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MgO/活性炭催化臭氧化降解有机物的作用机制

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摘要: 利用浸渍法制备了 MgO/活性炭(MgO/GAC-1) 催化剂, 研究了其在臭氧化降解敌草隆和乙酸中的活性, 并与已有研究中沉淀法制备的 MgO/活性炭(MgO/GAC-2) 作了稳定性对比. 结果表明, 在降解敌草隆和乙酸的过程中, MgO/GAC-1 能使臭氧化的效率提高约 15%~35%. 当溶液初始 pH 为中性或碱性时, MgO/GAC-1 可以有效减缓由于形成小分子有机酸而导致 pH 的下降问题, 从而保证臭氧的氧化效率. 当溶液初始 pH 为酸性时, MgO/GAC-1 在一定程度上可以提升溶液的 pH 值, 进而提升臭氧化的效率. 因此 MgO 对溶液 pH 值的调节作用可能是臭氧化效率提高的主要原因, 这是相关文献所忽略的. 尽管 MgO/GAC-2 有更大的比表面, 但 MgO/GAC-1 却具有更好的催化臭氧化降解性能. 在中性条件下降解乙酸重复 10 次实验的结果表明, MgO/GAC-1 具有更好的稳定性, 应用前景良好.

关键词: 臭氧; 氧化镁; pH; 草酸; 敌草隆; 稳定性

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Mechanism of MgO/GAC Catalyzed Ozonation of Organic Compounds

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Abstract: MgO/granular activated carbon (MgO/GAC-1) was prepared via an impregnation method, and its activity in ozonation of diuron and acetic acid was investigated. MgO/GAC-1 was also compared in stability to the same catalyst prepared via precipitation according to the literature (MgO/GAC-2). The results showed that MgO/GAC-1 could increase efficiency of ozonation by 15%-35% in the process of degradation of diuron and acetic acid. When the pH of the solution was neutral or alkaline, MgO/GAC-1 could effectively retard the decrease in pH owing to formation of small molecular organic acids, thus ensuring the efficiency of ozone. When the pH of the solution was acidic, MgO/GAC-1 could increase the pH of the solution to a certain extent, thereby enhancing the efficiency of ozonation. The adjusting effect of pH value is the reason why MgO can significantly improve the efficiency of ozonation, a fact that was ignored in the relevant literature. Although MgO/GAC-1 had a larger specific surface area, MgO/GAC-1 had better activity in ozonation. A recycling test also indicated that MgO/GAC-1 had better stability, showing a good prospect for application.

Key words: ozone; magnesium oxide; pH; acetic acid; diuron; stability

在惰性有毒有机物的处理中, 高级氧化技术以其降解的高效性和彻底性而受到人们的重视, 臭氧类高级氧化技术即是其中的一种重要方法^[1~7]. 在众多的臭氧类高级氧化技术中, 非均相催化臭氧化技术又以操作的简便性而得到人们的青睐^[8,9]. 当前非均相催化臭氧化技术报道的催化剂大多以一些 Lewis acids 为主, 比如一些过渡金属氧化物 MnO_2 ^[10]、 NiO ^[11]、 Co_3O_4 ^[12]、 Ag_2O ^[13]、 CeO_2 ^[14] 等, 对于固体碱催化剂的报道较少. MgO 作为典型固体碱催化剂在很多催化领域已有应用, 比如醇类的脱氢反应^[15]、催化降解有机物等^[16~19]. 在臭氧化领域, Moussavi 等^[16]利用沉淀法制备了 MgO, 并利用其催化臭氧降解了红色 198 偶氮染料. 然而他们没有考虑 MgO 对溶液 pH 的影响, 也没有考虑降解过程 pH 的变化情况, 不利于催化作用机制的澄清^[20~25].

本文以活性炭为载体(GAC)^[26~28], 利用浸渍

法制备了 MgO/GAC-1 催化剂, 考察了其在臭氧化乙酸(臭氧惰性小分子有机物的代表)和敌草隆(芳环类化合物的代表, 臭氧化降解过程 pH 变化较大)的性能, 重点分析了 MgO/GAC-1 对臭氧化过程溶液 pH 的变化情况, 并与臭氧化效率进行关联, 以便更好地解析其作用机制. 此外, 本研究中还从稳定性的角度对比了所制备的催化剂与 Moussavi 等^[19]报道的 MgO/GAC-2 催化剂.

