北京林业大学 Beijing Forestry University

2017年环境学院青年学术论坛暨
“水体污染源控制技术”北京市重点实验室年会

ZVI基材料的制备及其去除Cr(VI)性能的研究

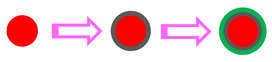
邱 斌

研究背景

含六价铬(Cr(VI))废水的处理思路：Cr(VI)（毒性强、易迁移）—电子供体→ Cr(III)（毒性低、易固定）

零价铁(Zero valent iron, ZVI）是一种去除Cr(VI)的理想材料，但其易氧化和受H^+侵蚀，导致了其电子的浪费；电性相斥， 不利于还原后Cr(III)的进一步去除。

解决方式：采用核壳结构提高ZVI的稳定性。



研究内容

（1） ZVI基复合材料的制备与表征

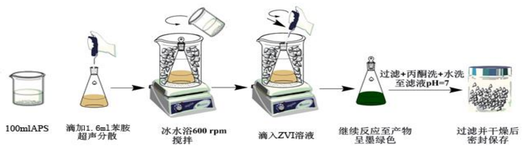
（2） ZVI基复合材料去除Cr(VI)的性能研究

（3） ZVI基复合材料去除Cr(VI)的机制解析

研究方法

(1)ZVI基复合材料

水热法+热裂解+表面聚合



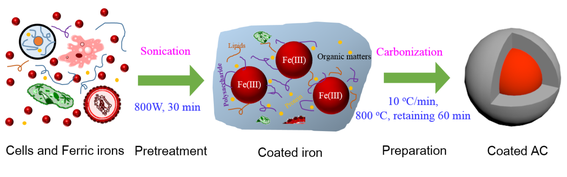
(2)多孔PANI材料的表征

- ❖ 形貌特征(SEM、TEM)
- ❖ 结构特征(BET、XRD、Raman)
- ❖ 化学性质(FT-IR、XPS、Zeta电位、SEM-EDS)

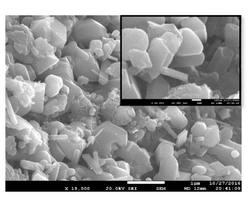
研究结果

1 ZVI@C复合材料

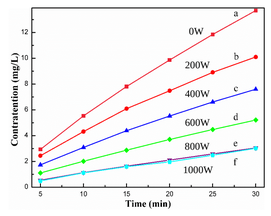
1.1 ZVI@C复合材料制备与表征



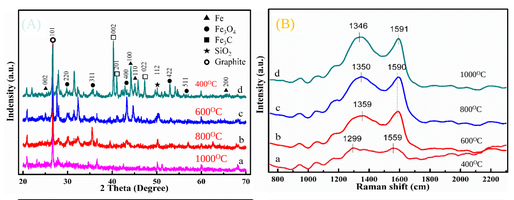
ZVI@C制备路线



ZVI@C形貌

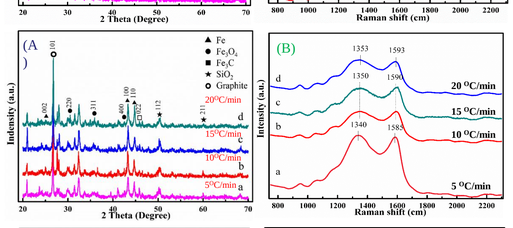


ZVI@C的稳定性



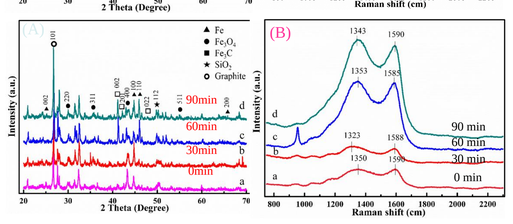
Samples	BET surface area (m^2/g)	Average pore size (Å)
UMCs-10-400-0	22.29	118.6
UMCs-10-600-0	20.38	81.1
UMCs-10-800-0	103.65	31.4
UMCs-10-1000-0	114.24	35.8

❖ 最佳碳化温度为800℃



Samples	BET surface area (m^2/g)	Average pore size (Å)
UMCs-05-800-0	91.39	33.4
UMCs-10-800-0	103.65	31.4
UMCs-15-800-0	78.04	32.8
UMCs-20-800-0	71.50	40.1

