

论文摘要集

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中文摘要集（32 篇）

01 我国城市垃圾渗滤液处理面临的膜浓缩液挑战及应对策略

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摘 要: 我国城市垃圾渗滤液处理工艺通常设有纳滤、反渗透等膜处理环节, 必然会产生有机物和盐分浓度更高、处理难度更大的“膜浓缩液”。目前膜浓缩液的常规处理方法是回灌至填埋堆体内或前端渗滤液处理单元, 腐殖质有机物、重金属、盐分等难降解污染物的不断积累, 势必会对渗滤液生化处理系统正常运行带来不利影响; 同时也会影响膜通量、增大设备运行压力、不断降低膜系统处理效率, 最终造成垃圾渗滤液处理系统的崩溃。膜浓缩液难处置正逐渐成为我国渗滤液处理行业发展的“瓶颈”难题。本文从垃圾源头分类、过程减量、末端利用出发, 探索性提出基于黑河腾冲线划分区域的膜浓缩液处理应对策略, 一方面完善生活垃圾源头分类-过程回收-末端利用体系, 狠抓餐厨垃圾分类与资源化, 逐步减量消除浓缩液; 同时好顶层设计与科学规划, 对垃圾压缩中转站、焚烧厂、填埋场、堆肥厂等渗滤液处理现有工艺, 进行优化、改造、升级, 重点突破膜浓缩液中腐殖酸和盐分累积难题。此外, 完善地方与行业标准, 强化科技支撑, 推进政产学研用科技成果转化; 因地制宜将膜浓缩液引入标准中, 在科学计算本地水体环境容量基础上, 制定渗滤液污染物排放及控制地方标准, 配套出台垃圾资源化与能源化产品质量标准。本文可为践行无膜浓缩液的渗滤液处理绿色新模式、以及渗滤液资源化回收新途径, 提供借鉴与参考。

关键词: 垃圾渗滤液; 膜浓缩液; 垃圾分类; 处理工艺; 策略

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02 两种潜流人工湿地对二级生化出水处理效果中试研究

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摘要：采用垂直和水平潜流两种湿地对武汉某污水处理厂二级生化出水进行处理，研究了在不同水力负荷条件下对污染物的去除效果，并进行了相关性分析。试验结果表明：两种湿地对出水 COD、NH₃-N、TN 和 TP 的去除效果无显著性差异。两种湿地在低水力负荷（0.25 m³/(m²·d)）条件运行下对 COD 和 TN 去除效果较好，在高水力负荷（1.00 m³/(m²·d)）条件运行下对 NH₃-N 和 TP 去除效果较好。相关性分析表明：两种湿地的水力负荷与 TN 去除率呈显著负相关，进水浓度很大程度上影响着湿地的净化效果，同时水质指标去除率之间存在一定的显著相关性。

关键字：垂直潜流；水平潜流；水力负荷；二级生化出水；处理效果

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03 余氯对城市污水处理厂生化系统的影响研究

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摘要: 新型冠状病毒爆发使含氯消毒剂的使用增多, 最终可能进入污水处理厂影响生物处理效果。本研究探讨不同浓度的余氯(游离氯和化合氯)对活性污泥处理效果的影响, 并观察活性污泥的性能和微生物多样性。结果显示, 与未投加余氯相比, 投加游离氯浓度大于等于 3 mg/L 或投加化合氯浓度大于等于 5 mg/L 时, 出水水质出现显著增加, 且化合氯对 COD 和 TN 去除抑制作用大于游离氯, 对 TP 去除抑制作用小于游离氯。投加余氯后, 活性污泥的沉降性能良好, 但芽孢杆菌属(*Bacillus*)的相对丰度随着游离氯投加量的增加而减少, 当化合氯投加量超过 1 mg/L 时, 芽孢杆菌属(*Bacillus*)几乎消失。芽孢杆菌属(*Bacillus*)的变化导致活性污泥脱氮效率的降低, 且化合氯抑制细菌脱氮功能高于游离氯。

关键词: 余氯; 活性污泥; 处理效果; 沉降性能; 微生物多样性

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04 给水管网疏松沉积物结构特征及其水质风险

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摘要: 自来水“黄水”是典型的饮用水输配过程水质恶化问题, 其产生的重要原因是管材的腐蚀及腐蚀产物的释放。饮用水输配管网中普遍存在以铁腐蚀产物为主要成分的疏松沉积物, 在正常情况下一般不会造成明显的浊度和色度升高, 但当水在管网中的水力停留时间较长, 特别是由于水源切换或处理工艺改变导致进入管网的水质化学特征发生显著改变时, 管内腐蚀产物层与原来的水质建立的平衡被打破, 腐蚀产物的释放加速, 疏松沉积物就会被释放或重新悬浮在饮用水中形成“黄水”。“黄水”问题严重影响着饮用水安全, 是自来水公司收到客户投诉的常见原因。然而, “黄水”问题通常被认为是感官性状问题, “黄水”中铁颗粒物的结构特点及其健康风险尚未引起重视, 在复杂的管网环境中形成铁颗粒物的结构会发生怎样的转变也尚不明确。

为此, 我们一方面从实际供水管网获取以铁颗粒物为主要组分的沉积物, 另一方面在实验室合成了不同物质共存条件下的铁颗粒物 (FeOOH), 通过系列大型仪器表征、细胞毒性测试和密度泛函理论计算等证实了管网中微量有机污染物可以影响铁颗粒物的形成过程并导致颗粒物毒性。结果表明:

(1) 管网疏松沉积物再悬浮是“黄水”的重要成因。在中国北方某城市频繁发生自来水“黄水”的7个小区的疏松沉积物中, 含量最高的金属元素都是铁元素、主要晶体成分是铁氧化物, 样品颗粒微观形貌大多具有锋利的针刺状结构; 样品 zeta 电位范围为-15~20 mV、平均粒径范围为 500~4000 nm、粗糙度范围为 0.25~7.81 nm。体外细胞毒性实验显示沉积物可产生一定的细胞毒性 (样品浓度 100 mg/L 时人体健康肝脏细胞存活率为 86.61~99.71%)。通过主成分分析发现, 疏松沉积物毒性与粗糙度的相关性比与粒度的高, 表明形貌对样品毒性的影响比粒径更大; FeOOH 是与疏松沉积物毒性相关性最大的晶体组分, 其对毒性的贡献可能是通过增加颗粒表面锋利程度造成的, 余氯不足时会因铁释放加剧和 FeOOH 含量增大造成更高的毒性风险。

(2) FeOOH 广泛存在于管网铁沉积物中并对颗粒物毒性高度相关。通过在二价铁离子形成针铁矿的过程中添加常见管网共存物质, 包括阳离子 (Al^{3+} 、 Mn^{2+} 、 Mg^{2+} 和 Ca^{2+})、阴离子 (磷酸盐、硅酸盐) 以及微量有机污染物 (持久性有机污染物 BPA 和 PFOA, 以及天然有机物 HA) 获得了系列 FeOOH 颗粒物, 发现在不存在共存添加物时, FeOOH 微观结构中具有不规则的海胆状结构, 不同共存物质显著影响了 FeOOH 的形貌, 尤其是在磷酸盐存在下的 FeOOH-P 中针刺消失表面最光滑, 在 BPA 影响下的 FeOOH-BPA 形成规则的海胆状结构且表面最锋利, 在 PFOA 和 HA 存在下形成表面较钝的珊瑚状结构, 其中大多样品符合表面越锋利毒性越大的规律。但是有趣的是, 尽管全氟辛酸存在下形成的 FeOOH 颗粒 (FeOOH-PFOA) 在所有样品中表面不是最锋利, 但毒性最高。密度泛函理论计算证实, 在 FeOOH-PFOA 颗粒中 F 诱导了 Fe 周围电子的迁移, 导致 FeOOH-PFOA 不仅能直接从 DNA 中夺捕获电子引发氧化损伤, 还能以 O_2 为电子供体产生 ROS 增强细胞的氧化应激损伤。

由此可见, 自来水管网“黄水”不止是感官性状问题, 管网中以铁颗粒物为主要成分的颗粒物还具有毒性风险 (如图 1a 所示), 管网中共存的其他微量污染物还能通过改变铁颗粒物的结构进一步增大颗粒物的毒性风险 (如图 1b 所示)。

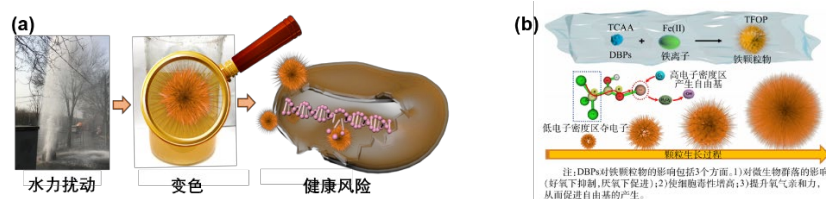


图1 (a) 管网颗粒物风险示意图, (b) 微量污染物增强颗粒物风险示意图

关键词：给水管网；疏松沉积物；黄水；毒性

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05 印染尾水中典型重金属铈对斑马鱼的急性毒性及肠道菌群影响研究

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摘要:近年来我国印染工业飞速发展, 印染尾水的排放量也与日俱增, 然而印染尾水中仍含有多种重金属, 对受纳水生态环境造成危害, 其中铈因其具有潜在致癌性而备受关注。斑马鱼作为生态毒理学研究的模式生物, 其生理免疫指标可以充分反映重金属对机体抗氧化系统的损伤情况, 而肠道微生物菌群在调节宿主生理功能的稳态以及对环境污染物的抗性中起着至关重要的作用。因此, 本研究基于重金属铈对斑马鱼急性毒性 LC₅₀ 的实验结果, 将斑马鱼分为四组, 设定模拟印染尾水中铈的浓度为 0 mg/L、10 mg/L、20 mg/L、40 mg/L, 每组设置三个平行实验, 对印染尾水中铈对斑马鱼的急性毒性效应及肠道微生物菌群的影响进行探究, 实验测定斑马鱼肌肉与肠道组织样品中过氧化氢酶 (CAT) 活性、谷胱甘肽过氧化物酶 (GSH-Px) 活性、丙二醛 (MDA) 含量、超氧化物歧化酶 (SOD) 活力、总抗氧化能力 (T-AOC) 和乙酰胆碱酯酶 (AChE) 活性等指标, 并对斑马鱼肠道样品进行微生物群落多样性组成谱分析, 结果表明: 重金属铈的急性暴露会引起斑马鱼抗氧化系统的各项指标异常, 神经系统紊乱, 肠道菌群失调, 并对斑马鱼机体的健康和生长产生不利的影响。

关键词: 斑马鱼; 印染尾水; 铈; 毒性效应; 肠道微生物

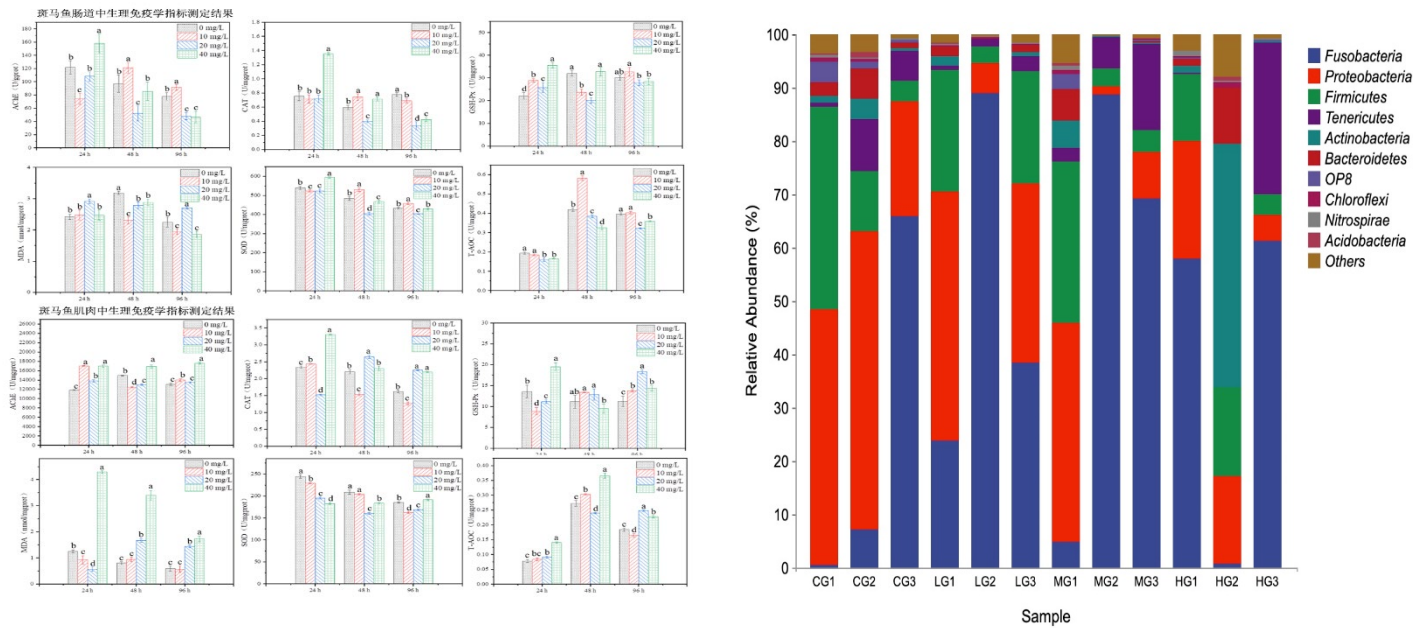


图1 斑马鱼肠道和肌肉中生理免疫学指标测定结果 (左); 斑马鱼肠道菌群的相对丰度 (右)

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06 煤化工废水处理中反渗透系统的膜污染空间分布特征解析

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摘要: 我国煤化工废水排放量大, 成分复杂难处理, 废水重复利用率低。以“双膜法”(超滤+反渗透)为主的膜结合工艺广泛应用在煤化工废水回用中。但是, 在分段式的反渗透工艺中, 由于沿程水质的变化, 导致不同空间位置的膜污染主要类型与特征存在差异, 识别反渗透系统的膜污染空间分布特征十分关键。本研究于煤化工厂进行废水和膜污染样品的采样。在一段(M1)和二段(M2)反渗透膜元件中各取一张膜, 将每张膜片分为图1所示的12个区域并依次编号, 以便后续膜表征。采用①SEM、AFM和接触角, ②XPS和ICP, ③TOC、3D-EEM和FTIR, ④ATP、HPC和序列统计分别表征表面性质、无机、有机和生物污染。

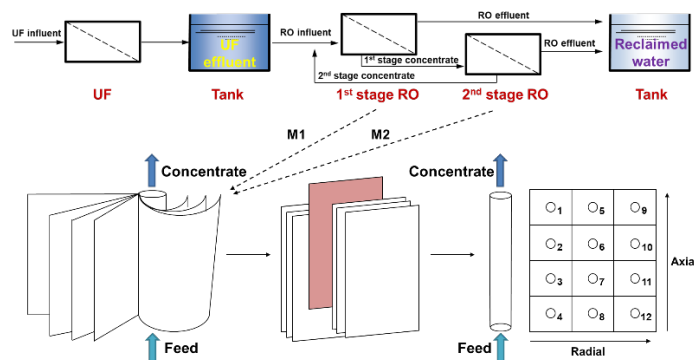


图1. 煤化工厂反渗透污染膜样品的采样示意图。

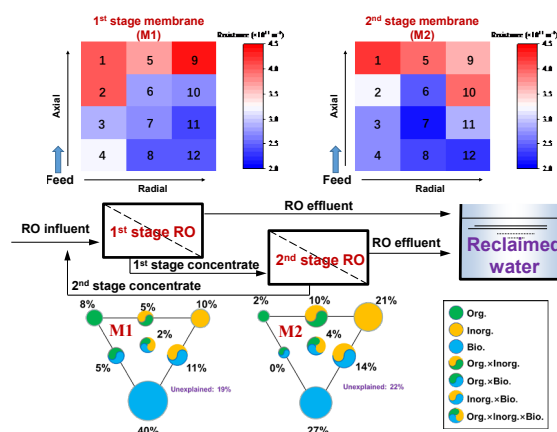


图2. 膜污染阻力分布情况及各类污染对膜通量下降的贡献率。

研究表明, 在两段反渗透膜的污染层中, Fe 都是含量最多的无机离子, Al 和 Si 次之, 随后是 Ca 和 Mg。这表明在污染层中可能形成 Fe、Al 和 Si 的胶体污染物, 而 Ca 和 Mg 易与胶体污染物加剧复合膜污染。一段污染层中, 腐殖酸含量较高; 二段污染层中, 蛋白含量较高。膜污染速率由一段到二段逐渐加重, 且两段反渗透膜均呈现从进水侧到浓水侧膜通量递减、膜污染愈重的变化规律。有机污染在膜面上的空间分布较为均匀, 无机污染、生物污染及其复合作用对膜通量下降的贡献较为显著。总体上, 从一段始端到二段末端, 膜污染的主要类型逐渐由生物污染, 向无机-有机和无机-生物复合污染转变。

