亚微米磁铁矿强化反硝化降解苯酚和喹啉

王竞*, 孙煜姣, 马姝, 王奉博

大连理工大学环境学院, 大连 116024

* 联系人, E-mail: jwang@dlut.edu.cn

2020-06-23 收稿, 2020-07-18 修回, 2020-08-07 接受, 2020-08-07 网络版发表

国家自然科学基金(21876018, 51278080)资助

摘要 导电性磁铁矿(Fe_3O_4)已被证实能促进厌氧微生物直接种间电子传递. 然而磁铁矿在厌氧水处理过程中会被铁还原菌利用而溶解, 造成大量磁铁矿随出水流失, 影响其长期介导作用. 基于此, 本研究在微氧连续运行的活性污泥反应器(activated sludge reactor, AS)中投加亚微米级($0.1\sim0.3\ \mu\text{m}$)磁铁矿建立 $\text{Fe}_3\text{O}_4/\text{AS}$ 复合体系(R2), 以强化反硝化生物降解苯酚和喹啉, 并探讨其作用机理. 结果表明, 在微氧条件下($\text{DO}=0.5\sim1.0\ \text{mg/L}$)运行80 d后, R2体系有效缓解了磁铁矿的还原溶解, 反应器中铁矿物主要以磁铁矿和针铁矿形式存在, 其出水 Fe^{2+} 浓度始终保持在 $0.2\ \text{mg/L}$ 左右; 当进水喹啉浓度为 $55\ \text{mg/L}$ 时, R2体系中化学需氧量、苯酚、喹啉、 $\text{NO}_3\text{-N}$ 、总有机碳和总氮去除率比对照组R1分别提高了38%、49%、65%、64%、23%和98%. 机理研究表明, R2中与反硝化和芳烃降解有关的菌属(如*Denitratissoma*和*Azoarcus*)丰度显著提升; 磁铁矿刺激了胞外聚合物(extracellular polymeric substances, EPS)的分泌(约为R1的2倍)和污泥微生物间的凝聚; 磁铁矿的加入显著提高了EPS中胞外电子穿梭体(血红素c和类腐殖酸)浓度以及污染物降解和氮还原相关的酶活性(R2 EPS中脱氢酶、硝酸盐还原酶和亚硝酸盐还原酶活性分别是R1的2.4、5.8和4.3倍), 从而加快了芳烃降解菌与反硝化菌之间的电子传递速率, 实现了 $\text{Fe}_3\text{O}_4/\text{AS}$ 体系更好的脱氮除碳性能.

关键词 磁铁矿, 反硝化, 苯酚, 喹啉, 胞外聚合物, 胞外电子传递

焦炭行业在生产过程中会产生和排放出大量水质成分复杂的焦化废水, 主要包含酚类、氨氮、氰化物、氮杂环芳烃(如喹啉等)及多环芳烃等污染物, 是一种典型的难降解有机废水^[1~3]. 化学需氧量(chemical oxygen demand, COD)和氨氮难以同时达标排放成为目前大多数焦化废水处理面临的难题, 未达标废水一旦进入环境会严重威胁人体健康和生态环境, 因此研发经济高效的焦化废水处理技术迫在眉睫.

针对焦化废水, 吸附、电解、膜分离以及臭氧氧化等物理化学法, 处理成本较高并且还会产生二次污染^[4]; 而具有处理量大、应用范围广、处理成本低等优点的生物法, 已成为焦化废水的主要处理工艺^[5]. 目

前焦化厂废水生物处理主要有厌氧-缺氧-好氧工艺(anaerobic-anoxic-oxic, A^2/O)、序批式活性污泥法(sequencing batch reactor activated sludge process, SBR)、曝气生物滤池法等. 但是这些常规的焦化厂废水生物处理工艺通常会导致出水COD、总氮和色度较高, 难以实现达标排放, 于是衍生出一些强化焦化废水生物处理新技术. 如在传统 A^2/O 后再增设一个好氧单元(A^2/O^2 工艺), 进一步去除 A^2/O 出水中COD和氨氮等污染物^[6]. 采用缺氧-好氧-水解-好氧(A/O/H/O 工艺)处理广东韶钢焦化废水, 结果发现该工艺在合理协调脱氮除碳过程的同时还可以实现氰化物的高效降解^[7]. 另外, 通过投加苯酚降解菌的生物强化技术也可提高焦化废