❖ 最佳升温速率为10℃/min

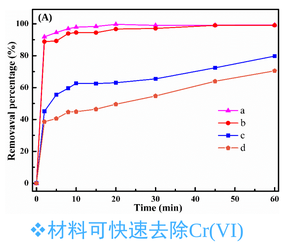


Samples	BET surface area (m^2/g)	Average pore size (Å)
UMCs-10-800-0	103.65	31.4
UMCs-10-800-30	118.93	61.7
UMCs-10-800-60	131.13	34.7
UMCs-10-800-90	124.15	51.3

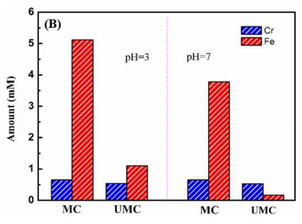
❖ 最佳保留时间为30min

ZVI@C的化学性质

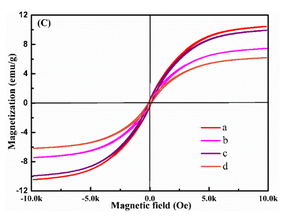
1.2 ZVI@C复合材料去除Cr(VI)性能



❖材料可快速去除Cr(VI)

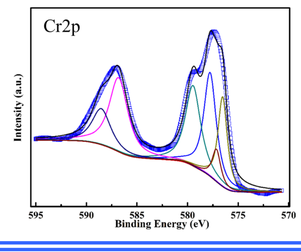


❖超声磁性碳的铁流失少



❖超声磁性碳的磁稳定性好

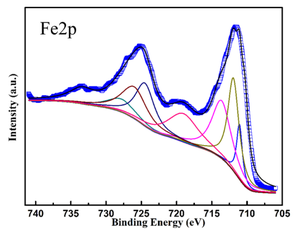
1.3 ZVI@C复合材料去除Cr(VI)机制



Fe(III) ← Fe(0)

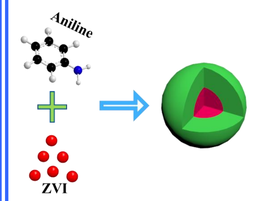
↓

Cr(VI) → Cr(III)