关键词: 煤化工; 反渗透; 膜污染; 空间分布; 统计学分析

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07 基于海水养殖尾水出路 with 排放标准解析的碳排放思考

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摘要: 21 世纪以来, 海水养殖业发展趋势迅猛, 多样化的海水养殖模式在带来经济效益的同时, 也会导致海水养殖业的环境污染范围与日俱增, 海水养殖带来的生态负荷和环境压力不容忽视。如何更好的发展海水养殖, 助力碳中和, 是绿色生态海水养殖面临的迫切问题。本文以海水养殖尾水的排放出路为切入点, 对比了国内外海水养殖尾水排放标准, 并对国内排放标准的修订提出相应的建议。此外, 笔者在已有的海水养殖业具体数据的基础上, 分析了目前我国海水养殖尾水排放以及处理回用的现状, 并针对其资源化利用存在的问题, 提出促进回用的方法与建议。本文主要研究结论如下: (1) 我国不断加强对养殖尾水排放的控制, 各省、自治区、直辖市人民政府相继制定了地方海水养殖水排放标准, 现行的国家标准是 2007 年发布的《海水养殖水排放要求》(SC/T 9103-2007)。(2) 近年来, 虽然我国多数养殖企业、养殖户采用直排入海的方式排放海水养殖尾水, 但排放方式正在逐渐由直排变为处理达标后排放。(3) 将海水养殖尾水回用的企业与养殖户占比不大, 尾水处理系统实际处理效率低等问题普遍存在。(4) 针对海水养殖尾水回用存在的问题, 重点提出发展规划、加强关于尾水资源化的法规体系建设、加大财政投入等操作性强的破解措施。

关键词: 碳排放; 海水养殖尾水; 排放标准; 处理回用

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08 基于 MATLAB 的对流弥散衰减方程求解与应用

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摘要: 根据污染物在饱和多孔介质中的随流迁移机理, 构建污染物对流-弥散-衰减(吸附及反应)耦合运移数学模型, 基于 MATLAB 平台采用差分法对模型进行编译、求解计算及可视化, 经实验数据拟合验证、实现了对污染物迁移时空分布规律的数值模拟。利用模型分析了不同水动力条件、含水介质特征、污染物特征对地下污染迁移扩散的影响, 为定量揭示污染物的运移转化风险提供了数学工具。

关键词: 对流弥散方程; MATLAB; 数学模型; 污染物迁移

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09 生物接触氧化法在给水处理工程中的应用

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摘要: 我国许多地区水域普遍受到了微污染, 通常表现为水体氨氮浓度升高、水中有机污染增多、溶解氧下降、藻类滋生等。当该类水体作为市政供水水源时, 采用常规水处理工艺难以达到饮用水水质要求, 增加生物预处理是一个必要的措施。生物接触氧化是一种简便易行的工艺、广泛应用于污水处理、给水预处理。本研究对生物接触氧化工艺原理及影响因素进行介绍, 调研了生物接触氧化工艺在市政给水处理方面的应用情况, 着重考察了代表性工程案例的设计参数及对污染物的去除效果, 分析了该工艺在应用过程中需注意的主要问题, 对生物接触氧化工艺在给水处理方面的未来研究热点进行展望。

关键词: 生物接触氧化; 市政给水; 设计参数; 去除效果

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10 MBBR 工艺对微污染水源水处理效果及微生物菌落选择性富集效

应

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摘要: 我国存在大面积的微污染水源水, 通常为氨氮、COD、藻类等超标。MBBR 工艺是一类可行的处理技术。本研究考察了 MBBR 工艺应用于微污染水源水处理效果, 发现对 $\text{NH}_4^+\text{-N}$ 、 $\text{NO}_2^-\text{-N}$ 、 BOD_5 和 COD 去除率在 50%、92.63% 60.44%和 26.14%左右, 出水符合 GB3838-2002 地表水Ⅲ类标准要求。对填料及水体中微生物菌落结构进行分析发现, 填料对 γ -变形菌 (Gammaproteobacteria)、杆菌纲 (Bacilli) 和硝化螺旋菌纲 (Nitrospira) 选择性富集了 1.52、14.38 和 14.12 倍, 为水中污染物的去除提供了微观证明。

关键词: 微污染水体; 移动床生物膜反应器 (MBBR); 填料; 菌落富集

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11 不同化学物质细胞毒性中活性物质和非活性物质的鉴别

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摘要: 随着现代工业产业的不断进步, 世界各类化合物的生产数量剧增, 这些化合物在促进各行业发展的同时, 可通过多种途径释放到环境中, 对各生态系统造成严重污染。它们也可以通过生物富集和食物链进入生物体内, 对动物和人类的健康构成严重的危害。因此, 急需对这些污染物进行毒性评估以确定其对生物和人类的潜在不良影响。体外细胞毒性试验是环境污染物风险评估中较为理想的体内毒性试验替代方法。然而, 许多化合物的细胞毒性作用模式(MOAs)尚未被研究。本文的目的是基于大量的不同化合物, 通过定量构效关系(QSAR)和结构警示来研究 MOAs 及其影响细胞毒性的因素。为达到目的, 从 Tox21 10K 化合物文库中编译了 8981 个化合物的细胞毒性数据, 对计算得到的细胞毒性和分子描述符进行了二项式和递归分析。结果表明, 细胞毒性与化学疏水性和过量摩尔折射密切相关, π 电子和 n 电子对的生物吸收和化学受体相互作用在细胞毒性中起重要作用。二项式模型中选择的这两个描述符对活性和非活性化合物的总体分类准确率为 69%。递归分析的决策树结果表明, 化合物可分为 25 组, 其结构特征可作为细胞毒性中活性和非活性化合物的结构警示。决策树中使用的描述符显示, 化学电离和生物利用度可以影响可电离和高度疏水化合物的细胞毒性。按照 Verhaar 分类法对 MOAs 进行比较, 表明在细胞毒性中, 许多惰性或弱惰性化合物是非活性化合物, 许多活性或特殊反应型化合物是活性物质 (例如, 黄体酮、雌激素、激素、核苷转运抑制剂、质子泵抑制剂、抗生素、抗癌药物、质子泵抑制剂、杀虫剂、杀菌剂、除草剂等)。这些化合物的体外毒性和体内毒性作用模式相同, 表明体外毒性试验可作为体内毒性试验的替代, 用于环境危害和风险评价。

关键词: 细胞毒性; 活性化合物; 疏水性; QSAR

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12 基于电催化氧还原电子转移调控的双氧水合成与电芬顿应用

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摘要: 化工、制药等重化工业产生大量高浓度有机废水, 处理难度大, 一直是废水处理领域世界性难题。芬顿反应是一种能有效处理废水的典型技术, 但需在酸性 pH 条件运行, 排放大量高危固废铁泥, 且过量消耗 H_2O_2 化学品。此外, 目前 95% 以上的 H_2O_2 生产主要依赖于大规模集中式的蒽醌工艺, 该过程能耗高污染排放量大, 且高浓度 H_2O_2 的运输存在爆炸风险。电化学氧还原(ORR)技术为解决以上问题提供了有效手段, 通过调控氧还原反应路径, 可操控反应产物为 H_2O_2 或 $\cdot\text{OH}$ (图 1a)。本研究基于调控金属单原子/单位点配位环境策略, 设计了高活性高选择性电催化氧还原产 H_2O_2 或 $\cdot\text{OH}$ 的金属单原子/单位点催化剂, 实现两电子合成 H_2O_2 或三电子生成 $\cdot\text{OH}$ 的选择性电子反应路径。

将具有 Co-N₄ 结构的酞菁分子与氧化碳纳米管进行组装, 调控钴单原子周围配位原子, 从而实现 ORR 性质调变。在 0.1 M KOH 条件下, CoPc/OCNT 催化剂的两电子选择性在 0.6~0 V vs RHE 电势范围内高达 96%~100%。基于前期工作研制的流动式气体扩散电极反应器, 进行连续地合成 H_2O_2 (图 1b), ORR 电流密度高达 100~170 mA cm⁻², H_2O_2 法拉第效率为 80~95%, 可连续产出 1.63 wt% 的 H_2O_2 , 产生速率为 4~5.8 mol h⁻¹ g⁻¹ (图 1c), 高于目前国际已报道的最高产率。通过将流出电解液回流到反应器, 可继续提高 H_2O_2 浓度, 可用于纸浆染料漂白, 芬顿反应去除难降解有机污染物等。

此外, Fe-N₄ 结构单原子是典型的四电子 ORR 催化剂, 设计了以缺陷三维多孔碳为基底, C, Cl 原子五配位的铁单原子催化剂, 实现了选择性地连续催化 O_2 还原生成 $\cdot\text{OH}$, 快速降解及矿化难降解有机污染物 (图 1d)。铁单原子催化 O_2 产 $\cdot\text{OH}$ 质量活性是颗粒态铁的 68 倍, 归一化反应动力学提高了 59 倍 (图 1e-f)。在酸性 pH 4 及中性 pH 6 条件下, 铁单原子的降解污染物的速率分别是均相芬顿反应的 1.4 倍和 10 倍。在 20 h 运行中, 降解污染物性能稳定, 金属溶出在 5~41 $\mu\text{g L}^{-1}$ 的痕量水平。单原子电芬顿阐明了新的反应机制, 为电芬顿技术的发展提供了新视角; 通过在非均相条件下实现传统均相芬顿的反应效率, 为解决传统均相芬顿过程 pH 范围窄、产生铁泥等难题提供了新的技术思路。

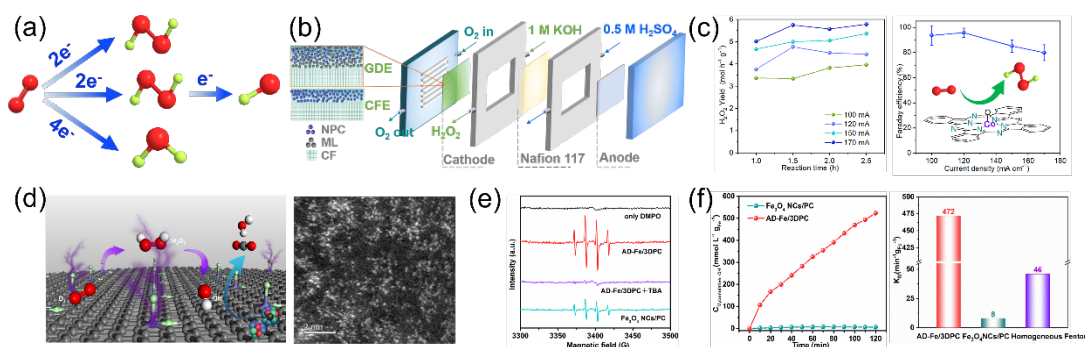


图 1. (a) 产物为 H_2O , H_2O_2 和 $\cdot\text{OH}$ 三种电催化氧还原路径; (b) 流动式反应池电化学合成 H_2O_2 ; (c) 电流密度 100~170 mA cm⁻² 产 H_2O_2 法拉第效率及产生速率; (d) 五配位铁单原子催化 O_2 产 $\cdot\text{OH}$ 示意图及球差电镜表征铁单原子; (e) 利用电子自旋共振技术定性检测 $\cdot\text{OH}$; (f) 铁单原子与颗粒铁的 $\cdot\text{OH}$ 质量活性对比, 及与均相体系对比的污染物降解动力学速率。

关键词: 单原子催化剂, 氧还原, 电芬顿, H_2O_2 , $\cdot\text{OH}$

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13 利用流化床结晶反应器从生物膜法(BSBR)富集的磷溶液中回收

蓝铁矿

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摘要: 目前城市污水磷回收广泛采用基于生物强化除磷(EBPR)工艺的污泥上清液或者浓缩液进行富集, 进而以鸟粪石结晶形成回收产品, 但其存在利用价值低、磷回收率不高等缺点。蓝铁矿因其经济价值高, 作为磷回收的新形式受到广泛关注。现有的以蓝铁矿的形式回收磷的研究中: 一种是从污泥中回收, 磷回收率约 90%, 纯度为 43.32-55.70%左右, 但存在产物复杂, 产物中除蓝铁矿外还有污泥, 难于分离利用; 另一种是从污水中回收, 由于城市污水中磷浓度极低, 难于直接进行结晶。本研究提出了一种新的磷回收工艺系统, 采用生物膜法(BSBR)+流化床反应器分别完成磷酸盐的富集和结晶, 可以实现对城市污水中磷酸盐的高效在线回收。本文以模拟城市污水经生物膜富集后的磷回收液为对象, 以流化床反应器开展诱导结晶回收蓝铁矿工艺研究, 获取不同控制条件下结晶工艺的回收性能、效率以及蓝铁矿的纯度。

工艺系统为间歇式运行, 流化床反应器的有效体积为 3L, 将 BSBR 反应器浓缩获得的高倍富集的磷回收液泵入流化床反应器, 用泵加入 NaOH 或者 HCl 溶液来调节 pH 在 7-7.5, 用泵来吹扫氮气来降低 ORP 为 -200mV, 使 pH 和 ORP 达到反应条件, 再调节循环泵调节使上升流速保持在 14.92m/L 进行循环反应, 再加入 Fe(II) 盐(Fe/P 摩尔比为 3/1), 通过单因素分析 HRT 和进水磷浓度得到最优的回收效率。采用 X 射线衍射(XRD)、扫描电子显微镜(SEM-EDS)和 X 射线光电子能谱技术(XPS)对回收的晶体颗粒进行表征。

本文研究了流化床反应器内的几个参数主要包括: HRT、进水磷浓度和结晶次数。反应器中 pH 控制为 7.5, ORP 为低于 -200mV, 上升流速为 14.92m/h, 对 HRT 和进水磷浓度进行单因素分析实验。HRT 过短, 蓝铁矿晶体自身无法生成晶核, 从而导致磷回收率低, 通过实验表明, 在 5h 时, 磷回收率达到了 95.3%, 纯度达到了 88.23%; 进水磷浓度会受到铁离子竞争和饱和度的影响, 从而影响磷回收率和纯度, 通过实验表明, 在进水磷浓度为 120mg/L 的时候, 磷回收率达到了 97.8%, 纯度达到了 88.26%。本文在最优的条件下, 对回收的晶体颗粒以自身为晶种进行多次循环, 可以发现晶体颗粒的平均粒径在成倍的增大, 在第 7 次循环结晶后, 磷回收率(95.2%)和纯度(87.91%)都保持很高的水平下, 蓝铁矿晶体粒径达到了 270.518 μm , 与目前一些以蓝铁矿形式回收的研究相比, 回收率、纯度以及平均粒径都高。

通过对最优条件下回收的晶体颗粒进行表征, 从 SEM-EDS 可以看出, 光学显微镜中显示了 5 微米和 50 微米尺寸下的晶体颗粒的形态呈板状, 与蓝铁矿大致形状相似, 能谱图中可以看出, Fe、P、O 这三个构成蓝铁矿的主要元素的相对含量占总元素的比例较高, 所得产物的元素组成非常接近蓝铁矿的元素组成。回收产物的 XRD 图谱在衍射角为 11.148°、13.144° 等角度时出现的一系列特征峰与蓝铁矿 PDF 标准图谱#83-2453 的出峰位置一致, 可以证明生成的为蓝铁矿晶体。XPS 总图谱中在结合能为 712.15 eV、531.43 eV、285.15 eV 和 133.74 eV, 分别对应于 Fe2p、O1s、C1s 和 P2p, 这说明在回收产物中存在 Fe、O、P 三种元素。通过进一步对精细图谱的分析, 在 Fe2p 精细图谱中, Fe2p 的高分辨率 XPS 显示了 711.8 eV 和 725.6 eV 的结合能分别属于 Fe2p_{3/2} 和 Fe2p_{1/2}, 得到的结合能接近 Fe(II)状态的结合能, 这表明回收产物中几乎所有的铁元素都是二价的, 占比高达 98%左右。通过上述表征, 可以证明得到的晶体颗粒为蓝铁矿晶体 $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ 。

关键词: 生物膜法; 含磷废水; 流化床结晶; 磷回收

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14 电化学提高石墨烯分离膜渗透性原理

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摘要: 近年来, 层状氧化石墨烯分离膜由于其优异的选择性和透过性在水处理领域得到了广泛的关注。该膜结构特点在于氧化石墨烯纳米片相互堆积形成二维孔道, 其氧化区域上的含氧官能团作为该孔道的撑挡(spacer), 而未被氧化的石墨烯区域构成近乎无摩擦的超快水传输通道。这是氧化石墨烯分离膜具有高水通量的根本原因。由此推测, 还原的氧化石墨烯膜由于可提供更多的无摩擦孔道而具有更高的渗透通量。这一推测已得到分子动力学模拟结果的证实。然而实验发现, 还原的氧化石墨烯膜的渗透通量往往低于氧化石墨烯膜的渗透通量。原因在于, 部分含氧官能团的去除大大减小了石墨烯片层之间的距离(interlayer spacing), 甚至使得部分石墨烯区域重新堆叠成石墨结构而无法用于水传输。针对此问题, 我们提出一种电化学分开堆叠的石墨烯并显著提高石墨烯膜渗透通量的方法。该方法利用电极化把石墨烯上的电子导到对电极上, 石墨烯由于缺少电子而电离势降低, 石墨烯纳米片之间的色散力减弱, 吸引力小于排斥力, 从而使堆积的石墨烯重新分开形成膜孔道。实验和分子动力学模拟都证实了该方法的可行性。电“活化”后的石墨烯分离膜的渗透通量是初始值的 3-10 倍, 是具有相同质量的氧化石墨烯分离膜通量的 2-5 倍。