引用格式: 王竞, 孙煜姣, 马姝, 等. 亚微米磁铁矿强化反硝化降解苯酚和喹啉. 科学通报, 2020, 65: 2914-2921

Wang J, Sun Y J, Ma S, et al. Submicron magnetite enhanced simultaneous denitrification and degradation of phenol and quinoline (in Chinese). Chin Sci Bull, 2020, 65: 2914-2921, doi: [10.1360/TB-2020-0752](https://doi.org/10.1360/TB-2020-0752)

水COD的去除率^[8]。但这些强化生物处理技术存在着构筑物增多,或投加菌有效性难以长期保持,基建和运行成本增高等弊端。

近年来,磁铁矿因廉价易得,且具备良好的导电性和磁性,被逐渐应用于废水生物处理领域^[9]。研究发现导电性磁铁矿能加速微生物直接种间电子传递(direct interspecies electron transfer, DIET)^[10],并促进相关酶活性和微生物生长,从而提高污染物的去除效率。但是磁铁矿在废水生物处理中存在以下两个问题:一是磁铁矿粒径,研究表明纳米级磁铁矿可进入微生物细胞内,进而损害微生物活性甚至造成细胞死亡^[11],而微米级及以上粒径的磁铁矿比表面积较小,与污泥菌体接触不充分,会削弱其强化效果。二是在厌氧生物反应器中,部分微生物如异化铁还原菌能利用磁铁矿,将其还原溶解成亚铁离子随出水流失^[12],从而使其介导作用不可持续。基于此,本研究在微氧(DO=0.5~1.0 mg/L)生物反应器中投加亚微米级磁铁矿颗粒,建立Fe₃O₄/AS复合体系以强化反硝化降解苯酚和喹啉,并探究其作用机理,以期对含氮、酚类和氮杂环类等难降解有机废水的高效生物处理提供理论依据。

1 实验

(i) 材料。苯酚(99%纯度)购于天津市大茂化学试剂厂,喹啉(98%纯度)购于阿拉丁试剂公司(上海),亚微米磁铁矿(0.1~0.3 μm)购于阿拉丁试剂公司(上海)。所用试剂均为分析纯。模拟焦化废水含有以下组分(mg/L):苯酚(220)、NH₄Cl(150)、KH₂PO₄(200)、CaCl₂(25)、MgCl₂(100)、NaHCO₃(500)、1 mL/L微量元素营养液(其组成见表S1),pH 7.0,喹啉、NaNO₃浓度根据体系不同运行阶段进行添加。接种污泥取自大连春柳河城市污水处理厂二沉池,污泥浓度(mixed liquid suspended solids, MLSS)为8 g/L,挥发性污泥浓度(mixed liquid volatile suspended solids, MLVSS)为6 g/L。

(ii) 批次实验。以250 mL血清瓶作为厌氧反应器,考察亚微米磁铁矿投加比例对污染物生物去除效率的影响。为防止高浓度苯酚和喹啉对活性污泥产生毒害作用,每个血清瓶中硝态氮120 mg/L、COD当量660 mg/L,其中苯酚100 mg/L,喹啉10 mg/L,其余由葡萄糖提供。量取125 mL活性污泥倒入血清瓶,使得反应体系MLSS为4 g/L,亚微米磁铁矿投加量分别为0.4、0.8、1.2和1.6 g/L,混匀体系,不添加磁铁矿的作为对照组。所有批次试验均在相同条件下进行:将用橡胶塞

密封的血清瓶置于35℃恒温摇床中,150 r/min,反应12 h。血清瓶胶塞处扎有针头,创造微氧的反应环境。所有反应体系均设置3个平行样,反应结束后测定各体系中COD、苯酚、喹啉及硝态氮的去除率。