1 材料与方法

1.1 材料与试剂

乙酸、敌草隆、六水合硝酸镁为分析纯, 甲醇

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为色谱纯,其他试剂均为分析纯,使用前不经过前处理. 活性炭为圆柱状,其他溶液均用二次去离子水配置,溶液 pH 用 $1.0 \text{ mol} \cdot \text{L}^{-1}$ 硫酸和 $1.0 \text{ mol} \cdot \text{L}^{-1}$ 氢氧化钠调节.

1.2 实验装置

本研究中所有实验采用的是半连续的方式进行,实验装置(图1)臭氧发生器和破坏器的型号为 CFS-1A 和 ODF-003 (Ozonia, Switzerland), 臭氧反应器(高为 75 cm, 内径为 5 cm)为一带恒温夹套的玻璃反应器,布气装置为反应器底部的砂芯,所有的实验均在室温条件下进行. 每次实验,模拟废水为 500 mL 的乙酸或敌草隆溶液. 在臭氧化乙酸中,乙酸浓度 $100 \text{ mg} \cdot \text{L}^{-1}$, 氧气流量 $0.67 \text{ L} \cdot \text{min}^{-1}$, 臭氧产量为 $46.9 \text{ mg} \cdot \text{min}^{-1}$; 在臭氧化敌草隆中,敌草隆浓度为 $25 \text{ mg} \cdot \text{L}^{-1}$, 氧气流量为 $0.1 \text{ L} \cdot \text{min}^{-1}$, 臭氧产量为 $9.0 \text{ mg} \cdot \text{min}^{-1}$. 尾气中的臭氧用 2% 碘化钾溶液吸收.

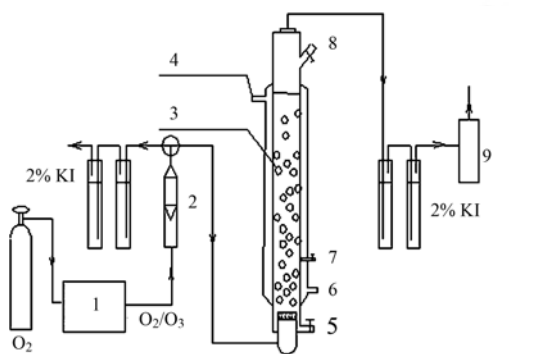


图1 实验装置示意
Fig. 1 Diagram of the experimental setup

1.3 催化剂的制备

采用浸渍法制备 MgO/GAC-1. 将 4.27 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 溶解于水中, 再加入 10 g 活性炭, 12 h 的浸渍后, 催化剂在 100°C 下干燥 24 h , 最后在 N_2 氛围下煅烧 4.0 h . 根据文献[19]利用沉淀法制备了 MgO/GAC-2, 步骤如下: 先将 5.0 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 溶解于 50 mL 水中, 然后加入 3.0 mL 的 NaOH ($1.0 \text{ mol} \cdot \text{L}^{-1}$), 在搅拌条件下形成凝胶状物质, 加入 10 g GAC 浸渍 30 min , 再把催化剂干燥煅烧生成 MgO/GAC-2.

1.4 分析方法

乙酸浓度采用的是 HPLC (ThermoFisher Dionex Ultimate3000, USAHypsil gold C₁₈) 色谱柱 ($250 \times 4.6 \text{ mm}$, 粒径 $5 \mu\text{m}$). 流动相为 $0.0134 \text{ mol} \cdot \text{L}^{-1}$ 的