关键词: 石墨烯; 分离膜; 渗透性; 层间距

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15 生物炭在暗发酵制氢过程中的应用及机制分析

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摘要: 暗发酵制氢一种重要的绿色产氢技术, 符合国家“双碳”目标和能源发展战略。然而, 产率低等缺点严重限制了暗发酵制氢的发展。本研究考察了生物炭对暗发酵产氢的作用, 并探讨了其作用机制。首先研究了生物炭对不同暗发酵产氢类型的影响, 结果显示, 投加 3 g/L 生物炭使乙醇型发酵的氢气产量和速率分别提高了 118.4%和 220.3%, 丁酸型发酵分别提高了 79.6%和 82.4%。为了探究其促进机制, 研究了生物炭对发酵条件和细胞代谢的影响。生物炭呈现碱性, 能够中和产生的有机酸, 延缓发酵液 pH 下降, 提高底物利用率; 含氧官能团能释放电子, 降低了发酵体系的氧化还原电势; 生物炭多孔性好, 能够吸附细胞; 生物炭释放了铁和镁等矿物质元素, 有利于产氢菌生长和氢化酶活性。进一步考察了原料和热解温度对生物炭在乙醇型发酵产氢过程中促进作用的影响。测定了五种生物质废弃物(咖啡渣、玉米秸秆、银杏叶、黄粉虫渣和甘蔗渣)制备的生物炭的理化特性和促进效能。甘蔗渣生物炭在乙醇型发酵中表现出最好的产氢促进效果。生物炭的物理化学性质, 如 pH 值、元素组成和表面特征, 受热解温度的影响显著, 但其促进能力没有显著变化。生物炭在乙醇型发酵产氢过程中的促进作用主要受原料类型影响, 受热解温度影响较小。提出了生物炭促进发酵产氢的复合机制, 即低温制备的生物炭通过影响氧化还原反应促进产氢, 而高温制备的生物炭通过促进细胞生长实现促进作用。本研究揭示了生物炭在暗发酵制氢中的促进作用, 探究了其关键促进因素及作用机制, 为开发绿色产氢促进技术提供了新思路。

关键词: 暗发酵制氢; 生物炭; 乙醇型发酵; 影响因素; 促进机制

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16 生物炭胶体颗粒与电活性菌的异团聚行为

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摘要: 生物炭是生物质在缺氧或厌氧条件下热解形成的一种含碳物质, 能够作为电活性菌的胞外电子传递介体, 促进污染物的生物还原。生物炭在受污染环境中的有效迁移和广泛分布有利于其与微生物和污染物接触反应, 使其能更有效地发挥介导电子传递的作用, 对污染修复效果至关重要。近年来研究发现, 施加到土壤环境中的生物炭通常会经物理风化逐渐破碎为生物炭胶体颗粒, 在土壤层中进行长距离迁移, 甚至扩散进入地下水中。这些生物炭胶体颗粒不可避免地会与环境中的广泛存在的电解质离子、天然有机质和微生物细胞发生相互作用, 导致异团聚和沉降等环境行为, 不仅影响其迁移归趋, 也可能影响其反应位点的暴露和反应活性。但是, 目前对于生物炭胶体颗粒与微生物细胞之间的异团聚行为尚不清楚。本研究选择小麦秸秆热解生物炭和典型电活性菌 *Shewanella oneidensis* MR-1, 通过团聚实验和动力学计算, 研究了生物炭胶体颗粒和 MR-1 细胞共存体系在不同水化学条件下的稳定性, 发现两者的异团聚速率随着电解质浓度的提高而加快。与 Na^+ 相比, 两者的异团聚行为对 Ca^{2+} 浓度变化更敏感, 在 NaCl 溶液中的临界聚沉浓度(33 mM)远高于在 CaCl_2 溶液中的临界聚沉浓度(1.2 mM)。此外, 根据生物炭能够作为 MR-1 胞外电子传递受体的特征, 考察了胞外电子传递相关影响因素(如电子供体浓度、Mtr 途径关键蛋白和生物炭的氧化还原活性)对生物炭与细胞异团聚的影响, 发现提高电子供体乳酸钠浓度后异团聚速率更高, 而当胞外电子传递基因缺失时异团聚速率降低。这是由于 MR-1 利用胞外电子传递将生物炭还原后提高了生物炭的其疏水性, 生物炭通过疏水亲和作用与细胞形成团聚体。生物炭的氧化还原状态显著影响生物炭和细胞在 Na^+ 条件下的异团聚行为, 而对两者在 Ca^{2+} 条件下的异团聚没有明显影响, 主要是由于 Ca^{2+} 容易与生物炭表面的羧基发生架桥作用, 削弱了静电作用的影响。此外, MR-1 细胞向生物炭表现出趋能运动, 且与胞外电子传递密切相关。与丧失胞外电子传递能力的突变株相比, 野生株的胞外电子传递能力更强, 表现出更明显的趋能运动, 导致细胞和生物炭发生更强的异团聚。本研究深化了对胞外电子传递影响微生物环境行为的认识, 为理解微生物与纳米颗粒的运移行为提供了新的思考。

关键词: 生物炭; 胶体颗粒; 电活性菌; 胞外电子传递; 异团聚;

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17 腐殖酸促进氧化还原波动条件下针铁矿转化产羟基自由基

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摘要: 在厌氧-好氧波动条件下, 针铁矿可氧化还原转化活化 O_2 产生 $\bullet OH$, 影响污染物在环境中的转化归趋。作为天然有机质的重要组成部分, 在土壤、沉积物和水生环境中腐殖酸(HA)通常与铁氧化物共存。前人研究发现利用 HA 的配合及电子穿梭作用, 可加速厌氧条件下铁氧化物的还原转化, 但 HA 对氧化还原波动条件下铁氧化物介导的产 $\bullet OH$ 行为的影响及作用机制尚不清楚。此外, 目前有关铁氧化物与 HA 相互作用及铁氧化物在厌氧-好氧波动过程中产 $\bullet OH$ 的研究大多以非生物源铁氧化物作为研究对象。实际上, 自然环境中存在许多由微生物参与形成的铁氧化物, 这些生物源铁氧化物往往具有与非生物源铁氧化物不同的形貌、比表面积和结晶度等特性, 影响其对污染物的吸附、电子转移及生物可及性等性质。探究生物源铁氧化物在氧化还原波动条件下的转化行为及其介导产 $\bullet OH$ 能力对于全面认识地下环境中活性氧物种的来源、浓度水平及铁碳等元素循环规律具有重要意义。本研究通过水解法合成化学针铁矿(Gt_{chem}), 利用 BoFeN1 菌株制备生物针铁矿(Gt_{bio}), 考察了厌氧-好氧交替条件下 HA 对上述针铁矿氧化还原转化产生 $\bullet OH$ 的影响及作用机制。经过 144 h 的厌氧还原和 32 h 的好氧化, Gt_{bio} /HA 体系的积累 $\bullet OH$ 浓度(47.1–71.3 μM)远高于 Gt_{chem} /HA 体系的积累 $\bullet OH$ 浓度(17.0–29.2 μM); 10–100 mg/L HA 分别使 Gt_{chem} 和 Gt_{bio} 体系的积累 $\bullet OH$ 浓度提高 40.5%–241%和 1.70%–54.0%。吸附态 Fe(II)对产 $\bullet OH$ 发挥重要作用, Gt_{chem} /HA 和 Gt_{bio} /HA 体系中由吸附态 Fe(II)氧化产生的 $\bullet OH$ 分别占产生 $\bullet OH$ 总量的 72.5%和 54.4%。在厌氧-好氧交替条件下, Gt_{bio} 和 Gt_{bio} /HA 体系磺胺(0.4 mg/L)降解率分别为 48.5%和 72.5%, 远高于 Gt_{chem} 和 Gt_{chem} /HA 体系磺胺降解率(15.2%和 34.3%)。游离或吸附态 HA 在厌氧-好氧交替条件下被部分矿化, 含氧官能团含量提高, 平均分子量降低。具有丰富含氧官能团的 HA 可作为电子穿梭体和 Fe(III)/Fe(II)配合剂, 促进 Gt_{chem} 和 Gt_{bio} 体系在厌氧阶段的异化 Fe(III)还原以及好氧阶段的 $\bullet OH$ 积累。 Gt_{bio} 因其较高的比表面积、低结晶度和掺杂有机质, 具有相比 Gt_{chem} 更高的异化还原和产 $\bullet OH$ 速率。

关键词: 腐殖酸; 针铁矿; 生物矿物; 氧化还原波动

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18 疫情期间武汉市污水处理厂消毒工艺运行分析与思考

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摘要: 2020 年初, 新型冠状病毒肺炎席卷全国。污水厂消毒单元作为排水系统的最后一道关卡, 必须要更严格地管理, 控制病毒的传播。本文总结了我国污水消毒标准的发展历程, 通过对武汉典型市政污水处理厂的调研, 总结了疫情期间各厂消毒单元的运行状况, 对其进行对比分析, 最后对污水厂在疫情期间的应急管理措施提出了建议。

关键词: 新冠肺炎; 污水厂; 运行; 消毒

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19 Fenton-臭氧组合工艺深度处理工业园区废水试验研究

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摘要: 工业园区产生的废水通常需要在生化处理后接深度处理过程使之达标排放。随着排放标准中对 COD 排放限值要求的升高, 已有深度处理设施往往需要提标升级改造。本研究将 Fenton 和臭氧两种深度处理方法进行组合, 探究“Fenton-臭氧”及“臭氧-Fenton”组合工艺对某工业园区污水处理厂生化出水的 COD 降解效果。发现 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 、 H_2O_2 、 O_3 的最优投加量分别为 200、200、45 mg/L, “Fenton-臭氧”组合工艺能将生化出水的 COD 从 150 mg/L 降至 40~50 mg/L, 满足 GB 18918-2002 一级 A 排放标准, 优于“臭氧-Fenton”组合工艺的 50~60 mg/L, 且出水可生化性升高。“Fenton-臭氧”组合工艺下每吨废水的运行成本为 1.63~1.68 元, 处理工业园区生化出水的环境效应显著, 有规模化应用的潜力。

关键词: 工业园区; 废水; 深度处理; Fenton; 臭氧; COD

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20 苯甲酸苯酯类液晶单体在水中的光化学转化研究

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摘要: 液晶材料在显示、相位调制、光开关等领域具有广泛应用。其中液晶单体(LCMs)是一类重要的液晶材料, 广泛应用于液晶显示屏(LCDs)中。现有研究发现, LCMs 在室内空气、室内灰尘以及沉积物样品中均有检出, 且一些 LCMs 具有持久性、生物富集性和毒性, 表明其具有潜在的环境风险, 需要引起人们的关注。一些 LCMs 在产品的使用、废弃产品的拆解、堆置和填埋等过程可释放最终进入水环境。光降解是水体中有机污染物重要的转化方式之一, 影响着污染物在水环境中的转化归趋。由于 LCMs 含有联苯、苯甲腈、苯甲酸苯酯等可进行光化学转化的基团, 因此进入到水环境中的 LCMs 很可能在日光的作用下发生光化学转化/降解。但是, 目前关于 LCMs 在水环境中的光化学转化尚未见报道, 不利于这类化合物的环境风险评价。

本研究以在 LCDs 中广泛使用的苯甲酸苯酯类 LCMs (4-乙基苯甲酸-4-氰基苯酯(CE), 4-乙基苯甲酸-3-氟-4-氰基苯酯(CFE))为例, 研究其在水中的光化学转化。结果发现, CE 和 CFE 在纯水、加叔丁醇、加组氨酸、加山梨酸、氮气饱和、加入山梨酸和氮气、加 DOM 中皆可发生光化学转化(暗对照无降解), 半减期分别为 27.84 和 12.04 min, 其在纯水中的量子产率(Φ)分别为 $(1.14 \pm 0.07) \times 10^{-1}$ 和 $(1.08 \pm 0.72) \times 10^{-1}$ 。在反应体系中加入 10 mM 叔丁醇($\cdot\text{OH}$ 淬灭剂)、1 mM 组氨酸($^1\text{O}_2$ 淬灭剂)均抑制了 CE 和 CFE 的光降解, 这表明纯水中发生了 $\cdot\text{OH}$ 和 $^1\text{O}_2$ 参与的自敏化光氧化反应。同时, 为了考察自敏化反应中 ROS 的生成过程, 基于量子化学计算方法研究了 CE 和 CFE 的激发态与基态氧分子($^3\text{O}_2$)之间发生能量或电子转移的可能性。发现在有溶解氧存在时, CE 和 CFE 的激发态会与 $^3\text{O}_2$ 发生能量转移生成 $^1\text{O}_2$, 并通过电子转移生成的 $\text{O}_2^{\cdot-}$ 再发生歧化反应得到 $\cdot\text{OH}$, 引发污染物的自敏化光解。实验上在 N_2 饱和、添加叔丁醇或组氨酸条件下, CE 和 CFE 的光解速率常数均低于溶解氧存在时的光解速率常数, 实验结果与计算结果一致。从图 1 可以看出, 添加山梨酸(0.1 mM)与山梨酸+ N_2 体系中, CE 和 CFE 的光解被显著抑制, 且它们的光解速率常数几乎相当, 与纯水中通入 N_2 去除 ROS 相比显著减少, 表明目标化合物的直接光解是激发三线态发生的。本研究还发现 DOM 的加入会明显抑制 CE 和 CFE 的光解。

本研究首次围绕典型 LCMs 在水中的光化学转化开展研究, 采用实验和量化计算方法阐明了 CE 和 CFE 的直接光解和自敏化光解机制, 研究结果对于认识水环境中 LCMs 的转化归趋及其生态风险评价具有重要意义。

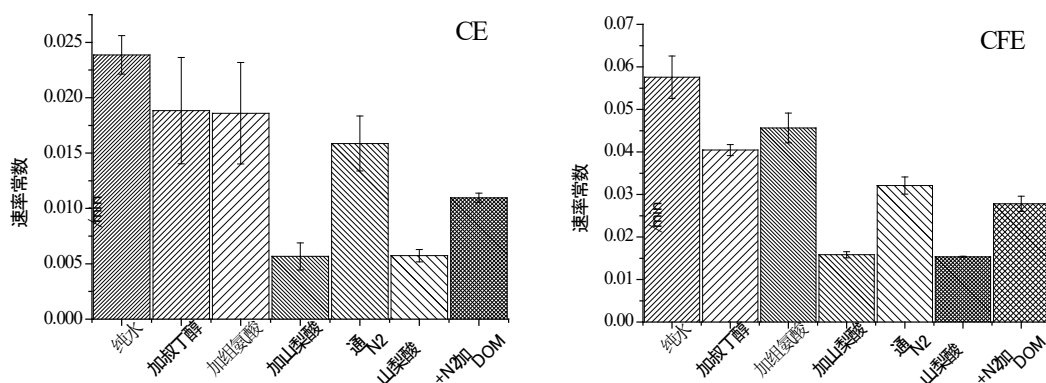


图 1 CE 和 CFE 在各个体系中的表观光解速率常数(k) (误差代表 95%置信区间, $n = 3$)

关键词: 液晶显示屏; 液晶单体; 光化学降解; 水环境; 量子化学计算

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21 腐殖质介导异化铁还原控制温室气体排放

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摘要: 减少甲烷排放对控制全球温室效应具有重要意义。在厌氧体系内, 铁还原菌可将有机质氧化产生的电子用于 Fe(III)还原, 这一过程称为异化铁还原(DIR)。在热力学上, Fe(III)优于 CO₂ 获得电子, 因此, DIR 可与产甲烷竞争电子供体, 从而抑制甲烷的产生。然而, 铁氧化物可溶性差, 在液相分散不均, 导致铁还原菌难以与铁氧化物的直接接触; 微生物还原生成的 Fe(II)会催化弱晶型铁氧化物向晶体铁氧化物的转化, 从而降低 DIR 的速率, 削弱对产甲烷的竞争; 此外, 具有(半)电导性的晶体铁氧化物可作为地杆菌和产甲烷菌之间的电子传递导体, 通过直接种间电子转移(DIET)途径加速甲烷的生成。由此可见, 控制铁氧化物转化及成矿物的作用对 DIR 效率及后续产甲烷具有重要的影响。本研究发现, 在微生物还原水铁矿的实验中投加腐殖质(HS)可显著提高异化铁还原效率, 减少甲烷的生成。除已被广泛报道的腐殖质通过醌基/氢醌官能团扮演“电子穿梭体”机制外, 本研究通过 X 射线吸收光谱(XAS)、原子力显微镜(AFM)等手段还发现腐殖质可在铁氧化物中铁的第二壳层生成新的 Fe-C/O 络合结构, 这种络合结构可有效减缓 Fe(II)在水铁矿表面的吸附作用, 延缓其对水铁矿矿化结晶的催化作用, 维持其参与 DIR 活性, 增强抑制甲烷生成的效果。据此得出启示, 在一些散逸性甲烷的排放源如稻田土中, 铁肥的施加及植物残体向腐殖质的转化可能对稻田土的甲烷排放具有重要影响。此外, 部分工程系统如污水处理厂的末端, 污水总量大但有机物浓度低导致其进行甲烷回收的价值低, 直接排放会产生大量散逸性甲烷, 合理利用腐殖质及铁氧化物可减少污水处理工艺中散逸性甲烷向大气中的排放。