(iii) 实验装置和基本参数。实验装置主要由反应器主体(圆形有机玻璃制成,有效容积1.5 L)、进水泵、循环泵、恒温水浴锅、曝气装置等组成,如图S1所示。模拟焦化废水从底部经蠕动泵送入反应器内,出水从反应器顶部排出;通过调节蠕动泵转速控制进水量,从而改变反应器的水力停留时间;通过调节进水瓶中曝气装置的曝气量,使反应器保持微氧状态;通过蠕动泵实现内循环扰动,使污泥与进水充分混匀;反应器外壁设有保温夹层软管,使反应器内温度一直稳定在35℃左右。

R1和R2中MLSS均为8 g/L,R2中添加2 g/L亚微米级磁铁矿颗粒,只添加活性污泥的R1为对照组。R1和R2体系中DO=0.5~1.0 mg/L,水力停留时间(HRT)12 h,35℃恒温条件下连续运行80 d。运行可以分为启动阶段(1~30 d)、驯化阶段(31~70 d)和稳定阶段(71~80 d),不同时间段的进水条件和检测指标见表S2。

(iv) 分析方法。根据《水和废水监测分析方法》(第四版)进行COD、MLSS、MLVSS、NO₃-N、NO₂-N、总有机碳(total organic carbon, TOC)以及总氮(total nitrogen, TN)等常规指标的检测。分别使用数字溶解氧仪(YSI, 模式55, 美国)和数字pH计(PHS-25, 莱西公司, 中国)测量DO和pH。采用邻菲罗啉分光光度法测定铁和总铁的浓度。苯酚、喹啉及其中间降解产物采用高效液相色谱分析;胞外聚合物(extracellular polymeric substances, EPS)、脱氢酶(dehydrogenases, DHA)和血红素c(heme c)、硝酸盐还原酶(nitrate reductase, NR)和亚硝酸盐还原酶(nitrite reductase, NIR)活性的测定,活性污泥的扫描电子显微镜(SEM)、X射线衍射(XRD)分析、16S rRNA基因高通量测序方法见补充材料。

2 结果与讨论

2.1 亚微米Fe₃O₄对苯酚、喹啉以及硝态氮去除的影响

批次实验结果表明,亚微米Fe₃O₄/AS复合体系(质量比 $W_{\text{Fe}_3\text{O}_4}:W_{\text{AS}}=0.25$)对COD、苯酚和喹啉的去除效率最高(图S2),故以该Fe₃O₄投加量进行后续实验。在反应器连续运行初期,R1和R2体系对COD、硝态氮、苯酚

的去除率均可达到80%~90%，推测低浓度喹啉可能未对微生物生长代谢产生明显抑制。两个体系对于喹啉的去除率分别为68%和77%(图1)。随着进水喹啉浓度的增大(17~40 mg/L)，R1和R2两个体系脱氮除碳效率差距逐渐增大，R2的降解优势开始显现。最终进水中喹啉浓度提升至40~55 mg/L时，R2对COD、苯酚、喹啉和硝态氮的平均去除率为93%、99%、84%和84%，比R1平均高出了38%、49%、65%和64%。这表明高浓度喹啉已经对R1中的降解菌群产生了明显的毒害作用，而 $\text{Fe}_3\text{O}_4/\text{AS}$ 复合体系仍具有良好的污染物降解性能和抗冲击负荷能力^[11,13]。反应器稳定运行后，R1和R2出水中的亚硝态氮浓度均在5 mg/L以下。

为了确定苯酚和喹啉在反应器中是否彻底矿化为 CO_2 ，对两个反应器稳定运行阶段的出水进行了TOC/TN分析。结果显示，R2对TOC、TN的去除率为86%、81%，分别比R1提高23%和98%，表明亚微米磁铁矿的加入可使苯酚和喹啉大部分矿化为 CO_2 和 H_2O (与图S3结果吻合)，降低反应器出水的TOC和TN，从而减轻废