磷酸缓冲液 ($\text{pH} = 3$): 甲醇 ($950:50$, 体积比). 流速为 $1.2 \text{ mL} \cdot \text{min}^{-1}$, 紫外检测波长为 210 nm , 柱温为 25°C . 敌草隆浓度采用的是 HPLC, 流动相为乙腈: 水 ($6:4$, 体积比), 流速为 $0.5 \text{ mL} \cdot \text{min}^{-1}$, 紫外检测器波长 254 nm , 柱温 30°C . 催化剂物相采用 X 射线仪 (XRD) 分析, 测定 X 射线为 Cu 靶 $\text{K}\alpha$ 射线 ($\lambda = 0.1542 \text{ nm}$). 管电压 45 kV , 管电流为 40 mA , 扫描范围 $10^\circ \sim 80^\circ$. 采用扫描电子显微镜 (SEM) 检测颗粒的形态, 用 BET 检测了样品的比表面积, 利用二氧化碳吸/脱附等温线分析了催化剂表面的碱性位强度和数量.

2 结果与讨论

2.1 催化剂的表征

XRD 分析结果表明(图2), 36.943° 、 42.920° 、 62.315° (JCPD45-0946) 是 MgO 的特征峰, 分别对应的是 (111)、(220)、(322) 晶面, 说明本方法成功将 MgO 负载在活性炭上. 在 BET 的测试中, MgO/GAC-1 的比表面积为 $612.23 \text{ m}^2 \cdot \text{g}^{-1}$, MgO/GAC-2 的比表面积为 $740.10 \text{ m}^2 \cdot \text{g}^{-1}$. 两者差别的原因可能是 $\text{Mg}(\text{OH})_2$ 凝胶法形成的 MgO 多数在 GAC 的表面, 而 MgO/GAC-1 会进入到活性炭的孔道中, 使得 MgO/GAC-2 比 MgO/GAC-1 的比表面积大.

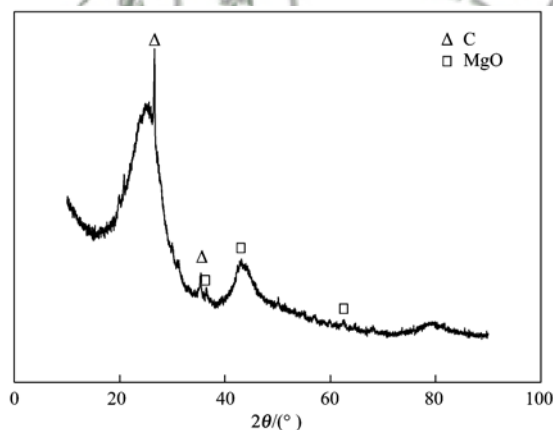
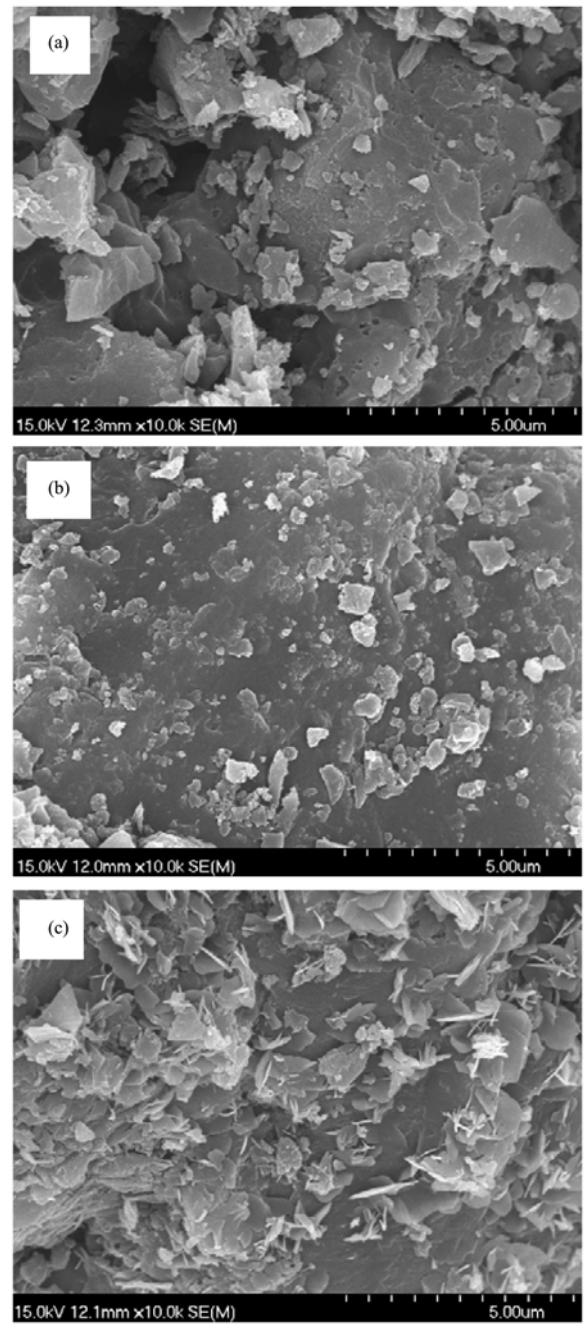