关键词: 腐殖质; 异化铁还原; 温室气体; 厌氧消化; 铁氧化物

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22 手性农药三唑醇和三唑酮不同对映体在水中的光解及其光致毒性

研究

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摘要: 三唑类杀菌剂是一种通过抑制麦角固醇合成而达到杀菌目的杀菌剂, 广泛用于全球农业生产中。三唑酮和三唑醇均为手性农药, 其中三唑酮含有 1 个手性中心, 具有 2 种对映体(S、R), 两种对映体活性相当; 三唑醇含有 2 个手性中心, 具有 4 种对映体, 分别为外消旋体 A(SR、RS)和外消旋体 B(SS、RR), 其中 SR 的杀菌活性明显高于其他三种单体。然而由于分离困难, 在实际应用中往往采用外消旋混合物。目前关于手性农药不同对映体在水中的光解机制和光致毒性尚不明确。鉴于此, 本文研究了三唑醇和三唑酮不同对映体及其混合物在水中的光化学转化行为, 并探究了转化过程中对明亮发光杆菌的毒性影响。光照条件下三唑酮的降解速率明显大于三唑醇, 这是因为三唑酮较三唑醇在 290 nm 以上区域能够吸收更多的光。三唑酮和三唑醇对映体混合物的表观光解速率常数分别为 3.77×10^{-2} 和 $1.54 \times 10^{-2} \text{ min}^{-1}$ (图 1), 半衰期分别为 18.38 和 45.01 min。尽管通常认为手性化合物在非手性环境下物理化学性质一致, 但其光解速率仍存在差别。研究发现三唑酮两个对映体的表观光解速率常数分别为 3.71×10^{-2} 和 $3.83 \times 10^{-2} \text{ min}^{-1}$, R-三唑酮 > 对映体混合物 > S-三唑酮。与三唑酮不同的是, 三唑醇具有两个手性中心, 具有两对对映体, 其表观光解速率常数两两一致, 分别为 1.71×10^{-2} (外消旋体 A)和 $1.46 \times 10^{-2} \text{ min}^{-1}$ (外消旋体 B), 且外消旋体 A > 对映体混合物 > 外消旋体 B。通常认为, 化合物降解是脱毒的过程, 然而在本研究中发现, 三唑酮和三唑醇经光照降解后, 光解液毒性反而增大。毒性试验表明, 在黑暗条件下, 两种农药对映体混合物对明亮发光杆菌几乎没有毒性。而在光照过程中, 两种农药的光解液对明亮发光杆菌的毒性随光照时间增加先迅速增加后逐渐趋于平稳, 毒性保持在较高水平。在 0-45 min 内, 三唑酮两种对映体和混合物的光致毒性表现出明显的差异, 但是随着光照时长的增加, 对映体与混合物光致毒性逐渐趋于一致(图 2a)。而三唑醇 4 种对映体与混合物的毒性变化整体一致, 但值得注意的是, 在 240 min 时, 4 种对映体的毒性表现出显著差异, 高杀菌活性的 SR 毒性明显低于其他对映体(图 2b)。总结来讲, 在评估农药环境风险时, 不仅应关注母体化合物的毒性, 更要考虑其光致毒性, 此外还应关注手性农药对映体之间的差异。

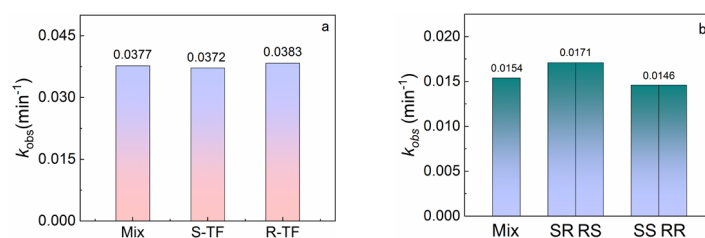


图 1 三唑酮(a)和三唑醇(b)对映体及其混合物在水中的表观光解速率常数

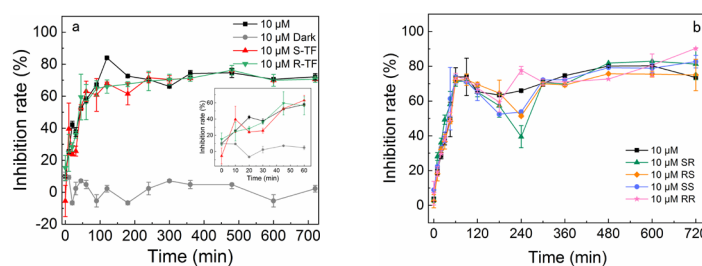


图 2 三唑酮(a)、三唑醇(b)对映体混合物及其对映体不同光照时长的光解液对明亮发光杆菌的发光抑制率

关键词：手性农药；三唑醇；三唑酮；光解速率常数；光致毒性

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23 CuFe₂O₄/生物炭阴极生物光电芬顿系统厌氧-好氧去除/矿化甲基

橙与 Cr(VI)

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摘要: 寻找清洁有效方法去除/矿化含有一定浓度重金属(如 Cr(VI))的偶氮染料(如甲基橙, MO)废水, 一直是人们关注的热点和难点。本研究以 CuFe₂O₄/生物炭复合材料为阴极, 通过构建生物光电芬顿系统(BPES), 设置先厌氧后好氧的运行模式, 彻底矿化/去除混合模拟偶氮染料废水中的 MO 与 Cr(VI)。结果表明, 4 h 内 CuFe₂O₄/生物炭阴极可使初始浓度 20 mg/L 的 MO 脱色率达到 95%, 矿化率达 56%, 同时完全去除 10 mg/L 的 Cr(VI), 分别是单一 CuFe₂O₄、单一生物炭以及空白碳毡作阴极时的 1.75 倍、1.55 倍和 1.22 倍, 1.33 倍、2.35 倍和 1.31 倍, 1.04 倍、4.48 倍和 2.06 倍。CuFe₂O₄/生物炭复合有效避免 CuFe₂O₄团聚, 降低电荷转移内阻, 从而提高催化活性。运行 12 周期后, CuFe₂O₄/生物炭阴极仍保持 90%以上的污染物去除率。研究结果为清洁高效地去除/矿化偶氮染料废水提供了有效方法和借鉴。

关键词: CuFe₂O₄/生物炭; 光电芬顿; 生物电化学; 厌氧-好氧; 复合污染

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24 基于 f-CNH/GR/AuNPs/SPE 的细胞电化学方法研究全氟化合物

及其替代品的毒性效应

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摘要: 全氟化合物是一类脂肪烃碳链上氢原子被氟原子全部取代的化合物, 在造纸、皮革、涂料、灭火泡沫、农药等多个领域被广泛应用。其中, 全氟辛烷磺酸 (PFOS) 和全氟辛酸 (PFOA) 的应用范围最广也被研究的最多。随着全氟化合物对人体健康和生态环境的危害日益凸显, 国际社会开始对其使用进行管制或限制。近年来, PFOA、PFOS 的替代品开始被生产和使用, 常见的替代品如六氟环氧丙烷二聚体 (HFPO-DA)、六氟环氧丙烷三聚体 (HFPO-TA)、氟调聚羧酸 (FTCA)、氟调聚磺酸 (FTSA)、氟调聚醇 (FTAS) 等已在多种环境介质中检出。全氟化合物及其替代品已成为国际公认的一类新型污染物。然而, 全氟化合物替代品的环境危害和生物毒性尚不清楚, 其安全性尚需进一步研究。因此, 对其毒性进行快速、灵敏检测, 成为保护生态环境与人类健康的迫切需求。

细胞电化学是基于电化学与细胞生物学发展起来的一个新的研究领域, 主要通过研究细胞的电化学位行及规律, 揭示细胞的结构-功能关系并评价外源物质对细胞产生的影响。本研究团队近年来建立了基于核苷酸代谢的细胞电化学方法, 通过直接检测细胞核苷酸代谢产物 (鸟嘌呤/黄嘌呤) 的电化学信号来研究细胞活性, 进而评价污染物对细胞的毒性效应。与传统污染物毒性检测方法相比, 该方法具有无需标记、灵敏、快速等优点, 可为全氟化合物及其替代品的毒性检测及早期预警提供有效手段。然而, 当前电化学检测所用细胞多为人体癌细胞, 与之相比, 鱼类细胞可以更加直接地反映污染物对水生生物的毒性作用。草鱼肾脏细胞 (CIK) 作为水生毒理学研究的重要模型细胞, 对污染物毒性感应灵敏。因此, 制备对 CIK 细胞具有良好催化性能的纳米修饰电极是提高毒性检测灵敏度的关键。

综上, 本研究利用酸化单壁碳纳米角 (f-CNH)、石墨烯 (GR) 和金纳米粒子 (AuNPs) 对丝网印刷电极 (SPE) 进行修饰, 制备了对 CIK 细胞电活性物质具有优异催化性能的纳米复合修饰电极 f-CNH/GR/AuNPs/SPE; 采用扫描电子显微镜、X 射线能谱、拉曼光谱、X 射线衍射等对 f-CNH/GR/AuNPs/SPE 的形貌和结构进行了表征, 结果表明: f-CNH/GR/AuNPs 具有石墨烯的片层结构与碳纳米角的典型大丽花结构; 其主要由 C、O、Au 三种元素组成, 其中, C 和 O 来自于 f-CNH 和 GR, Au 归因于 AuNPs; f-CNH/GR/AuNPs 拉曼光谱图中的 G 峰强度显著增大, D 峰和 G 峰强度比减小, 其石墨化程度增强; f-CNH/GR/AuNPs 与 f-CNH 的 XRD 谱图中的出峰位置基本一致, 表明碳结构未发生明显变化。进一步以草鱼肾脏 (CIK) 细胞为模型, 通过优化检测条件, 构建了基于 f-CNH/GR/AuNPs/SPE 的细胞电化学方法。测定了不同浓度的 PFOA、PFOS 及其替代品 HFPO-DA、HFPO-TA、6:2 FTCA 对 CIK 细胞的毒性, 结果发现, 不同污染物的细胞毒性 (Y) 与其浓度对数 (X) 之间具有良好的线性关系, 线性方程分别为: $Y = 47.67X - 78.92$ ($r = 0.985$)、 $Y = 46.04X - 60.65$ ($r = 0.985$)、 $Y = 49.49X - 63.09$ ($r = 0.993$)、 $Y = 48.07X - 43.60$ ($r = 0.987$) 和 $Y = 42.55X - 69.04$ ($r = 0.963$)。根据线性方程计算得到 PFOA、PFOS、HFPO-DA、HFPO-TA、6:2 FTCA 的对 CIK 细胞的 IC_{50} 值分别为: 501.19、251.19、194.98、89.13、630.96 μM , 毒性顺序为: HFPO-TA > HFPO-DA > PFOS > PFOA > 6:2 FTCA, 可以看出, HFPO-TA 及 HFPO-DA 并非环境友好型全氟化合物替代品, 其生物毒性效应不容忽视。同时, 将所得结果与常规细胞毒性检测方法 (MTT 法) 进行了比较, 发现两种方法所得毒性规律一致, 但细胞电化学方法所得 IC_{50} 值更低, 表明该方法更为灵敏。本研究为环境污染物毒性检测提供了灵敏、简单、快速的技术方法, 为全氟化合物及其替代品的毒性效应和生态风险评价提供了基础数据和科学依据。

关键词: 全氟化合物及其替代品; 草鱼肾脏细胞; 电化学; 细胞毒性; 碳纳米角

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25 电辅助增强纳米碳基纳滤膜脱盐性能

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摘要: 纳滤(NF)膜作为一种荷电膜,对多价离子(如: Ca^{2+} 、 Mg^{2+} 、 SO_4^{2-} 等)表现出很好的截留性能,但其对单价离子(如: Na^+ 、 Cl^- 等)的截留率却相对较低,并且,在保持高的水渗透性的同时获得高的离子截留,特别是对单价离子的截留性能,是当前NF膜面临的一大挑战。在本研究中,我们制备了新型的碳纳米管和氧化石墨烯基NF膜,并通过电辅助的策略实现了膜水渗透性和截留性能的显著提高。以聚苯胺/碳纳米管NF膜为阴极并施加2.5 V电压,膜的NaCl截留率达82.4%,显著高于传统纳滤膜的截留率(通常<60%),Donnan位阻孔模型研究揭示了膜截留性能的增强归因于电辅助下膜表面电荷密度的增加;进一步以氧化石墨烯/碳纳米管复合NF膜为阴极并在膜分离层两侧施加3.0 V电压,膜的通量和截留率同时提高,通量由未加电时的 $9.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ 增加到 $17.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, NaCl 截留率则由52.4%提高到78.3%,数值模拟研究揭示膜性能的增强是由于电场作用下的电动效应引起的。本研究有助于深入地理解NF膜的分离过程,并且对于高性能NF膜的设计以及NF技术在脱盐和水处理领域的发展具有重要的指导意义。

关键词: 纳滤膜; 碳纳米管; 石墨烯; 电压; 离子截留

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26 平板陶瓷膜处理地表水源水中试研究

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摘要: 为探究陶瓷膜在处理高浊度、重有机污染地表水源水时的工艺特性, 对预臭氧-混凝-沉淀-平板陶瓷膜超滤净水工艺进行中试试验, 考察了组合工艺的净水效果以及产水通量、过滤周期、反冲洗模式对陶瓷膜跨膜压差变化的影响规律。结果显示, 该组合工艺出水浊度可控制在 0.1 NTU 以下, 对原水中 COD_{Mn}、DOC、UV₂₅₄ 的去除率分别为 58%、49%、45%。运行过程中陶瓷膜跨膜压差变化趋势呈现出三个阶段: 短期快速上升(滤饼层生长)-中期平稳上升(滤饼层成熟)-末期快速上升(滤饼层密实)。产水通量对陶瓷膜污染速率影响较大, 当 80、100、120、150 L m⁻² h⁻¹ 恒通量运行时, 陶瓷膜前期跨膜压差上升速率分别为 0.18、0.42、1.20、2.04 kPa/h。反冲洗周期对膜污染速率影响相对较小, 反冲洗时“高强度短时间”优于“低强度长时间”模式, 因此适当延长过滤周期、增大反冲洗强度可节省自用水量并保证反冲洗效果。此外, 采取定期排浓措施可减缓膜池内有机物浓度累积, 从而有效延长陶瓷膜稳定运行时间及化学清洗周期。在产水通量 80 L m⁻² h⁻¹、过滤周期 1 h、反冲洗强度 400 L m⁻² h⁻¹、排浓周期 4 h 的较优工况下, 陶瓷膜在连续 12 天运行中无需化学清洗, 跨膜压差仅上升 20 kPa, 表明陶瓷膜组合净水工艺具有良好的应用潜力。

关键词: 平板陶瓷膜; 净水; 通量; 反冲洗; 跨膜压差

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27 查干湖水质富营养化评价及微生物多样性分析

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摘要: 查干湖是吉林省最大的天然淡水湖, 在维护生物多样性和流域生态环境安全等方面发挥着重要作用。本文对查干湖 2018—2020 年汛期(6 月-9 月)水质的理化指标(透明度、COD_{Mn}、总磷、总氮、叶绿素 a)进行分析, 同时利用 Illumina MiSeq 平台高通量测序技术解析浮游细菌(16s)和浮游生物(18s)的群落结构, 以期探究查干湖水质与微生物群落变化之间的联系, 为查干湖富营养化控制提供理论依据。采用综合营养状态指数法对查干湖进行评价, 结果表明, 评价项目的赋分值由大到小依次为 EI(SD)>EI(TN)>EI(COD_{Mn})>EI(TP)>EI(Chla), 查干湖水体透明度低, 总氮、总磷和有机物浓度较高, 2018-2020 年汛期富营养化状态分别处于中度、轻度和轻度。浮游细菌由厚壁菌门(Phylum Firmicutes)、蓝藻门(Cyanobacteria_Chloroplast)、放线菌门(Actinobacteria)、拟杆菌门(Bacteroidetes)、变形菌门(Proteobacteria)、浮霉菌门(Planctomycetes)和疣微菌门(Verrucomicrobia)等门类组成。浮游动植物由无分类真核生物(norank_Eukaryota)、绿藻门(Chlorophyta)、硅藻门(Bacillariophyta)、节足动物门(Arthropoda)、壶菌门(Chytridiomycota)和丝足虫门(Cercozoa)等门类组成。浮游细菌和浮游生物的多样性排序均为: 2019>2020>2018。2019 和 2020 年的浮游细菌群落结构和丰度较为相似, 2018 年浮游细菌群落结构和丰度存在显著差异。同样地, 2019 和 2020 年的浮游生物群落结构和丰度较为相似, 2018 年浮游生物群落结构和丰度存在显著差异。