水排放对生态环境产生的不利影响^[14]。

2.2 机理分析

2.2.1 EPS

EPS对污泥絮体的结构和功能具有重要作用^[15]，如对有机污染物、重金属、氮和磷具有一定的吸附能力^[16]，含有胞外降解酶，且可促进细胞间电子传递^[17]等。亚微米磁铁矿能刺激活性污泥分泌更多的EPS，R2活性污泥EPS中多糖和蛋白质的浓度几乎是R1的2倍，如图S4所示。SEM分析进一步表明R2中亚微米磁铁矿紧密地附着在微生物表面(图2(b))，增强了活性污泥微生物间的凝聚，为潜在种间电子传递创造了有利的空间条件，并发挥高效吸附降解污染物和抵御有毒物质的能力。根据三维荧光光谱中激发/发射(E_x/E_m)荧光峰的位置^[18]，可见R1和R2污泥EPS中具有2个相同的荧光峰类型，Peak A(330/400 nm)和Peak B(260/300 nm)，分别为可作为电子穿梭体的类腐殖酸物质^[19,20]和表征微生物代谢活性的类溶解性微生物产物(图2(c), (d))。R2

图1 两个体系中COD(a)、苯酚(b)、喹啉的去除率(c)以及亚硝态氮出水浓度和硝态氮的去除率(d)

Figure 1 Removal efficiencies of COD (a), phenol (b) and quinolone (c), effluent concentration of nitrite nitrogen and removal efficiencies of nitrate nitrogen (d) in the two systems

图2 R1(a)和R2(b)中污泥SEM图以及R1(c)和R2(d)中EPS三维荧光光谱

Figure 2 SEM images of sludge in R1 (a) and R2 (b), and three-dimensional fluorescence spectrum of EPS in R1 (c) and R2 (d)

中Peak A和Peak B的荧光强度均显著高于R1, 表明导电性磁铁矿的加入能增强活性污泥中微生物的代谢活性; 并提高EPS中介体浓度, 促进微生物间的胞外电子传递, 有助于有机污染物的生物降解.

2.2.2 NR、NIR、DHA和heme c

NR和NIR是生物反硝化过程中的关键酶^[21]; 而活性污泥中DHA和heme c含量直接关系到有机物的转化速率^[22]. R2污泥总的NR和NIR活性分别是R1的2.2和4倍; R2污泥EPS中NR和NIR活性分别是R1的5.8和4.3倍(图3). 污泥EPS中具有NR和NIR活性表明反硝化反应可在胞外发生. 反应器连续运行80 d后, R2中DHA含量是R1的2.4倍. R2中NR、NIR和DHA均显著高于R1, 有利于R2体系中反硝化菌更充分地利用进水苯酚和喹啉作为电子供体, 加速硝态氮还原为氮气的过程.

Heme c作为细胞色素c的活性中心, 能够间接地反映出细胞色素c的浓度^[23]; 而细胞色素c可作为电子传递的通道, 协助微生物在同种或不同种微生物之间甚至微生物与胞外矿物之间完成电子传递过程^[24]. R2反应器中无论是污泥总的还是污泥EPS中heme c含量均高于R1, 分别是R1的1.8和3.1倍. 因此, 亚微米磁铁矿

可加速R2体系中苯酚、喹啉降解菌和反硝化菌之间的胞外电子传递速率, 实现更好的脱氮除碳效果. 另外, 将以上酶活性分别乘以两个体系污泥和EPS中蛋白质含量, 得到污泥EPS中heme c、NR和NIR对脱氮除碳的相对贡献度. 结果表明, R2污泥EPS中heme c、NR和NIR占总的比率分别是对应R1的1.6、5.5和1.5倍, 表明亚微米磁铁矿的加入不仅刺激污泥产生更多EPS, 还显著地提高了EPS中相应胞外酶对污染物的去除效率.

