成：



Cr(III)和 Cr(VI)可替换 Fe^{3+} 与 SO_4^{2-} 进而固定在矿物中以较稳定的形式存在。

3 结论

研究了矿物修复、电修复及矿物强化电修复 3 种方法对于 Cr(VI)污染土壤的处理效果，得到以下结论：

1) 矿物强化电修复对 Cr(VI)修复效果最好。矿物两侧填充、电势梯度 0.4 V/cm 的装置运行 7 d，Cr(VI)总体去除率 100%，TCr 总体去除率 95.7%。

2) 电势梯度是影响 Cr(VI)治理的主要因素。矿物填充位置相同时，电势梯度从 0.2 V/cm 升至 0.4 V/cm，TCr 总体去除率提升 10%以上。

3) 修复稳定性实验表明，矿物强化电修复实验

组中电极板与模拟土壤的 Cr(VI)返溶量接近于零，说明该修复方法对于 Cr(VI)治理具有长效性。

4) Cr(III)和 Cr(VI)替换 Fe^{3+} 与 SO_4^{2-} 进而固定在矿物中，是保持 Cr(VI)治理效果长效性的主要原因。

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Enhanced Electro-Remediation of Cr(VI) Contamination by Magnetite/Pyrrhotite Composite Mineral and Analysis of Cr-Containing Products

ZHOU Chuanye, JI Xiang, LU Anhuai, DING Hongrui, GE Xiao, WANG Changqiu, LI Yan
(School of Earth and Space Sciences, Peking University, Beijing 100871, China)

Extended Abstract

Introduction Electrokinetic remediation is a promising method for Cr(VI) treatment. Electrokinetic remediation operates based on a low-intensity electric field across the soil, which mobilizes contaminants towards the electrodes. Some previous studies tried to improve the mobility and availability of contaminants for extraction. However, the technology faces some challenges such as interference from non-target contaminants. It is thus necessary to develop the electrokinetic remediation with other technologies like chemical agents and permeable reactive barriers. Some minerals can be used to remediate Cr(VI) due to their properties like surface effect and redox effect. The existing researches on minerals for Cr(VI) remediation mainly focus on zero-valent iron (ZVI) materials. ZVI usually requires loading materials to minimize agglomeration. In this paper, a magnetite/pyrrhotite composite material (*i.e.*, pyrrhotite naturally dispersed in magnetite) was introduced to the electrokinetic remediation systems, mitigating shortage of electron donors in Cr(VI) contaminants and stabilizing Cr in the form of Cr-containing minerals. The impacts of mineral filling position and potential gradient on the Cr(VI) remediation performance were investigated, and the Cr-containing products were analyzed.

Methods The mineral enhanced electro-remediation devices consisted of acrylic reactors (length 100 mm, diameter 50 mm), and plate-shaped electrodes (length 80 mm, width 50 mm). The minerals were filled on the both sides or in the middle. The applied potential gradient was 0.2 V/cm or 0.4 V/cm, provided by a model CHI 1000C Electrochemical workstation. In the remediation process, the samples were taken at 12, 24, 36, 48, 72, 96, 120, 144 h, and 168 h, respectively. The concentrations of Cr(VI) were determined by a model Thermo Fisher EVOLUTION 220 UV visible spectrophotometer based on the national standard GB7467–87. The total Cr (TCr) concentrations were determined by a model SPECTROBLUE SOP inductively coupled plasma optical emission spectrometer, in accordance with HJ 776–2015 method. The mineral phase was tested by a model PANalytical X-pert3 powder X-ray diffractometer (XRD), and the element analysis was performed on a model Thermo ARL ADVENT XP+X-ray fluorescence spectrometer (XRF). The scanning electron microscopy images and energy dispersive X-ray spectroscopy mapping of Cr-containing products were performed by a model FEI Quattro S environmental scanning electron microscope (ESEM) at 15 kV. The Raman spectra were determined on a model Renishaw inVia Reflex Laser micro-Raman spectrometer with a 532 nm laser. After remediation, the reaction devices were maintained at room temperature for six months. Subsequently, the contaminated simulated soil underwent a second washing with ultrapure water to mimic leaching of harmful components into the environment under specific conditions. The concentrations of Cr(VI) and TCr were measured to evaluate the stability of the remediation. The electrodes were removed from the

devices, weighed, and placed in 250 mL beakers. The volume of leaching agent and water was determined at a liquid-to-solid ratio of 10:1 (L/kg). After adding the leaching agent, the beakers were sealed with a film and mounted vertically in a horizontal oscillation device (THZ-D). The oscillation settings were adjusted to 120 cycles per minute with an amplitude of 40 mm. The leachates were then filtered through a 0.45 μm microporous membrane, collected and analyzed for Cr(VI) and TCr concentrations. This process assessed the contribution of electrodes adsorption to Cr(VI) removal, following the guidelines of HJ 557–2010.

Results and discussion The XRF and XRD analysis demonstrate that the minerals in magnetite/pyrrhotite composite are mainly composed of 70% magnetite and 26% pyrrhotite. Moreover, the mineral material does not contain other heavy metals. The mineral and electrokinetic remediation both are effective in the treatment of Cr(VI)-contaminated simulated soil. However, reducing the Cr(VI) concentration below 200 mg/L proves a challenge. In contrast, the mineral-enhanced electro-remediation system reduces the Cr(VI) concentration to 200 mg/L within 24 h and progressively approaches zero at seventh day. Also, the removal efficiency of Cr(VI) at both the anode and cathode doubles, compared to electrokinetic remediation. The effects of potential gradient and mineral filling position on the remediation of Cr(VI) were investigated. The results reveal that the experimental systems with a higher potential gradient exhibit the superior removal efficiency for TCr, compared to those with a lower potential gradient. The removal efficiency of TCr in a high potential group exceeds that in a low potential group by more than 10% under identical mineral filling conditions. Moreover, within the same potential gradient, the mineral filling position exerts a minimal influence on the remediation outcome. The stability analysis of Cr-containing products demonstrates a reduction in the Cr(VI) re-dissolution ratio by over 54% in the mineral-enhanced electro-remediation group, compared to the electrokinetic remediation group, indicating that the generated Cr-containing products are relatively stable and resistant to re-dissolution. Based on the analysis by Raman spectroscopy, XRD, and ESEM, Cr in stable mineral phases is correlated to Fe distribution.

Conclusions Mineral-enhanced electro-remediation was the most effective approach for Cr(VI) removal. After 7 d operation of the device filled with minerals on both the sides and with a potential gradient of 0.4 V/cm, the overall removal efficiency of Cr(VI) and TCr was 100.0% and 95.7%, respectively. A potential gradient is the main factor affecting Cr(VI) treatment. The overall efficiency of total Cr was increased by more than 10% when the potential gradient was increased from 0.2 V/cm to 0.4 V/cm. The results of stability experiment showed that the amount of Cr(VI) re-dissolved from the electrodes, and the simulated soil in the mineral-enhanced remediation was close to zero, indicating that the remediation method had a long-term effect on the Cr(VI) treatment. The replacement of Fe^{3+} and SO_4^{2-} by Cr(III) and Cr(VI) in minerals was the main reason for maintaining the long-term effect of Cr(VI) treatment. This study could demonstrate the enhanced effect of magnetite/pyrrhotite composite mineral on the Cr(VI) removal, providing an effective approach for the long-term and stable remediation of Cr(VI)-contaminated sites.

Keywords magnetite/pyrrhotite composite mineral; mineral-enhanced effect; electro-remediation; chromium(VI) contamination