关键词: 查干湖; 富营养化评价; 高通量测序; 综合营养状态指数法; 微生物群落结构

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28 厌氧氨氧化菌利用内部碳源降解硝酸盐的研究

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摘要: 厌氧氨氧化 (Anaerobic ammonium oxidation, Anammox) 菌通常被认为是一种只能利用外源电子供体 (氨氮 ($\text{NH}_4^+\text{-N}$), 甲酸, 乙酸等) 降解亚硝酸盐 (NO_2^-) 的化能自养菌。本研究首次发现了在以硝酸盐 (NO_3^-) 为唯一氮源的情况下, Anammox 菌利用内部碳源作为电子供体进行 NO_3^- 还原的反应。并提出 Anammox 菌可能是利用硝酸盐异化还原为氨 (Dissimilatory reduction of nitrate to ammonia, DNRA) 的路径进行的 NO_3^- 还原。批次实验中, 在未添加任何外源性电子供体的条件下, 48 h 内约 50 mg/L 的 NO_3^- -N 被 4400 mg/L 的 Anammox 菌还原成了氮气 (N_2), 期间检测到了微量的 NO_2^- -N (最大浓度 2 mg/L)。乙炔作为一种抑制剂, 主要抑制的是 Anammox 反应过程中 $\text{NH}_4^+\text{-N}$ 和一氧化氮 (NO) 反应的这一阶段。通过添加乙炔, 在 NO_3^- -N 降解的过程中检测到了明显 $\text{NH}_4^+\text{-N}$ 的累积。通过对比有无添加碳酸氢盐 (HCO_3^-) 的情况发现, 未添加 HCO_3^- 时 NO_3^- -N 的降解速率明显降低。与此同时, 在有无添加 HCO_3^- 的情况下, Anammox 菌中糖原的含量从初始的 142.20 ± 0.61 mg/g VSS 降低到了 133.22 ± 1.21 mg/g VSS 和 129.79 ± 1.21 mg/g VSS。在长期的反应器实验中, Anammox 菌对 NO_3^- -N 维持着稳定的降解率, 其最大去除率达到了 55.4%。上述结果表明, Anammox 菌通过 DNRA 的途径对 NO_3^- -N 进行降解, Anammox 菌先后将 NO_3^- -N 转化为 NO_2^- -N 和 $\text{NH}_4^+\text{-N}$, 之后通过常规的 Anammox 反应过程将 NO_2^- -N 和 $\text{NH}_4^+\text{-N}$ 转化为 N_2 。内部的碳源物质 (糖原) 在 NO_3^- -N 的降解过程中提供了电子供体。这个结果将会提高 Anammox 菌在复杂环境中的生存能力, 并且使仅通过 Anammox 菌脱氮实现可能。

关键词: 厌氧氨氧化; 硝酸盐降解; 硝酸盐异化还原为氨; 内部碳源

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29 Fe⁰/FeO_x 负载的硅藻土作为高效磁性吸附剂回收水体中的磷

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摘要: 以乙二醇为还原剂, 采用水热法将零价铁/铁氧化物纳米颗粒成功负载在了硅藻土表面及孔道内 (Fe⁰/FeO_x-DE), 并对其作为一种新型磁性吸附剂回收水体中磷的性能进行了探究。硅藻土原矿对磷的吸附量为 3.51 mg P/g, 制备得到的 Fe⁰/FeO_x-DE 材料的吸附量提高到了 37.0 mg P/g。34.3 emu/g 的饱和磁化强度也方便实现固液分离。TEM 和 XRD 表明已实现了 Fe⁰/FeO_x 纳米颗粒的成功负载, 且该制备方法有效地提高了纳米颗粒的分散性。溶液 pH 对磷回收性能的影响较大, pH 为 7 ~ 9 时效率最高。吸附实验数据符合 Langmuir 等温模型和准二级动力学模型, 热力学研究表明吸附过程是自发的吸热过程。使用 NaOH 溶液为再生液, 重复 3 次之后 Fe⁰/FeO_x-DE 对磷的结合率仍保持在 66.8%。在共存离子实验中, 除 SO₄²⁻ 外, Fe⁰/FeO_x-DE 对 P 表现出较好的选择吸附性。静电吸引、化学沉淀和配体交换可以较好地解释吸附机理。吸附结束的含磷复合材料后续可直接用作肥料或土壤改良剂, 从而实现磷回收。

关键字: 硅藻土; 零价铁; 铁氧化物; 磁性; 磷回收

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30 厌氧消化中间产物对噬菌体 MS2 的灭活特性及机理研究

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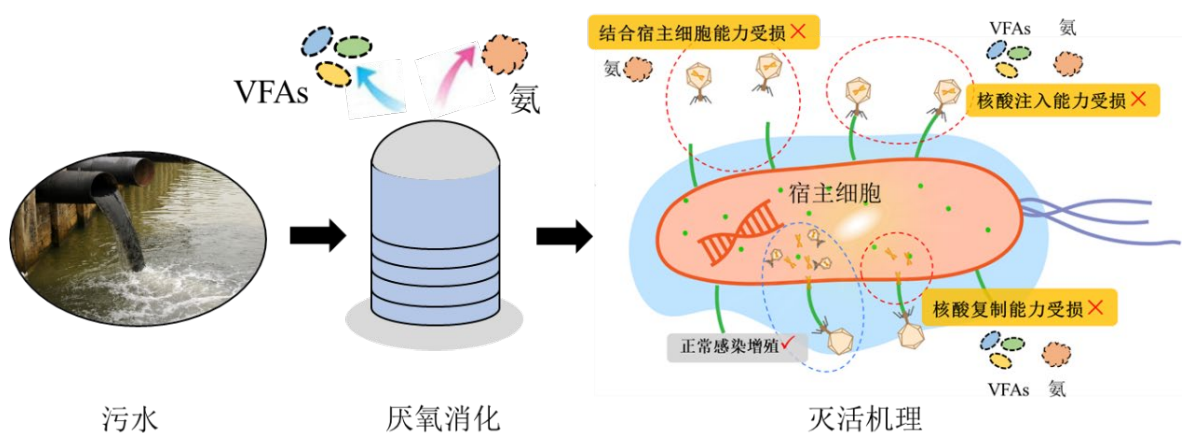
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摘要: 污水处理是降低病毒传播风险和确保污水安全再利用的关键步骤。作为一种新型的污水处理技术, 厌氧消化工艺过程产生的中间产物具有生物毒性, 为在灭活污水中的病毒提供了可能。本研究以噬菌体 MS2 为研究对象, 探究了典型的厌氧消化中间产物挥发性脂肪酸 (VFAs) 和氨对病毒的灭活特性及机理。灭活特性结果表明, 不同链长的 VFAs 对病毒的灭活能力没有显著差异, 游离 VFAs 浓度在 17~20 mmol/L 范围时对病毒的灭活效果最好, 在 pH 为 5.0~6.0 范围内时, 低 pH 不仅通过直接作用和影响游离 VFA 浓度提高病毒灭活, 而且提高了游离 VFA 对病毒灭活的能力; 氨对 MS2 的灭活速率与游离氨 (free ammonia, FA) 浓度成正相关, 25℃、35℃时, 温度的升高不仅通过热效应和影响游离氨浓度提高病毒灭活, 而且提高了游离氨对病毒的灭活能力。灭活机理结果表明, VFAs 通过破坏病毒核酸注入和复制功能来致使病毒失活, 在最佳灭活浓度下, VFAs 会提升对病毒核酸注入功能的破坏, 从而提高对病毒的灭活速率。氨对病毒的灭活机理是破坏了病毒与宿主细胞结合功能、核酸注入功能和复制功能。本研究结果表明厌氧消化工艺在去除污水中病毒以确保水安全回用方面具有较大潜能。

关键词: 厌氧消化; 挥发性脂肪酸; 氨; 灭活; 噬菌体 MS2

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31 不同形式的碳对硫酸盐还原菌修复 Cd 污染水体沉积物的影响

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摘要: 沉积物作为水环境中重要的组成部分, 对重金属在水生生态系统中的迁移、形态转化以及食物链传递均起到了关键作用。当水体沉积物受到自然或人为扰动时, 积累于沉积物中的重金属则会被再次活化并释放到上覆水中, 严重威胁着水体生态环境以及人类健康, 亟待修复治理。在诸多沉积物重金属修复方法中, 微生物修复因具有环境友好、成本低等优势, 被认为有着较好的发展前景。其中, 硫酸盐还原菌 (SRB) 能够将硫酸盐还原成为硫离子, 随后与重金属形成稳定沉淀, 从而达到固定重金属的效果。不过, 由于 SRB 会受到环境条件的限制, 导致其修复效率仍有待提高。因此, 寻找能够刺激 SRB 生长的协同物质以促进重金属的修复, 成为近年来的研究热点。碳是微生物生长的重要营养源, 同时一些含碳基质能够为 SRB 提供电子, 是影响 SRB 生长代谢的重要因素之一。

本研究选取液态有机碳 (甲醇、丙酮酸、乳酸), 以及固态生物质炭 (椰壳炭和桃壳炭) 作为 SRB 的刺激因子, 探究不同形式的碳对 SRB 修复 Cd 污染沉积物 (100mg/kg) 的影响。沉积物中重金属的迁移率和毒性主要取决于其地球化学形态, 因此, 本研究采用 BCR 连续提取法监测沉积物中 Cd 的形态变化。此方法将重金属分为四个形态, 其稳定性顺序为: 可交换态 < 可还原态 < 可氧化态 < 残渣态。结果表明, 大多数修复体系展现出了 Cd 的稳定化趋势, 其中, 丙酮酸条件下的沉积物中可交换态 Cd 的降低以及可还原态和残渣态 Cd 的上升最为显著。这说明丙酮酸能够有效刺激 SRB 的重金属固定化作用, 另外, 该体系上覆水中硫酸盐含量下降最多 (92.4%) 也证明了这一点。然而, 桃壳炭的添加却导致沉积物中 Cd 的可交换态增大和可还原态减少, 这可能是由于固态生物质炭对体系的还原环境造成了破坏, 从而导致 SRB 的硫酸盐还原过程受到抑制。此外, 本研究利用方格星虫肠液对沉积物进行体外消化浸提, 用于评估沉积物中 Cd 的生物可利用性。结果显示, 所有修复体系沉积物中 Cd 的生物可利用性均有所下降, 其中椰壳炭体系下降的幅度最大 (54.20%), 这可能归因于椰壳炭上的多孔结构能够吸附重金属。综合分析 Cd 的生物可利用性和化学形态变化发现, 添加液态有机碳对 SRB 固定沉积物中的重金属有一定积极作用, 且丙酮酸的作用最为有效。固态生物质炭对 SRB 的硫酸盐还原没有促进, 不过椰壳炭因自身的多孔性质实现了重金属的修复, 而桃壳炭对 SRB 以及沉积物重金属修复都没有起到作用。可见, 不同形式的碳对 SRB 修复沉积物重金属污染的影响不同, 选择合适的刺激因子才能达到促进修复的效果。

关键词: 不同形式的碳; 硫酸盐还原菌; 水体沉积物; 重金属修复

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32 纳米氧化锰改性生物炭催化 Fenton 反应协同吸附法去除水体中

EDTA-Cu(II)的研究

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摘要: 金属配合物在水中表现出更高的稳定性, 使金属的去除更具挑战性。在本研究中, 制备了一种低成本、高效的、多功能的纳米氧化锰改性生物炭用于 EDTA-Cu(II) 的去除。基于锰氧化物改性生物炭 Fenton 协同吸附法可有效去除 Cu 和总有机碳, 其中, Cu 去除率为 94.67% (吸附量为 16.55 mg/g), TOC 去除率为 92.79%。该材料在款的 pH 范围和一定浓度条件的共存离子条件下, 仍具有有意的去除性能。机理分析表明, 多功能纳米氧化锰改性生物炭催化 Fenton 反应生成的羟基自由基作通过同步脱羧作用使 EDTA-Cu(II) 络合结构破坏, 产生 EDDA-Cu、IDA-Cu、NTA-Cu、EMDA-Cu 和 Gly-Cu 等中间产物; 在自由基的作用下进一步产生可被改性生物炭吸附的低分子量有机质 Cu 络合物。改性生物炭具有高效、稳定、成本低和应用广泛等优点, 吸附协同 Fenton 法在络合铜的去除中展现了有意的性能, 其为更多络合态金属的去除奠定了良好研究的基础。

关键词: 络合态铜; 吸附; Fenton 反应; 协同作用; 去除途径

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英文摘要（30 篇）

01 Deciphering the influence of multiple anthropogenic inputs on taxonomic and functional profiles of the microbial communities in

Yitong River, Northeast China

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Abstract: Rivers are essential for human civilization and they are threatened by multiple anthropogenic stressors. Microbes are suggested as sensitive bioindicators that actively respond to various disturbances in rivers. We conducted physicochemical parameters analysis, 16S rRNA amplicon sequencing and real-time quantitative polymerase chain reaction to explore the impact of human inputs on the bacterioplankton communities within a tributary of the largest river flowing through a megacity in northeast China. Agriculture largely accounted for the alteration of diversity and functions of the microbial communities. Furthermore, nutrients were significantly declined at the reservoir outlet, and WWTP effluent discharge caused changes in the river microbial community. $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ were the main environmental factors that drive the shift of the bacteria community, and rare taxa played a more important role in the response to environmental changes compared with the abundant ones. The occurrence of the human-specific fecal indicator was mostly derived from agriculture, and its increase in relative abundance was observed in the effluent. Thus, our study provides guidance for ecological assessment and management of rivers by revealing the response pattern of river bacterioplankton to multiple types of anthropogenic stressors.

Keywords: Anthropogenic inputs; Wastewater treatment plant effluent; River ecosystem; Bacterioplankton communities; 16S rRNA gene sequencing

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02 Development of a quantitative structure-activity relationship model for predicting generation quantum yield of hydroxyl radical from dissolved organic matter

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Abstract: Dissolved organic matter (DOM) was shown to generate hydroxyl radicals ($\bullet\text{OH}$) through the excited triplet states of DOM in natural water. In this study, the $\bullet\text{OH}$ quantum yields ($\Phi_{\bullet\text{OH}}$) of 17 DOM-analogs and a commercial DOM, Suwannee River fulvic acid (SRFA), were determined by photochemical experiments. The calculated $\Phi_{\bullet\text{OH}}$ values for the selected DOM-analogs vary from $(1.01 \pm 0.33) \times 10^{-5}$ to $(59.02 \pm 1.43) \times 10^{-5}$. A quantitative structure-activity relationship (QSAR) model for predicting $\Phi_{\bullet\text{OH}}$ was constructed and the established model was proven to have a proper goodness of fit, robustness and predictive ability. The QSAR model was successfully used to predict the $\Phi_{\bullet\text{OH}}$ value of SRFA. Mechanistic interpretation showed that the electron distribution and the electronegativity of DOM are the most important factors that determine the generation of $\bullet\text{OH}$. The results of this study are of importance for understanding the generation of $\bullet\text{OH}$ from DOM and provide a potential tool for the prediction of $\Phi_{\bullet\text{OH}}$ of DOM isolated from natural waters of different sources.

Keywords: Dissolved organic matter; Hydroxyl radical; Quantum yield; Quantitative structure-activity relationship

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03 Study on the treatment efficiency of cosmetics production wastewater and membrane fouling mechanism using electrode ultrafiltration membrane bioreactor

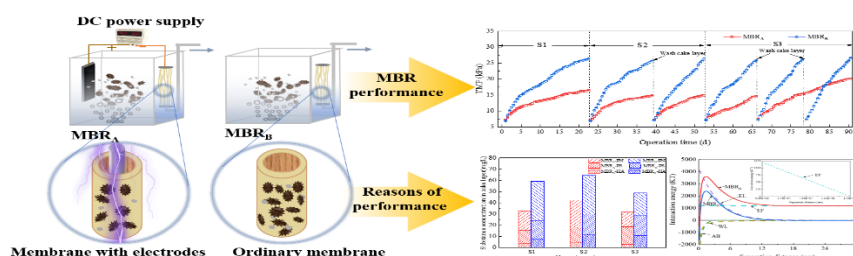
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Abstract: Membrane fouling affects membrane flux and removal efficiencies of the pollutants in the membrane bioreactor (MBR) and it is an urgent task to solve the membrane fouling problem. In this study, electrode ultrafiltration membrane bioreactor made of hollow fiber membrane built-in electrodes was used to relieve the membrane fouling and treat actual wastewater of cosmetic production. Removal efficiencies of the pollutants, sludge activity and the composition changes of extracellular polymeric substances (EPS) were analyzed, and the formation mechanism and control measures of membrane fouling were explored. The results showed that removal efficiency of COD was 85.1% in the electrode ultrafiltration membrane bioreactor A (MBRA) when the current intensity was 10 mA under 800mg/L of influent COD, and its removal efficiency increased by 4.43% compared with ultrafiltration membrane bioreactor B without external current (MBRB). The electric field membrane effect formed by applied current could reduce the content of PN, PS and HA in the cake layer and they only accounted for 61.27%, 78.37% and 34.85% of cake layer in the MBRB. The resistance growth rate of cake layer in the MBRA was much lower than that in the MBRB, and the transmembrane pressure (TMP) reduced by 50%, which greatly extended membrane operation cycle and reduced the frequency of membrane cleaning. After 90 days of operation, specific surface areas of electrode ultrafiltration membrane and ordinary ultrafiltration membrane declined by 56.9% and 78.8%, respectively. Therefore, the electrode ultrafiltration membrane had strong anti-fouling performance, and its service life was significantly increased.