2.2.3 微生物群落和Fe转化

对R1和R2的微生物群落组成进行了属水平分析, 如图4(a)所示. 变形菌门(*Proteobacteria*)下的雌甾二醇降解反硝化菌属(*Denitratisoma*)、热单胞菌属(*Caldimonas*)和固氮弓菌属(*Azoarcus*)为优势菌属. 在R2中的相对丰度为20.5%、11.2%和8.7%, 分别是R1相应菌属丰度值的1.9、1.8和138倍. 其中, *Denitratisoma*是红环菌科的一个新属, 是一类异养反硝化菌, 能直接将亚硝态氮转化为氮气^[25]; *Azoarcus*, 近年来研究发现其具有在反硝化条件下去除复杂有机物的能力, 尤其是芳香族化合物, 被认为携带有苯环开环基因^[26-29]. 工业污水中分离的*Azoarcus*被证明在好氧和厌氧条件下, 能通过

图3 R1和R2活性污泥、EPS中硝酸盐还原酶(a)、亚硝酸盐还原酶活性(b)和脱氢酶和血红素c含量(c)
Figure 3 Activity of nitrate reductase (a), nitrite reductase (b) and contents of dehydrogenase, heme c (c) in activated sludge and EPS of R1 and R2

图4 R1和R2中属水平微生物群落组成(a)以及亚微米磁铁矿和R2中污泥XRD图谱(b)
Figure 4 Microbial community composition at genus level in R1 and R2 (a), and XRD pattern of submicron magnetite and sludge in R2 (b)

相同的途径降解杂环胺中的吡啶^[30]。根据最大似然法构建进化树,发现*Caldimonas*和*Denitratisoma*具有很近的亲缘关系,推测*Caldimonas*的功能与*Denitratisoma*类似,可能与生物脱氮有关。因此, R2中富集了与反硝化脱氮和芳香族有机物降解有关的优势菌属,促使R2具有更好地污染物去除性能。

XRD谱图分析表明,在微氧条件下运行时, $\text{Fe}_3\text{O}_4/\text{AS}$ 体系中有部分磁铁矿经过转变生成了针铁矿(图4(b))。陶巍和王进^[31]的研究表明针铁矿可以作为反硝化生物滤池的填料,促进不同微生物之间的电子转移速率,加速微生物对硝酸盐的还原过程。Tan等人^[32]研究发现针铁矿的加入可以促进藻类厌氧产甲烷过程。因此,新生成的针铁矿和磁铁矿均可作为电子传递的载体,促进R2体系脱氮和有机物降解。另外,为了考察 $\text{Fe}_3\text{O}_4/\text{AS}$ 复合体系中Fe溶出情况,分析了R1和R2出水中的 Fe^{2+} 浓

图5 苯酚/喹啉降解菌与反硝化菌间潜在直接种间电子传递示意图
Figure 5 Proposed DIET diagram between phenol/quinoline degrading bacteria and denitrifying bacteria

度, 结果如图S5所示. 在微氧条件下连续80 d的运行过程中, R1和R2出水中 Fe^{2+} 浓度稳定在0.2 mg/L左右, 始终低于1 mg/L; 运行80 d后, R2中总铁含量仅随出水流失31.8%, 与厌氧条件下磁铁矿的大量溶出相比, 微氧条件能有效缓解磁铁矿的溶解, 从而持续地强化毒性难降解污染物的微生物降解和反硝化脱氮能力.

综上, 除了自身可作为电子传递载体之外, 亚微米磁铁矿还能够提高反应器活性污泥EPS中电子穿梭体的浓度, 如heme c和类腐殖酸. 电子穿梭体与磁铁矿发挥协同作用, 加快芳香烃降解菌与反硝化菌之间的胞外电子传递速率, 从而有效地强化 $\text{Fe}_3\text{O}_4/\text{AS}$ 复合体系

的脱氮除碳效果(图5).

3 结论

亚微米磁铁矿在微氧条件下可有效地缓解其还原溶解, 刺激活性污泥分泌更多EPS, 增强微生物间的凝聚, 而且显著提高了EPS中胞外电子穿梭体浓度, 以及污染物降解效率、氮还原相关的酶活性和功能菌群丰度, 加快了芳烃降解菌与反硝化菌之间的电子传递速率, 从而有效强化 $\text{Fe}_3\text{O}_4/\text{AS}$ 体系对COD、苯酚、喹啉和 $\text{NO}_3\text{-N}$ 的去除性能, 为研发焦化废水及其他难降解有机废水高效处理技术提供了理论依据.