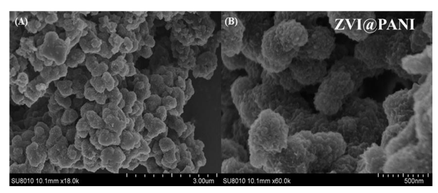


2 ZVI@C@PANI复合材料

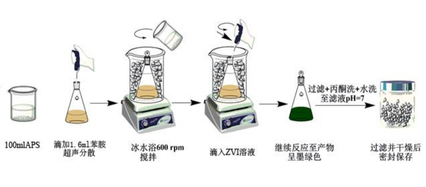
2.1 ZVI@PANI复合材料制备及应用



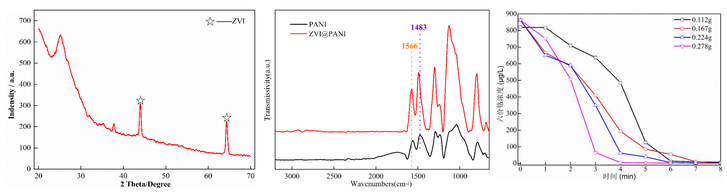
ZVI@PANI制备机理

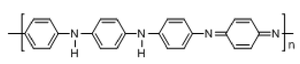


ZVI@PANI形貌



ZVI@PANI制备方法





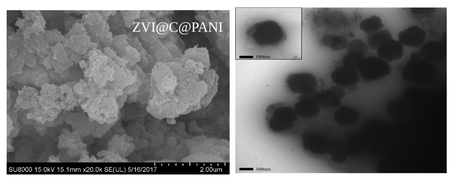
PANI为中间氧化还原态可作为电子供体，与ZVI一起快速还原Cr(VI)。

ZVI@PANI的化学性质与除铬性能

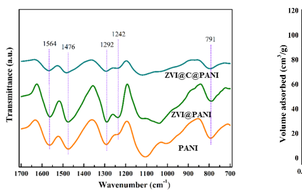
2.2 ZVI@C@PANI复合材料

2.2.1 ZVI@PANI复合材料制备与表征

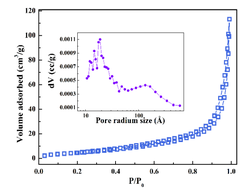
ZVI@C@PANI制备方法



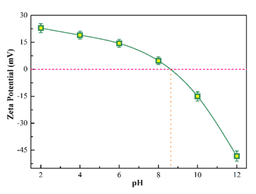
ZVI@C@PANI形貌与空间结构



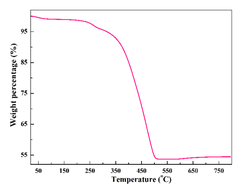
FI-RT:富含-NH-的EB态



BET：介孔结构-物质传递



Zeta:适宜的等电点



TGA:充足的ZVI

2.2.2 ZVI@C@PANI复合材料去除Cr(VI)性能

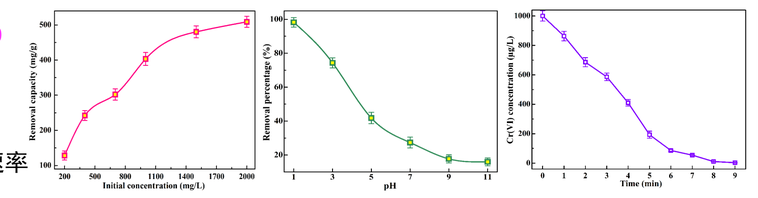
- ❖ Cr(VI)去除速率快

ZVI@C@PANI (5 ~6min) < PANI (60 min)

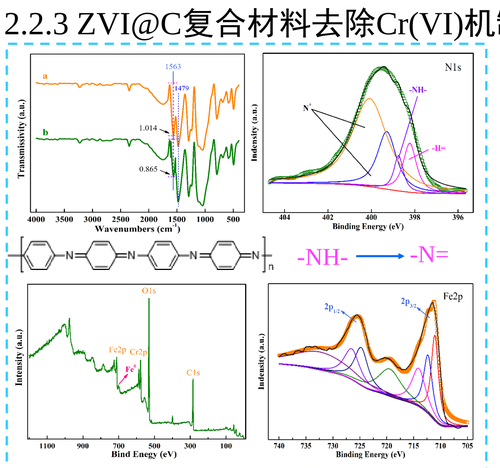
- ❖ Cr(VI)去除容量大（202 mg/g）

ZVI@C@PANI> PANI (190 mg/g)

- ❖ 酸性条件明天提高Cr(VI)去除速率



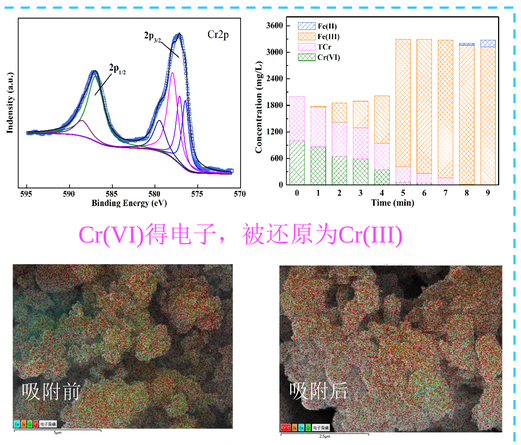
2.2.3 ZVI@C复合材料去除Cr(VI)机制



-NH- → -N=

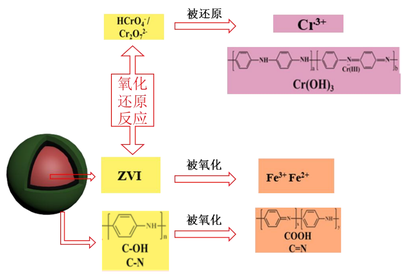
Fe(0) → Fe(III)

e⁻



Cr(VI)得电子，被还原为Cr(III)

Cr(III)被吸附到材料表面



$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$ E^0= +1.33 V

$CrO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$ E^0= +1.48 V

$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$ E^0= +1.35 V

$H_2CrO_4 + 6H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$ E^0= +1.33 V

研究结论

- ☐ 污泥等生物质可为碳源制备ZVI基碳材料；
- ☐ 超声预处理可增加污泥中溶解性碳源的释放，提高制备的磁性碳的稳定性；
- ☐ 核壳结构的ZVI复合材料可实现对废水中Cr(VI)的快速去除，并将Cr(VI)还原为Cr(III)，实现对Cr(VI)的脱毒；
- ☐ 三层核壳结构的ZVI@C@PANI中C@PANI对ZVI核起到了缓释的作用，提高了ZVI作为电子供体的能力。

课题来源

- 北京林业大学青年教师科学研究中长期项目. 用于污水深度处理的环境功能材料研发与应用 (NO. 2016ZCQ03)