Keywords: wastewater treatment; membrane bioreactor; electrode ultrafiltration membrane; membrane fouling; extracellular polymeric substances

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04 The effect of ZVI/Fe³⁺ coupling on the performance of anoxic sludge and its recycling

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Abstract: The ordinary activated sludge process had low mud-water separation efficiency and low removal efficiencies of the pollutants. Zero-valent iron (ZVI) and Fe³⁺ were added into the activated system and combined to improve flocculation ability and effluent quality in anoxic zone. The effects of ZVI/Fe³⁺ on the removal efficiencies of nitrogen and phosphorus were discussed, and the contact angle, Zeta potential and particle size of the sludge were analyzed. The changes of ZVI crystal structure and element valence were investigated using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The results showed that ZVI mainly improved the removal of COD and phosphorus by enhancing electron transfer rate of sludge, and Fe³⁺ promoted the hydrolysis and acidification of sludge. Nitrate nitrogen was removed by ZVI/Fe³⁺ under biological and chemical action. Removal efficiencies of COD and TP were the highest (72.66% and 98.66%, respectively) under 10 g/L of ZVI and 10 mg/L of Fe³⁺, and removal efficiency of nitrate nitrogen was directly proportional to ZVI content. The flocculation performance of single Fe³⁺ was better than that of single ZVI. Sludge particle size, Zeta potential and hydrophilicity increased under the combined action of ZVI/Fe³⁺. Fe₂O₃ and Fe₃O₄ were formed on the surface of ZVI, which improved removal efficiencies of the pollutants and sludge flocculation. The addition of Fe³⁺ did not change main crystal structure and surface element valence of ZVI. ZVI could be recovered and the reused ZVI still had the ability to remove the pollutants.

Keywords: ZVI; Iron ions; Sludge properties; Pollutants removal efficiency; Charge transfer

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05 Goldfish Growth Inhibition and Gut Microbial Community Shift Induced by Exposure to Carboxylated Multi-Walled Carbon Nanotubes

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Abstract: Exposure to carbon nanotubes can affect animal growth and gut microbiota are closely related with lipid metabolism of animals, but the roles of gut microbiota in the adverse effects of carbon nanotubes on fish growth remain unknown. In this study, juvenile goldfish (*Carassius auratus*) was exposed to 0-1000 µg/L carboxylated multi-walled carbon nanotubes (MWCNT-COOH) for 28 d to investigate the correlations of fish gut microbial community shift with the induced toxicities. MWCNT-COOH was found to induce histopathological and oxidative damages to liver. Fish body weight and liver weight decreased after the MWCNT-COOH exposure at any dose for 14 d or longer time ($p < 0.05$). Pyrosequencing of 16S rRNA gene amplicon showed that the MWCNT-COOH exposure greatly disturbed gut microbial community structure of the fish by increasing the relative abundance of Bacteroidetes phylum and *Bacteroides* genus and inhibiting Proteobacteria and Firmicutes phyla and *Vibrio* genus. Correlation and network analyses consistently indicated that the liver weight and body weight changes were positively correlated with the alterations of Firmicutes/Bacteroidetes ratio and negatively correlated with the increase of Bacteroidetes and *Bacteroides* abundance. Our results suggested that MWCNT-COOH inhibited fish growth by modulating the intestinal microbiota and subsequently disturbing the lipid metabolism.

Keywords: goldfish; gut microbial community; MWCNT-COOH; lipid metabolism; pyrosequencing

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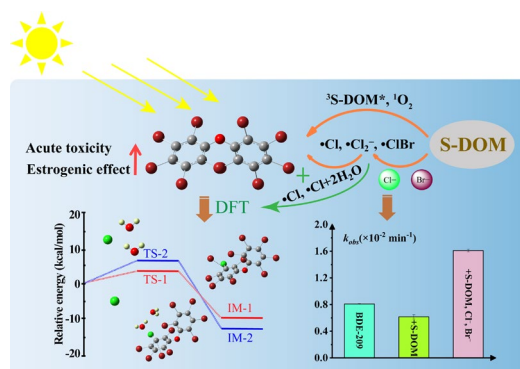
06 Photo-induced degradation and toxicity change of decabromobiphenyl ethers (BDE-209) in water: Effects of dissolved organic matter and halide ions

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Abstract: BDE-209 is a widely used brominated flame retardant that is ubiquitous in the aquatic environment, especially in marine water. However, photodegradation of BDE-209 in seawater is still not fully understood. In this work, the photodegradation kinetics of BDE-209 in water was studied and the effects of seawater dissolved organic matter (S-DOM) and halide ions (Cl^- , Br^-) were evaluated. S-DOM inhibited the degradation of BDE-209 through dynamic quenching and light shielding effect. However, with the coexistence of S-DOM, Cl^- and Br^- , the photodegradation of BDE-209 was significantly promoted. The promotional effect is attributed to the generation of excited triplet state S-DOM, singlet oxygen, and reactive halogen radicals. The results of density functional theory calculation showed that $\bullet\text{Cl}$ addition reaction on C-Br sites of BDE-209 is the main reaction pathway of BDE-209 with chlorine radical, which leads to the generation of mixed Cl/Br substituted intermediates. The acute toxicity and estrogenic effects of BDE-209 solution were enhanced during simulated sunlight irradiation. These results indicate that the environmental factors in seawater play important roles in the photodegradation of BDE-209, and contribute to the potential ecological risks of PBDEs in the marine environment.

Keywords: Dissolved organic matter; Decabromobiphenyl ethers; Halide ions; Photodegradation; Toxicity effect



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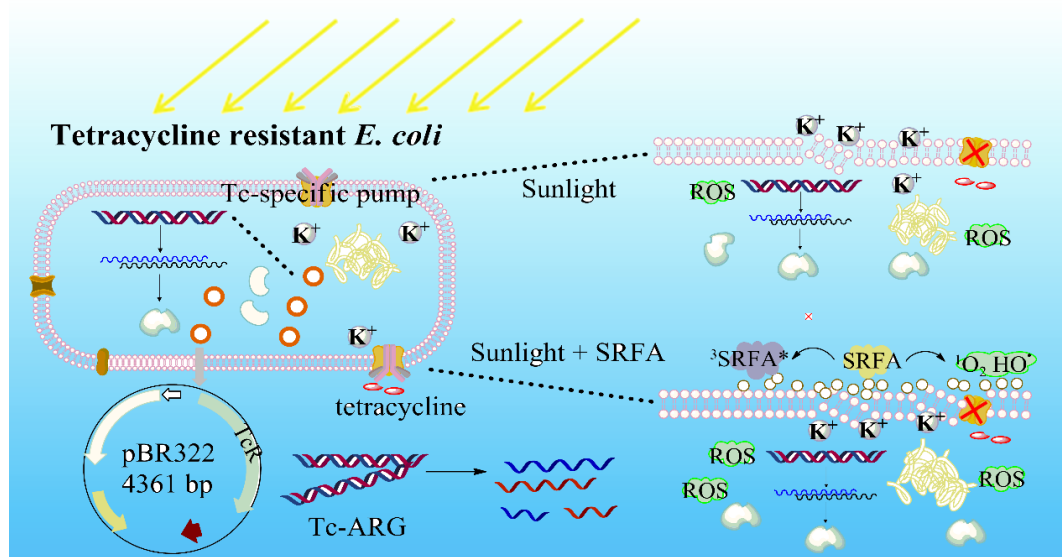
07 Simulated sunlight-induced inactivation of tetracycline resistant bacteria and effects of dissolved organic matter

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Abstract: The transmission of antibiotic resistance in surface water has attracted much attention due to its increasing threat to human health. The role of sunlight irradiation and the effect of dissolved organic matter (DOM) on the transmission of antibiotic resistance are still unclear. In this study, photo-inactivation of antibiotic resistant bacteria (ARB) was investigated using antibiotic resistant *E. coli* (AR *E. coli*) that contained the tetracycline resistance gene (Tc-ARG) as a representative. The results showed that AR *E. coli* underwent significant photo-inactivation due to the membrane damage induced by direct irradiation and by the generated reactive oxygen species. Simulated sunlight irradiation specifically suppressed the expression of tetracycline resistance, which is attributed to the destruction of tetracycline-specific efflux pump. Tetracycline inhibited the photo-inactivation of AR *E. coli* due to its selective pressure on tetracycline resistant *E. coli* and competitive light absorption effect. Suwannee River fulvic acid (SRFA), a representative DOM, promoted the inactivation of AR *E. coli* and further inhibited the expression of tetracycline resistance gene due to the generation of its excited triplet state, singlet oxygen, and hydroxyl radical. The extracellular Tc-ARG also underwent fast photodegradation under light irradiation and in the presence of SRFA, which leads to the decrease of its transformation efficiency. This study provided insight into the sunlight-induced inactivation of ARB, which is of significance for understanding the transmission of tetracycline resistance in surface water.

Keywords: Antibiotic resistant bacteria; Photo-inactivation; Tetracycline resistance; Dissolved organic matter; Reactive oxygen species



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08 Genomics study of a steroid-estrogen-degrading bacterium

S.nematodiphila DH-S01

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Abstract: Environmental estrogen is considered to be a category 1 carcinogen by the World Health Organization. Removal of environmental estrogen is an urgent environmental hot issue. We isolated a strain that can degrade the steroid estrogen estrone (E1) and 17 β -estradiol (E2) from the sewage treatment plant and named it DH-S01. The genomic structure and genetic characteristics of this strain was investigated. The genome of this strain consists of a 52,56,558 bp circular chromosome with 4,874 coding genes in total. Among the metabolic genes, there are fixed as many as 853 genes related to the metabolism of terpenoids and ketones. 13 related genes involved in the degradation process of steroid estrogen, encoding 9 types of sterol estrogen degrading enzymes, including benzene ring-opening catechol 1,2-dioxygenase, 1 type of sterol core degrading enzyme and 7 types of sterol side chain degrading enzymes. The existence and expression of 9 types of sterol estrogen degrading enzymes encoded by these genes, such as acetyl-CoA synthase, acyl-CoA transferase and acyl-CoA dehydrogenase, were verified by PCR and RT-PCR. Under E1 and E2 sole carbon source culture conditions, 6 and 5 sterol oestrogens degrading enzyme-related genes were increased respectively. Cultivation experiments showed that the degradation rates of E1 and E2 in the strains reached 93.47% and 93.2%, respectively. This study upheld the ability of this strain to degrade steroid estrogen at the genomic level.

Keywords: *S.nematodiphila*; Estrogen; Degrading enzyme; gene

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09 Phosphate enrichment from municipal wastewater by BSBR

process

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Abstract: The annual phosphorus recovered by the sewage treatment plant can meet 15-20% of human phosphorus demand. At present, the side-flow phosphorus recovery process based on enhanced biological phosphorus removal (EBPR) process has the disadvantage of low recovery efficiency. Koderá; Tian et al. enriched the phosphate recovery solution to 110-130 mg·L⁻¹ with the biofilm method at the influent phosphorus concentration of 5-16 mg·L⁻¹ and the carbon source dosage of 500-900 mg·L⁻¹. The phosphorus concentration of urban sewage influent in China is generally low, and the concentration in the southern region is about only 3-5 mg·L⁻¹. Studies have shown that under low phosphorus loading/low concentration, the growth of phosphate accumulating organisms (PAOs) may be inhibited, leading to glycogen accumulating organisms (GAOs) as a dominant species, thus, leading to the collapse of the biological phosphorus removal system. In this research, a BSBR reactor with alternating anaerobic and aerobic mode was operated under the condition of low phosphorus concentration (2.5 mg·L⁻¹) to investigate the phosphate enrichment, recovery efficiency, and carbon source consumption. Also, the variation of the dominant microbial community in the system was reviewed by high-throughput sequencing to verify the feasibility and performance of BSBR for the treatment of municipal wastewater with low phosphate concentration.

A BSBR reactor with an effective volume of 8L and phosphorus concentration of 2.5 mg·L⁻¹ was simulated. In the aerobic stage, the phosphorus was absorbed and discharged. In the anaerobic stage, the recovery solution and the substrate solution (COD=100 mg·L⁻¹) were pumped into the reactor to release phosphorus. At the end of the anaerobic phase, the phosphorus recovery solution flowed into the recovery tank (the recovery solution was reused),the BSBR process completes one cycle. Then, changed the system to the aerobic stage again for the phosphorus absorption and moved in circles. After several cycles, high-enriched phosphorus recovery solution was obtained.

After 40 days, the phosphorus removal rate in the aerobic stage can be stabilized at more than 80% when the biofilm was cultured under conditions of 10 mg·L⁻¹ phosphorus concentration in aerobic influent, 4-6 mg·L⁻¹ dissolved oxygen in aerobic phase, and 200 mg·L⁻¹ COD in anaerobic phase. After acclimation, the influent phosphorus concentration was reduced to 2.5 mg·L⁻¹, the anaerobic COD concentration was kept to 100 mg·L⁻¹, and the dissolved oxygen was controlled to 6-8 mg·L⁻¹. The phosphorus concentration in the effluent could be maintained below 0.5 mg·L⁻¹. After about 60 cycles, the average phosphorus concentration of the phosphorus recovery solution in the recovery tank can reach 75.8±2.9 mg·L⁻¹, and the enrichment factor has reached 30.3 times. The average phosphorus recovery efficiency reached to 64.5% based on the total dissolved phosphorus, and the average recovery rate of TP reached to 72.8%. The C_{upt}/P_{rel} (COD per gram of phosphorus recovered) was 37.3±2.6 mg-P/mg-COD. The various indexes indicated that this phosphorus recovery system is better than the previous literatures.

High-throughput sequencing showed that the dominant phyla were *Proteobacteria*, *Bacteroidota*, and *Chloroflexi*. The relative abundance of *Proteobacteria* increased from 22.64% of the seed sludge to 70.05% of the domesticated sludge after 40 days of cultivation and finally stabilized at 58.05% with the decrease of influent phosphorus concentration from 10 mg·L⁻¹ to 2.5 mg·L⁻¹. Previous studies have shown that *proteobacteria* is a phylum that contains common PAOs groups such as *Rhodocyclaceae* and *Moraxella*: the key microorganisms in biological phosphorus removal and exogenous biodegradation. At the genus level, there were 18 genera with abundance > 2%. After 130 days of stable operation in the reactor, the dominant genera *Candidatus Competibacter*, *Flavobacterium*, *Saprospiraceae*, *Thiothrix*, et al., were determined *Flavobacterium* and *Thiothrix* were reported as PAOs, and their relative abundance increased from 0.49% and 0.00% to 16.88% and 3.30%, respectively.

Keywords: BSBR, Biofilm, Phosphorus recovery, Municipal wastewater, microbial community

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10 Combining chlor(am)ine-UV oxidation to ultrafiltration for potable water reuse: Promoted efficiency, membrane fouling control and mechanism

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Abstract: Wastewater reuse has been progressively popular as a practical method for protecting aquatic environment and water sources. In this work, the chlor(am)ine-UV oxidation was employed to enhance membrane system performance during potable water reuse. The achievements were comprehensively evaluated from the aspects of membrane fouling mitigation and organic matter removal. The various dosages of chlorine and UV irradiation were applied and the effects of typical inorganic species in wastewater effluent were considered as well. It was suggested that the chlor(am)ine-UV oxidation could significantly promote the normalized flux by 94.9% under the condition of 10 mg·L⁻¹/960 mW·cm⁻² (chlorine dose and UV irradiation density). And the certain lower concentration of inorganic pollutant in wastewater effluent could further prevent the membrane fouling accumulation, especially for the reversible and total fouling resistances. The model fitting of filtration flux revealed that the combination of pore blockage and cake filtration was responsible for the mechanisms of fouling formation, and the transition moment was adjusted by the oxidation process. The characteristics of dissolved organic matter were modified as well, which were positive for the improvement of membrane effluent quality and security. The results demonstrated that the combination of the chlor(am)ine-UV oxidation and ultrafiltration could be a promising alternative for efficient wastewater recycle and reuse.