参考文献

- Ronen Z, Vasiluk L, Abeliovich A, et al. Activity and survival of tribromophenol-degrading bacteria in a contaminated desert soil. *Soil Biol Biochem*, 2000, 32: 1643–1650
- Öberg K, Warman K, Öberg T. Distribution and levels of brominated flame retardants in sewage sludge. *Chemosphere*, 2002, 48: 805–809
- Hassenklöver T, Predehl S, Pilli J, et al. Bromophenols, both present in marine organisms and in industrial flame retardants, disturb cellular Ca^{2+} signaling in neuroendocrine cells (PC12). *Aquat Toxicol*, 2006, 76: 37–45
- Shan M, Yang P, Pan D, et al. Study on coke dry quenching production and recycling of coking wastewater. *Front Environ Sci*, 2012, 1: 7–9
- Xing L, Zhang J, Jiang A, et al. Characteristics of pollutants degradation during catalytic ozonation of coking wastewater. *Chin J Environ Eng*, 2017, 11: 2001–2006
- Min Y G, Cui L P, Xue Y L. The practice of coking wastewater with A_2/O_2 process (in Chinese). *Technol Water Treat*, 2012, 38: 123–125 [闵玉国, 崔利平, 薛英连. A_2/O_2 工艺处理焦化废水工程实践. *水处理技术*, 2012, 38: 123–125]
- Huang H J, Wei C H, Wu C F, et al. Characteristics of cyanide degradation in A/O/H/O coking wastewater treatment (in Chinese). *Chem Prog*, 2011, 30: 1141–1146 [黄会静, 韦朝海, 吴超飞, 等. 焦化废水生物处理A/O/H/O工艺中氰化物的去除特性. *化工进展*, 2011, 30: 1141–1146]
- Wang J, Yuan H, Shi L Y, et al. Research on the bio-augmentation treatment process of coking wastewater (in Chinese). *Ind Water Treat*, 2017, 37: 41–45 [王津, 苑辉, 侍浏洋, 等. 焦化废水生物强化处理工艺研究. *工业水处理*, 2017, 37: 41–45]
- Liu Y, Li J, Guo W, et al. Use of magnetic powder to effectively improve the performance of sequencing batch reactors (SBRs) in municipal wastewater treatment. *Bioresour Technol*, 2018, 248: 135–139
- Aulenta F, Rossetti S, Amalfitano S. Conductive magnetite nanoparticles accelerate the microbial reductive dechlorination of trichloroethene by promoting interspecies electron transfer processes. *ChemSusChem*, 2013, 6: 433–436
- Ma B, Wang S, Li Z, et al. Magnetic Fe_3O_4 nanoparticles induced effects on performance and microbial community of activated sludge from a sequencing batch reactor under long-term exposure. *Bioresour Technol*, 2017, 225: 377–385
- Ambuchi J J, Zhang Z, Shan L, et al. Response of anaerobic granular sludge to iron oxide nanoparticles and multi-wall carbon nanotubes during beet sugar industrial wastewater treatment. *Water Res*, 2017, 117: 87–94
- Ni S Q, Ni J, Yang N, et al. Effect of magnetic nanoparticles on the performance of activated sludge treatment system. *Bioresour Technol*, 2013, 143: 555–561
- Li Y, Peng Y, Gu G, et al. Degradation of organic compounds in coal coking wastewater treated by the $\text{A}_1\text{-A}_2\text{-O}$ biofilm system. *Acta Sci Circum*, 2004, 24: 242–248
- Zhang P, Feng B, Chen Y P, et al. *In situ* characterizations for EPS-involved microprocesses in biological wastewater treatment systems. *Crit Rev Env Sci Technol*, 2019, 49: 917–946
- Yan L, Zhang S, Hao G, et al. Simultaneous nitrification and denitrification by EPSs in aerobic granular sludge enhanced nitrogen removal of ammonium-nitrogen-rich wastewater. *Bioresour Technol*, 2016, 202: 101–106
- Xiao Y, Zhang E, Zhang J, et al. Extracellular polymeric substances are transient media for microbial extracellular electron transfer. *Sci Adv*, 2017, 3: e1700623
- Chen W, Westerhoff P, Leenheer J A, et al. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ Sci Technol*, 2003, 37: 5701–5710
- Newman D K, Kolter R. A role for excreted quinones in extracellular electron transfer. *Nature*, 2000, 405: 94–97

- 20 Lovley D R, Coates J D, Blunt-Harris E L, et al. Humic substances as electron acceptors for microbial respiration. *Nature*, 1996, 382: 445–448
- 21 Zheng X, Wu R, Chen Y. Effects of ZnO nanoparticles on wastewater biological nitrogen and phosphorus removal. *Environ Sci Technol*, 2011, 45: 2826–2832
- 22 Su C Y, Li W G, Huang Z, et al. Influence on activated sludge characteristics of anthraquinones before and after pre-treatment by heterogeneous Fenton-like (in Chinese). *China Environ Sci*, 2015, 35: 2351–2359 [宿程远, 李伟光, 黄智, 等. 蒽醌类物质经多相类芬顿预处理前后对活性污泥特性的影响. *中国环境科学*, 2015, 35: 2351–2359]
- 23 Schwarzenbach R P, Stierli R, Lanz K, et al. Quinone and iron porphyrin mediated reduction of nitroaromatic compounds in homogeneous aqueous solution. *Environ Sci Technol*, 1990, 24: 1566–1574
- 24 Shi L, Dong H, Reguera G, et al. Extracellular electron transfer mechanisms between microorganisms and minerals. *Nat Rev Microbiol*, 2016, 14: 651–662
- 25 Mao Y, Xia Y, Zhang T. Characterization of *Thauera*-dominated hydrogen-oxidizing autotrophic denitrifying microbial communities by using high-throughput sequencing. *Bioresour Technol*, 2013, 128: 703–710
- 26 Wang D, Wang G Y, Li Y N, et al. Structure of phenol-degradation anaerobic denitrification microbial community in coking contaminated soil (in Chinese). *Environ Sci Technol*, 2018, 41: 6–10 [王迪, 王国英, 李亚男, 等. 焦化土壤中降解苯酚的厌氧反硝化菌群结构. *环境科学与技术*, 2018, 41: 6–10]
- 27 Song B, Palleroni N J, Kerkhof L J, et al. Characterization of halobenzoate-degrading, denitrifying *Azoarcus* and *Thauera* isolates and description of *Thauera chlorobenzoica* sp. nov. *Int J Syst Evol Microbiol*, 2001, 51: 589–602
- 28 Liu B B. Molecular identification and identification of dominant functional bacteria in efficient wastewater treatment bioreactors (in Chinese). Doctoral Dissertation. Shanghai: Shanghai Jiao Tong University, 2006 [刘彬彬. 高效废水处理生物反应器中优势功能菌的分子识别与鉴定. 博士学位论文. 上海: 上海交通大学, 2006]
- 29 Schink B, Philipp B, Müller J. Anaerobic degradation of phenolic compounds. *Naturwissenschaften*, 2000, 87: 12–23
- 30 Rhee S K, Lee G M, Yoon J H, et al. Anaerobic and aerobic degradation of pyridine by a newly isolated denitrifying bacterium. *Appl Environ Microbiol*, 1997, 63: 2578–2585
- 31 Tao W, Wang J. The operation performance of denitrifying biological filter filled with synthetic goethite, granular activated carbon and quartz sand (in Chinese). *Guangdong Chem Ind*, 2017, 44: 27–28 [陶巍, 王进. 人工合成针铁矿与颗粒活性炭、石英砂作为反硝化生物滤池填料的比较. *广东化工*, 2017, 44: 27–28]
- 32 Tan J, Wang J, Xue J, et al. Methane production and microbial community analysis in the goethite facilitated anaerobic reactors using algal biomass. *Fuel*, 2015, 145: 196–201

补充材料

图S1 实验装置和工艺流程图

图S2 不同浓度亚微米磁铁矿复合污泥体系对有机污染物的去除效果

图S3 R1和R2出水产物分析

图S4 R1和R2活性污泥中EPS组分

图S5 R1和R2中 Fe^{2+} 溶出浓度

表S1 人工模拟废水的微量元素成分

表S2 反应器不同的运行阶段

本文以上补充材料见网络版csb.scichina.com. 补充材料为作者提供的原始数据, 作者对其学术质量和内容负责.