Keywords: Chlor(am)ine-UV oxidation; ultrafiltration; membrane fouling; potable water reuse; micropollutants

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11 Efficient acetate production in photo-assisted microbial electrosynthesis system by urea-treated MnFe₂O₄/g-C₃N₄ cathode incorporating with *Serratia marcescens*

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Abstract: Photo-assisted microbial electrosynthesis system (MES) is a promising technology to reach the sustainable carbon neutrality goal by combining photocatalysis with bioelectrochemical system for valuable biofuels (e.g. acetate) production from inorganic carbon. It is thus imperative to explore efficient photocatalysts with excellent biocompatibility for acetate production. Manganese ferrite (MnFe₂O₄) combined with graphitic carbon nitride (g-C₃N₄) is a biocompatible candidate (MnFe₂O₄/g-C₃N₄) but with poor photocatalytic performance. Herein, the MnFe₂O₄/g-C₃N₄ after urea treatment achieved reproducible and superior transient photocurrent responses, 2.8 (MnFe₂O₄/g-C₃N₄ without urea treatment), 14.1 (MnFe₂O₄) and 18.5 (g-C₃N₄) times of the controls. Moreover, photoluminescence further demonstrated the high carrier separation efficiency of the urea-treated MnFe₂O₄/g-C₃N₄. Urea treatment broadened the light absorption range of the heterojunction, which in turn sufficiently utilized visible light for acetate production from inorganic carbon through a Z-scheme mechanism. The assembling of the urea-treated MnFe₂O₄/g-C₃N₄ with *Serratia marcescens* achieved a 8.5 ± 0.6 mM/d acetate production with a CE_{acetate} of 96 ± 3% under simulated sunlight, appreciably higher than the controls of MnFe₂O₄/g-C₃N₄ without urea treatment (acetate: 3.6 ± 0.3 mM/d; CE_{acetate} : 71 ± 4%), abiotic MnFe₂O₄/g-C₃N₄ (absence of any acetate), absence of illumination (acetate: 3.3 ± 0.3 mM/d; CE_{acetate} : 67 ± 3%). Cyclic voltammetry demonstrated the more positive reduction onset potential (−0.31V) and the higher maximum reduction peak current (−2.77 mA) for acetate on the urea-treated MnFe₂O₄/g-C₃N₄ photocathode, compared to the urea-untreated control (potential: −0.31V; current: −1.27 mA), confirming the improved interaction between electrotroph and photocatalysts for acetate production by urea treatment. This is the first study that evaluated the enhanced photocatalytic performance of MnFe₂O₄/g-C₃N₄ photocatalyst by urea treatment, and thus provides an alternative and ingenious strategy for efficient acetate production from CO₂ sequestration.

Keywords: microbial electrosynthesis system, MnFe₂O₄/g-C₃N₄, urea treatment, photo-assisted, electrotroph

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12 Water quality characteristics and microbial diversity analysis of

Mopanshan Reservoir

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Abstract: Water source reservoir plays a vital role in ensuring the drinking water health of urban residents and maintaining sustainable economic development. In order to explore the water quality characteristics of Mopanshan Reservoir and the relationship between water quality and microbial community changes, the physical and chemical indexes of water quality of Mopanshan Reservoir were analyzed, and the characteristics of microbial diversity and community structure were analyzed by using high-throughput sequencing technology. The results showed that the main exceeding standard index of water quality of Mopanshan Reservoir in 2019 was total nitrogen. Except April, the total nitrogen in other months exceed the standard, and the concentration was 1.25 ~ 2.22 mg / L. The microbial communities in the water body and sediments in the reservoir center and before the dam were composed of 441 genera. The microbial diversity in sediment was higher than that in water, The order of microbial diversity was N1 > N2 > S2 > S1, Redundancy analysis (RDA) showed that total nitrogen (TN), dissolved oxygen (do) and water temperature (WT) were the main water quality factors affecting the microbial community structure of Mopanshan Reservoir. The purpose of this study was to provide theoretical basis and data support for the microbial safety indication of water supply in Mopanshan Reservoir.

Key Words: Mopanshan Reservoir, Characteristics of water supply quality, High throughput sequencing technology; Microbial community structure; Microbial diversity

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13 Prediction of organic compounds adsorbed by PE and CPE

microplastics in freshwater based on QSAR method

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Abstract: Microplastics (MPs), a growing class of emerging pollutants in the environment, have attracted widespread attention due to their adsorption properties. Recent research on MPs has mainly concentrated on seawater, and little work has been conducted on freshwater. Investigating and predicting the adsorption behavior of organic pollutants by MPs are necessary in freshwater. In this study, the adsorption behavior of 13 organic chemicals by polyethylene (PE) and chlorinated polyethylene (CPE) MPs was determined under freshwater conditions. Results shows the majority of the organic chemicals exhibit no distinctive differences in their adsorption on two MPs. However, the adsorption of polycyclic aromatic hydrocarbons (Phenanthrene and Naphthalene) and 1,2,3,4-tetrachlorobenzene on CPE is obviously stronger than that on PE, and the result is a counter for two pesticides (Tricyclazole and Triadimefon). Quantitative structure activity relationship (QSAR) analysis was performed for the prediction of adsorption capacity. A QSAR model with acceptable performance ($R^2 = 0.8586$) was built to predict the adsorptive affinity (expressed as $\log K_d$) of organic compounds on the PE MPs via multivariable linear regression (MLR) on forty-nine determined and collected data. The model suggests that the octanol/water partition coefficient ($\log K_{ow}$) and excess molar refractive index (E) play dominant roles in the adsorption process. The higher the hydrophobicity of the compound, the greater the adsorption capacity of PE to it, and the interaction of the n and π electrons of the compound with the microplastic also has an effect on adsorption. A QSAR model with satisfactory performance ($R^2 = 0.9302$) was also established for $\log K_d$ values from CPE MPs in freshwater by using 13 adsorption data determined. The result shows that the octanol/water partition coefficient ($\log K_{ow}$) and the most negative charge on Cl atom ($Q_{\max, \text{cl}}$) play a decisive role in the adsorption. Again, the higher the hydrophobicity of the compound, the stronger the CPE adsorption capacity for it. Compounds with Cl atoms in them may repel the Cl groups in CPE. The findings can provide a scientific basis for the risk assessment of waters contaminated by MPs and organic pollutants.

Keywords: Microplastics; Adsorption; Quantitative structure activity relationship; Multivariable linear regression

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14 Development and evaluation of a ceramic diffusive layer based DGT technique for measuring organic micropollutants in seawaters

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Abstract: Diffusive gradients in thin-films (DGT) technique has been well demonstrated as a robust tool for measuring organic micropollutants (OMPs) in the aquatic environment. However, potential adsorption of the OMPs on organic polymer filters and flow rate of waters can affect the measuring results of the DGT method, hence tedious work should be conducted to reduce these interferences. In the present study, a novel DGT technique coupled with a ceramic diffusive layer was developed to measure the OMPs in seawaters. The ceramic diffusive layer exhibited adsorption inertness to the OMPs with various logK_{ow} values. Moreover, the ceramic diffusive layer based DGT technique was proved to be less affected by the flow rate than the traditional DGT with agarose diffusive layer. The developed DGT device exhibited kinetic accumulation for the targets during a 6-d deployment, and measurement of the OMPs by the DGT method was independent with pH and ionic strength. Finally, the developed DGT sampler was applied in coastal waters of Dalian, and eight OMPs were detected with levels ranging from 1.58 to 13.1 ng/L. The development of the ceramic diffusive membrane can lead to simplification of the DGT applications, promoting the progress of the OMPs monitoring technology.

Keywords: Ceramic diffusive layer; Diffusive gradients in thin-films; Organic micropollutants; Seawater

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15 Tracking *Cryptosporidium* in urban wastewater treatment plants in a cold region: occurrence, species and infectivity

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Abstract: This study was designed to investigate the occurrence, species, infectivity and removal efficiency of *Cryptosporidium* spp. across typical wastewater treatment train. Samples from different process units were collected seasonally and synchronously from four wastewater treatment plants (WWTPs) in Northeastern China. Live *Cryptosporidium* oocysts was identified in most samples from both influent (97.50%) and effluent (90.00%) wastewaters of the four WWTPs, at an average density of 26.34 oocysts L⁻¹ and 4.15 oocysts L⁻¹, respectively. The overall removal efficiency was 84.25%, and oocysts were mainly removed (62.01%) by the modified secondary sedimentation process. Ten *Cryptosporidium* species were identified in the effluent samples. *C. andersoni*, *C. bovis*, and *C. ryanae* were the three most prevalent species. Oocyst viability assays indicated that the primary and secondary wastewater treatments did not reduce excystation rate (varied in the range of 63.08-68.75% in 2 hour), but the excystation rate declined to 53.31% in the effluent after disinfection. It is worth noting that the *Cryptosporidium* oocysts displayed higher infection intensity in the cold season (winter and spring) compared to that in summer and autumn. The influences of environmental temperature on virulence factors of *Cryptosporidium* were further examined. We found that more extracellular secretory proteins (ESPs) were bound on the oocyst surface and that several virulence genes were expressed relatively strongly at low temperatures, both of which could facilitate oocyst adhesion, invasion, and host immune evasion. This work can be considered an important step towards more accurate panoramic recognition of *Cryptosporidium* risk reduction in WWTPs, and especially highlights the potential health risk associated with *Cryptosporidium* in cold regions/seasons.

Keywords: WWTPs; *Cryptosporidium*; occurrence; species; infectivity; low temperature.

Graphic Abstract

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16 Low-intensity ultrasound assisted iron-dependent autotrophic denitrification by alleviating cell-iron mineral aggregation induced by Fe(II)-oxidizing products

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Abstract: Autotrophic iron-dependent denitrification (AIDD) process has garnered increasing interests as a proposed alternative to remove nitrogen from wastewater with a low carbon to nitrogen ratio. However, recent studies have shown an inevitable deterioration of AIDD performance caused by the aggregation of microbial cells and iron-bearing minerals, making it difficult to achieve a long-term stability of this process. Here, this work develops a simple method to resolve such a problem by adopting low-intensity ultrasound treatment. Batch results reveal that the aggregation of cells and iron-bearing minerals in Fe(II) oxidation process induced a cumulative inhibition on the activity of AIDD sludge. Extracellular polymeric substances played a glue-like role in the cell-iron mineral aggregates, where microbial cells were caged. Sonication was found to efficiently recover the AIDD activity by disintegrating such aggregates rather than stimulating the microbial metabolism. Moreover, the low-intensity ultrasound assisted AIDD bioreactor exhibited an advantageous nitrogen removal performance compared to the control bioreactor. An intermittent sonication of 5 min promoted the nitrogen removal efficiency of the AIDD bioreactor from 39.0% to 68.4% and maintained relatively stable operation for two weeks. Overall, the ultrasonic treatment seems to be a promising way to support the development of AIDD process.

Keywords: Autotrophic iron-dependent denitrification (AIDD); low-intensity ultrasound; wastewater treatment; extracellular polymeric substances; cell-mineral aggregates

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17 Reduced graphene oxide carbonized aerogel as electrodes in supercapacitive E-Fenton system for sulfamethoxazole degradation

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Abstract: Novel reduced graphene oxide carbonized aerogel (RGO-CA) was used as the electrodes in a neutral supercapacitive Electro-Fenton (SEF) system to achieve degradation of sulfamethoxazole (SFX). Poriferous RGO-CA material was fabricated by a multistage carbonization method, leading to a good conductivity (28.42 Sm^{-1} with 5 mg mL^{-1} GO), high surface area ($2321 \text{ m}^2 \text{ g}^{-1}$) and a specific capacitance of 310 F g^{-1} at 0.2 A g^{-1} in a two-electrode setup. The maximum energy density of RGO-CA was 19.8 W h/kg at a power density of 125 W kg^{-1} and 90.2% capacitance was retained after 10000 cycles of charge-discharge at 5 A g^{-1} . After 24 h treatment in SEF system, the total degradation rate of SFX was 98.1%. The total organic carbon (TOC) removal efficiency of SFX was 90.2%. This RGO-CA electrode demonstrated a great potential for the SEF system to remove antibiotics in water.

Keywords: Carbonized aerogel; Supercapacitive; Electro-Fenton; Antibiotic reduction; Porous electrode

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18 Oxygen and nitrate/nitrite: the key parameters for the enrichment of denitrifying methanotrophs

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Abstract: Denitrifying anaerobic methane oxidation (DAMO) process uses methane as electron donor to reduce nitrate/nitrite to dinitrogen, which is a potentially efficient, low-cost and clean biological nitrogen removal technology. However, incredibly slow microbial growth and process start-up severely limit the application of this promising process. To achieve rapid microbial enrichment and reactor start-up, a series hollow-fiber membrane biofilm reactor (HfMBR) was operated to investigate the influence of oxygen and substrates nitrate/nitrite on the enrichment of DAMO microorganisms. The reactor was run for 90 days and finally achieved the nitrate removal rate of 9.1 mg N L⁻¹ d⁻¹ without nitrite and ammonia accumulation. Compared with the inoculum, the abundance of DAMO archaea and DAMO bacteria increased 92.9 and 136.6 times respectively at the end of the enrichment, and the relative abundance increased 65.4 and 340.7 times, respectively. 40-240 μm biofilms were formed in the series HfMBR at the end of the enrichment and the biomass decreased from the first to the fifth unit in sequence. The results indicated that oxygen and low nitrate concentration significantly inhibited the growth of DAMO archaea while DAMO bacteria could tolerate high dissolved oxygen concentrations and low substrate concentrations. This work provided theoretical guidance for the rapid enrichment of DAMO microorganisms and contributed to the application of methane-dependent denitrification process.

Keywords: denitrifying methanotrophs, rapid enrichment, oxygen, nitrate/nitrite.

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19 Pilot-scale evidence of mainstream nitrogen removal via a novel anammox coupling with partial-denitrification: Identification of mechanisms and microbial community

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Abstract: The increasingly stringent nitrogen discharge limit with minimized energy consumption and carbon footprint has become a great challenge for wastewater treatment. Anammox is regarded as the most attractive biological treatment, which converts ammonia ($\text{NH}_4^+\text{-N}$) and nitrite ($\text{NO}_2^-\text{-N}$) to nitrogen gas (N_2) directly under anaerobic condition. However, it still faces the major bottleneck of instable nitrification as pretreatment for oxidizing $\text{NH}_4^+\text{-N}$ to only $\text{NO}_2^-\text{-N}$. Partial-denitrification (PD) coupling with anammox (PD/A) is emerging as a promising technology due to the relatively stable $\text{NO}_2^-\text{-N}$ production, less organic carbon demand, and high-level nitrogen removal performance. Current studies have been based on small-scale reactors in the laboratory with simulated wastewater. In this study, the pilot-scale PD/A for municipal wastewater treatment was developed for the first time. The microbial mechanisms and population structure were comprehensive analyzed.

Methods and materials: The municipal wastewater from wastewater treatment plant in Beijing was used as influent. The average $\text{NH}_4^+\text{-N}$ and COD was 47.8 mg/L and 152.3 mg/L during the experiment. Two sequencing batch reactor with working volume of 10 m³ and 8 m³ were started up for nitrification and PD/A, respectively. The nitrifying SBR was operated as anoxic and aerobic condition. The PD/A SBR was operated under a consisted anoxic stage, which was fed with the effluent of nitrifying SBR and the raw water with a volume ratio of 3:1.

Result and discussion: A pilot scale PD-A process was established by adding anammox activated sludge to a stable PD reactor; When the influent TN is about 37.6mg/L, the removal rate of TN can get 74.9%. Otherwise, the contribution ratio of anammox in TN removal is 64.5%. The stable $\text{NO}_2^-\text{-N}$ accumulation in the PD process is the key factor of denitrification in the system with the NTR more than 80% in the typical cycle; *Thauera* is always dominant in the microbial community with the relative abundance 13.58%; *Candidatus brocadia* is the main anammox functional bacteria in the system. In long term operation, its proportion in the microbial community has increased from 0.96% to 1.55%. The abundance increase is an important guarantee of anammox activity under the water quality and temperature fluctuation; Compared with the traditional nitrification/ denitrification process, the PD-A has lower sludge output, which would reduce the energy and cost for sludge treatment in the practical application process and can get higher economic value and environmental benefits.

Therefore, the novel integration of PD/A has great potential for efficient low-strength wastewater treatment with low land occupancy and desirable effluent quality, which required low organic carbon source and aeration energy.