Summary for “亚微米磁铁矿强化反硝化降解苯酚和喹啉”

Submicron magnetite enhanced simultaneous denitrification and degradation of phenol and quinoline

Jing Wang^{*}, Yujiao Sun, Shu Ma & Fengbo Wang

School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

^{*} Corresponding author, E-mail: jwang@dlut.edu.cn

A large amount of coking wastewater will be generated and discharged during the production process of the coke industry. Such a refractory organic industrial wastewater contains ammonia nitrogen, cyanide, phenols, nitrogen heterocyclic aromatic hydrocarbons (such as quinoline, etc.), and polycyclic aromatic hydrocarbons, etc. Common biological treatment technology is often faced with the problem that it is difficult to meet the discharge standard of COD and ammonia nitrogen at the same time, which will pose a huge threat to human health and the ecological environment. At present, the biological treatment of coking plant wastewater mainly includes anaerobic-anoxic-oxic (A^2/O), sequencing batch reactor activated sludge process (SBR), biological aerated filter, etc. However, these conventional biological treatment processes usually lead to the higher concentration of COD and total nitrogen (TN) in the effluent, which is difficult to meet the discharge standards. As a result, some new technologies for enhanced biological treatment of coking wastewater have been derived. For example, adding an aerobic unit (A^2/O^2 process) after the traditional A^2/O or adding bioenhanced technology of phenol degrading bacteria can also improve the removal rate of pollutants (such as COD and ammonia nitrogen) in coking wastewater. However, these enhanced biological treatment technologies have many disadvantages, such as the increase of structures, the difficulty of maintaining the effectiveness of adding bacteria for a long time, and the high cost of capital construction and operation. In recent years, magnetite has been widely used in biological wastewater treatment because of its low cost, good conductivity and magnetism, and the micro-oxygen system can maintain its long-term mediating effect. In order to enhance the denitrification biodegradation of phenol and quinoline, the Fe_3O_4/AS composite system (R2) was established by adding submicron (0.1–0.3 μm) magnetite to the micro-oxygen continuous activated sludge reactor (AS). And explore its mechanism of action. The results show that after 80 d of operation under microaerobic conditions ($DO = 0.5-1.0$ mg/L), the iron minerals in R2 reactor mainly exist in the form of magnetite and goethite, and the concentration of Fe^{2+} in effluent was always kept at about 0.2 mg/L, which effectively alleviated the reduction and dissolution of magnetite. When the concentration of quinoline in influent was 55 mg/L, the removal rates of COD, phenol, quinoline, NO_3-N , total organic carbon (TOC) and total nitrogen in R2 were 38%, 49%, 65%, 64%, 23% and 98% higher than those in the control group R1 respectively. In addition, R2 had the better capabilities of mineralization and denitrification, and its removal rate of TOC and TN was increased by 23% and 100% respectively than that of R1, realizing the complete mineralization and removal of most of the pollutants. The mechanism research showed that the abundance of bacteria (such as *Denitratisoma* and *Azoarcus*) related to denitrification and aromatic degradation in R2 increased significantly; the addition of magnetite improved the secretion of extracellular polymer substances EPS (about twice as much as R1) and the cohesiveness of sludge microorganisms. Moreover, the concentration of extracellular electron shuttles (heme c and humic acid) in the EPS and the activities of enzymes related to pollutant degradation and nitrogen reduction were significantly increased (the dehydrogenase, nitrate reductase and nitrite reductase activities in EPS of R2 were 3.1, 5.8 and 4.3 times respectively). The addition of Fe_3O_4 significantly improved the degradation of quinoline and the activity and recovery of microorganisms, achieved better denitrification and carbon removal performance.

magnetite, denitrification, phenol, quinolone, extracellular polymeric substances, extracellular electron transfer

doi: [10.1360/TB-2020-0752](https://doi.org/10.1360/TB-2020-0752)