Key words: Municipal wastewater treatment, biological nitrogen removal, pilot-scale, anammox, denitrification

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20 Fabrication of H3PW12O40/g-C3N4 catalysts for enhanced hydrolysis of polysaccharides

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Abstract: A series of heteropolyacid (HPA) functionalized graphitic carbon nitride (g-C₃N₄) HPA/g-C₃N₄ (n wt%, n means the loading amount of HPA on g-C₃N₄, n = 20, 25, 30 and 35) was synthesized, which was evaluated their catalysts in conversion of polysaccharides as cellobiose, sucrose, starch and cellulose. The high yield (58.6%) of 5-hydroxymethylfurfural (5-HMF) was obtained in one-pot upon H3PW12O40(HPW)/g-C₃N₄(30) at 100 % cellulose conversion, which was contributed to the nature of HPW/g-C₃N₄(30) with (1) the coexistence of Brønsted acidic and basic sites favoring for cellulose hydrolysis, isomerization of glucose to fructose, hence hydration to 5-HMF; (2) electron-transfer between g-C₃N₄ and HPW promoting depolymerization of cellulose, which combined pre-oxidation and hydrolysis in one-pot. Meanwhile, extra proton was generated during the oxidationreduction between HPW and g-C₃N₄; (3) nitrogen groups and hydrophobic cages in g-C₃N₄ to adsorb cellulose molecules around active sites of HPW. HPW/g-C₃N₄ was determined as an efficient, recyclable solid catalyst with high stability and long duration for highly selectively to 5-HMF in one-pot HPW/g-C₃N₄(30) in 10 cycles with highly promising in cellulose conversion

Keywords: Heteropolyacid; g-C₃N₄; Cellulose; 5-HMF; Cascade reaction

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21 Engineering Enhanced Anaerobic Digestion via Ethanol-type

Fermentation Pretreatment: Mechanisms and Applications

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Abstract: Conversion of organic wastes to methane via anaerobic digestion has been practiced for more than 160 years. However, the technical bottlenecks derived from the thermodynamic limitations of interspecies hydrogen/formate transfer (IHT/IFT) between syntrophs and methanogens resulting in the slow fermentation rate, low methane conversion efficiency and poor stability of system still limit its large-scale application. No engineering strategy to speed up IHT/IFT for dramatically changing the performances of anaerobic digestion has been developed. However, simple strategy of pretreating organic wastes to produce ethanol for accelerating and stabilizing anaerobic digestion has been recently documented in the laboratory and engineering-scale digesters (Fig. 1). Molecular methods reveal that the change of methanogenic communities is not towards the promotion of IHT/IFT. The most likely interpretation of these results is that ethanol may not favor IHT/IFT but direct interspecies electron transfer (DIET), a novel working mode of interspecies electron transfer that depends on the electrically conductive pili (e-pili) or multi-heme *c*-type cytochromes as the electrical connection components. However, further summary and clarification to understand the enhanced mechanisms and advantages of this engineering strategy are required. In this study, we summarized the current evidence that anaerobic digestion could be enhanced by initially pretreating organic wastes to produce ethanol, discussed the link between ethanol and DIET, and emphasized how this engineering strategy would be better applied in the future.

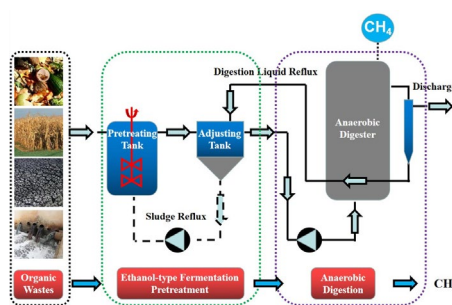


Figure 1. Schematic diagram on engineering strategies for enhancing anaerobic digestion via ethanol-type fermentation pretreatment.

Keywords: Anaerobic Digestion; Methane Production; Direct Interspecies Electron Transfer (DIET); Ethanol Fermentation; Pretreatment

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22 Insight into synergies between ozone and in-situ regenerated granular activated carbon particle electrodes in a three-dimensional electrochemical reactor for highly efficient nitrobenzene degradation

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Abstract: This study compared the removal and mineralization of nitrobenzene (NB) by electrolysis using granular activated carbon (GAC) as three-dimensional (3D) electrodes, ozonation, and the combination of electrolysis, GAC, and ozone (E-GAC-O₃). A highly synergetic effect was demonstrated by combining electrolysis, ozone, and GAC, and able to achieve 95.58% of TOC removal within 120 min due to abundant production of •OH in the E-GAC-O₃ process. Interestingly, further study revealed 92.30% of NB removal was due to the oxidation of •OH, and the E-GAC-O₃ process could achieve a much higher energy efficient ratio for •OH production compared with other processes. Besides, the mechanism of •OH generation was explored through quantitatively estimating the contribution of different reaction paths involved in E-GAC-O₃ process. Results demonstrated that electrochemical oxidation of hydroxyl ion, peroxone reaction, GAC catalyzed ozone reaction, and electro-reduction of ozone reactions were responsible for 12.50%, 37.50%, 8.75%, and 31.25% of •OH generation, respectively. Moreover, the durability of GAC in E-GAC-O₃ process was systematically investigated by reusing GAC for 50 times. It is worth noting that GAC possessed a very stable activity for transforming ozone into •OH with almost unchanged functional groups and pore texture during long consecutive recycles in E-GAC-O₃ process, while the cathode insulation experiment revealed that replenishing of free electrons from both cathode and inside of GAC was critical for maintaining the stability of GAC. These findings should be widely considered in the combination of electrolysis using 3D electrodes and ozone technologies to obtain further improvement of their potential and applicability in industrial practice. Finally, the removal efficiency of other ozone-refractory organics, Ibuprofen (IBP), Benzotriazole (BTA), and N,N-Dimethylformamide (DMF) were also investigated while the effects of different water matrices on NB removal in E-GAC-O₃ process was studied. All the results suggest that the E-GAC-O₃ process was efficient and sustainable for refractory organic wastewater treatment.

Keywords: Electro-peroxone, granular activated carbon, ozonation, advanced oxidation process, three-dimensional electrode

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23 Microbial diversity, community composition and metabolic function in Xiangjiang River: the relationship with nutrients

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Abstract: Microbial communities are central components in river ecosystem. They are involved in the transportation and transformation of certain pollutants including nutrients that discharged to the surface water. The microbial diversity and composition in rivers can reflect the quality of surface water systems. Yet most of current research focus on the bacterial diversity and less on the eukaryotes which also play key role in nutrient cycle. In this study, 10 sampling sites along Xiangjiang river were selected, covering the total reaches of Changsha City, China. Both bacterial and eukaryotic diversity and composition in water and sediments samples were investigated using 16S/18S rRNA amplicon sequencing. Typical water quality parameters including $\text{NH}_4^+\text{-N}$, TN, TP and COD of the water samples were analyzed to explore the correlation with microbes.

The results showed that the sediments had a higher diversity and richness than water samples. *Proteobacteria*, *Acidobacteria*, *Actinobacteria* were the dominant bacteria in sediments. While in water samples, the most abundant taxa are *Proteobacteria*, *Actinobacteria* and *Firmicutes*, with *Chloroplastida* was the dominant eukaryotes, indicating that more phototrophic microbes existing in the water column. To predict the ecological function genes of the bacterial community in different habitats, the FAPROTAX database was applied. The results showed that bacteria in the water samples had more chemoheterotrophic gene, aromatic compounds degradation genes and phototrophic gene than the sediment samples. While the latter had more nitrogen-transformation involved genes, suggesting that sediments are more active in the global nitrogen cycle.

Key words: Xiangjiang River; bacterial diversity; eukaryotic diversity; nutrients

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24 Effects of anthropogenic activities on microbial diversity and its community spatial distribution characteristics of surface water in Xiangjiang River and the tributaries in Changsha

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Abstract: Urban river is a unique ecosystem which plays an important role in the aquatic ecological environment and the Migration and transformation of nutrients in it. Human activities, besides of sewage discharge, leading to significant changes in the chemical and biological constituents of surface water, such as eutrophication. River microorganisms, which have attracted wide attention, play a major role in the biogeochemical nutrition cycle. However, the effects of human activities on the spatial diversity of microbial communities in urban rivers are inadequate yet. In this paper, Illumina MiSeq sequencing technology based on 16S ribosomal RNA gene and 18S ribosomal RNA gene was used to analyze the spatial distribution and structural characteristics of planktic microeukaryote and planktic prokaryotes in the coastal waters of Xiangjiang River and the tributaries in Changsha, respectively. Redundancy analysis showed that the distribution of microbial community was affected by many environmental factors. The results indicated that the physicochemical parameters (TN, NH₃-H, TP, DO, pH and COD_{Cr}) had significant effects on the microbial diversity ($P < 0.05$). Meanwhile, it was found that the microbial community in the water had obvious spatial variability. The phytoplankton microeukaryotes in the water were composed of Chlorophyta, SAR, Ascomycota, Rotifers, etc. Chlorophyta dominated the upper and middle reaches of the river, while Mmidiophyceae and Symbiophytella increased significantly in the lower main stream. The composition of planktonic prokaryotes was Proteobacteria, Firmicutes, unclassified bacteria, Actinobacteria, Cyanobacteria, Bacteroidetes and so on. Proteobacteria and Firmicutes dominated in the upper and middle reaches, while Proteobacteria and Firmicutes decreased in the lower reaches, while Actinobacteria increased. Moreover, the diversity of planktonic prokaryotes was significantly higher than that of corresponding microeukaryotes. Our study improved the understanding of microbial ecology in urban rivers during urbanization and provides data support for future work.

Keyword: Anthropogenic effects; Surface water; Microbial diversity; Community spatial distribution

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25 Interfacial synthesis ZIF-8@HPAN membrane for highly efficient humic acid removal

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Abstract: In this study, a ZIF-8 thin layer deposited on the surface of a hydrolyzed polyacrylonitrile (HPAN) membrane was used for highly efficient humic acid removal. The thin ZIF-8 layer was synthesized by using a two-step interfacial synthesis method, based on liquid-liquid interfacial coordination polymerization. The formation of a continuous ZIF-8 layers was confirmed by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, and atomic force microscopy. The effects of the synthesis conditions including reaction time, precursor concentration, and other operating conditions on the ZIF-8 composite membrane performance were studied using humic acid solution as organic waste. The results showed that when the reaction time was extended, or when the precursor concentration was increased, the ZIF-8 layer deposited on the membrane surface became denser. Compared with the unmodified HPAN substrate, the composite membrane deposited with the ZIF-8 layer showed better processing ability for organic matters due to the strong electrostatic interaction of organic matter with the ZIF-8@HPAN membrane and the ZIF-8 particles unique structural characteristics, which shows a great application prospect for humic acid treatment compared with other membrane technologies.

Keywords: interfacial synthesis; ZIF-8; synthesis conditions; humic acid; membrane performance

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26 Microalgae tolerant of boron stress and the accumulation of lipid and starch

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Abstract: Boron (B) is an indispensable microelement for the formation of ribonucleic acid; however, excess B has different toxic effects on living creatures. This study investigated the signal regulation during B-containing wastewater treatment by microalgae. As the core element of quorum sensing signal molecules, B stress triggered mitogen-activated protein-kinase signaling cascade up-regulation and induced B efflux translocator ABCC up-regulation and physiological metabolism enhancement to adapt the adverse situation. Microalgae growth was uninfluenced by 25 mg B/L, and the maximum B removal rate was 1.22 mg/(L·d). B was bonded to protein and carbohydrate after being uptake. The toxicity of 50 mg B/L resulted in cell viability reduction, organelle damage, and low B removal efficiency. During the B removal process, microalgae also accumulated lipid and starch, their productivity was 188.65 mg/(L·d) and 305.35 mg/(L·d), respectively. This study provides a clue of B-containing wastewater treatment and inspires the signal role in biological remediation.

Keywords: Boron toxicity; Microalgae; Signal regulation; Lipid productivity; Wastewater treatment

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27 Rapid charge transfer and pollutant degradation via Z-scheme nitrogen-defect-rich g-C₃N₄ nanosheets embedded with NiCo₂O₄ nanoparticles as efficient photoactivator of peroxymonosulfate

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Abstract: Limited peroxymonosulfate (PMS) activation efficiency resulted from slow metal reduction has been a challenge in SO₄^{•-}-based oxidation of organic pollutant. Herein, a Z-scheme nitrogen-defect-rich g-C₃N₄ embedded with NiCo₂O₄ catalyst (NiCo₂O₄/g-C₃N₄-N_{vac}) was elaborately designed to accelerate Ni(III)/Ni(II) and Co(III)/Co(II) cycles for PMS activation. The NiCo₂O₄/g-C₃N₄-N_{vac} exhibited remarkable enhancement with a tetracycline hydrochloride (TCH) degradation rate constant (0.1168 min⁻¹), higher than those of NiCo₂O₄/g-C₃N₄ (0.0724 min⁻¹) and g-C₃N₄ (0.0233 min⁻¹), respectively. Theoretical and experimental results suggested that N vacancies modulated electric structure to build Z-scheme-charge-transfer platform for rapid reduction of Ni(III) and Co(III), thereby accelerating PMS activation for remarkable removal of refractory pollutants. NiCo₂O₄/g-C₃N₄-N_{vac} exhibited excellent degradability and corresponding electrical energy per order (EE/O) in different water matrix was evaluated. Additionally, TCH degradation behavior, pathways and toxicity of products were analyzed, respectively. This work provided an novel paradigm to design the efficient photo-activator of PMS for environmental remediation.

Keywords: Sulfate radical-photo-Fenton-like; nitrogen vacancies; g-C₃N₄; NiCo₂O₄; Z-scheme.

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28 Fabrication of oxygen defect-rich pencil-like ZnO nanorods with CDots and Ag co-enhanced photocatal

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Abstract: In this work, oxygen defect-rich pencil-like ZnO nanorods were prepared by a simple hydrothermal method, and Ag and CDots co-catalysts were further introduced for modification. The morphology, structure, UV-vis diffuse reflectance, photoluminescence (PL) and electrochemical properties of the as-prepared photocatalysts were studied by a series of analytical techniques and measurements. The results indicated that pencil-like morphology and the existence of oxygen defects increased the carrier concentration and promoted charge carrier separation of ZnO. The introduction of Ag and CDots co-catalysts further improved the electron-hole pairs separation and visible light utilization of photocatalysts. Gaussian three-peak fitting of the PL spectra proved that the introduction of co-catalysts also affected the relative content of various oxygen defects in the catalyst. As a typical pollutant, tetracycline hydrochloride (TCH) was used to detect the photocatalytic performance of as-prepared catalysts. CDots/Ag/ZnO possessed the strongest TCH removal and mineralization performance, and the possible degradation mechanism and pathways of TCH were proposed. Furthermore, the consequence of the biotoxicity assessment showed that the ternary photocatalyst had good biocompatibility and low biotoxicity.

Keywords: CDots/Ag/ZnO ternary photocatalyst; Tetracycline hydrochloride; Water purification; Oxygen defect; Biotoxicity assessment.

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29 Degradation of carbamazepine by UV / persulfate / sulfite system

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Abstract: This study uses sulfite(S(IV)) as a reductant to enhance Ultraviolet-ray(UV) persulfate(PS) compound system to remove carbamazepine(CBZ). The results show that compared with the UV/PS system, the UV/PS/S(IV) system can raise the degradation efficiency by 10.1%. UV / PS/ S(IV) system under pH=3~11 environment, can exceed 92% in the degradation rate of CBZ, with wide pH adaptability. When the molar ration of PS:S(IV) is 2:1, the highest degradation rate of CBZ is 98.1%. Chloride ion(Cl^-) and Carbonate ion(CO_3^{2-}) show an overall inhibitory effect on the degradation rate of CBZ. The reaction rate constant of the UV/PS/S(IV) system to degrade CBZ decreases with the increase of the initial concentration of humic acid(HA). The results of free radical identification shows that the contribution rate of sulfate radicals to the degradation of carbamazepine was between 63% and 69%, and it is the main active oxygen species in this reaction. The study on the mechanism of UV/PS/S(IV) system in terms of degradation of CBZ shows that sulfate radicals the active sites of the olefin double bond of the CBZ structure, and then are oxidized to form oxygen-containing derivatives in 10 sorts. The degradation pathway is mainly hydroxyl substitution reaction. This system has good potential in the degradation of such emerging refractory pollutants as carbamazepine.

Keywords: UV/persulfate/sulfite; carbamazepine; sulfate radicals; degradation pathways; water quality parameters

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30 Investigating the biological stability of drinking water in aged household connection pipes during supply water quality switching

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Abstract: The switch of supply water quality has become one of the common practices worldwide as constant efforts at the operational level have been made to improve drinking water quality via using better source water and/or upgrading water treatment processes. While the treated water at the treatment plants is of higher quality, it is shown that the irregular changes in supply water quality might result in water quality deteriorations during distribution, posing potential risk to consumers' health. However, until now, our understanding of the impacts of biological stability in drinking water distribution systems (DWDSs), especially premise plumbing, during switching supply water quality is still limited. The objective of this study was to determine the effects of supply water quality switching exhibit on biostability of drinking water in aged household connection pipes (HCPs). The aged HCPs from two locations in a distribution area supplied by conventionally treated water were assembled into test rigs, and were fed with three types of water, i.e. conventionally treated water (KA), mixed water (MX), and remineralized RO permeate (RE), over a period of 18 weeks. ATP assessment and 16S rRNA amplicon sequencing were applied on influents, effluents after one-week stagnation in HCPs and biofilm samples before and after the pilot experiments. An increase of the concentration of ATP was observed over the first 8 weeks in the effluents fed with MX and RE, followed by re-stabilization as compared to the influents, suggesting the detection of transition effects in terms of active biomass. In addition, 16S rRNA amplicon analyses results revealed that the drinking water microbiome was structurally different in influents as compared to effluents after stagnation, and location was also one of the main factors drove the clustering of effluent samples, which suggests that the destabilization of microbiome in HCPs exhibits effects on the drinking water delivering in the DWDSs during supply-water quality switching.

Keywords: 16S rRNA amplicon sequencing; Drinking water microbiome; supply water quality switching

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