图2 MgO/GAC 的 XRD 图

Fig. 2 XRD pattern of MgO/GAC

在 SEM 的表征图中可以看到(图3), 在放大倍数 10.0×10^3 的条件下, 图3(a)中的活性炭表面有较多的空穴, 凹凸不平; 而 MgO/GAC-1 表面更细致并有一些小颗粒, 说明 MgO 负载在了活性炭的表面, 图3(b)部分填补了活性炭的表面空穴位置. 图3(c)中的 MgO/GAC-2 样品活性炭的表面出现了很多针状物质, 可能生成的 $\text{Mg}(\text{OH})_2$ 胶体很难进入活性炭的孔道内部, 导致 MgO 基本存在于活



(a) GAC, (b) MgO/GAC-1, (c) MgO/GAC-2

图3 催化剂的 SEM 图

Fig. 3 SEM of the catalyst (a. GAC, b. MgO/GAC-1, c. MgO/GAC-2)

性炭的表面.

图4为催化剂的CO₂脱附. 相对于MgO/GAC-1, MgO/GAC-2碱性位略强^[29], 但从峰面积可以看出MgO/GAC-1比MgO/GAC-2的碱性位数目更多. 以上差异预示两者在臭氧化过程中的性能可能会有些差异.

2.2 臭氧化降解敌草隆

pH是影响臭氧化效率的一个重要因素, 图5

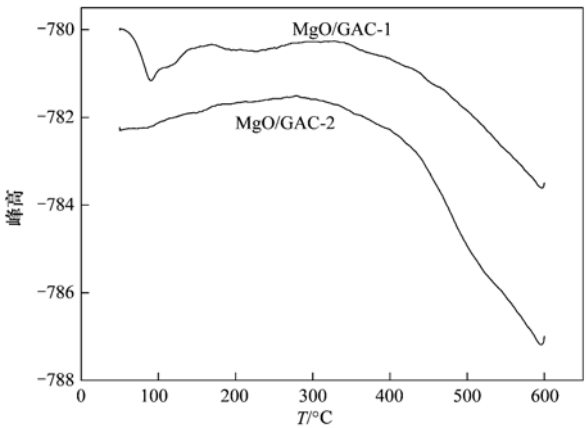


图4 两种催化剂的 CO₂-TPD 的图谱

Fig. 4 CO₂-TPD graphics of the two catalysts

为不同初始pH条件下臭氧及催化臭氧化敌草隆过程pH的变化情况. 当初始pH为5.0和7.0时, 由于中间产物小分子有机酸的生成, 单独臭氧化过程溶液的pH不断下降, 15 min后溶液的pH下降3.5左右. 但在MgO/GAC-1/O₃中, 溶液pH在前10 min时pH变化至6.3后基本稳定不变, 初始pH为5.0时溶液的pH值反而升高了. 当初始pH为9.0时, 单独臭氧下pH在15 min后降到7.5, 而催化臭氧化过程20 min后pH下降到8.5后就基本稳定了, 说明MgO/GAC-1有效抑制了反应液pH的下降. 当pH为11.0时, 两者均会导致溶液pH的明显下降, 但相比单独臭氧化, 催化臭氧化过程pH的下较缓慢, 30 min后要比单独臭氧化的pH约高一个单位, 并维持在8.5左右. 臭氧化水处理中, 一

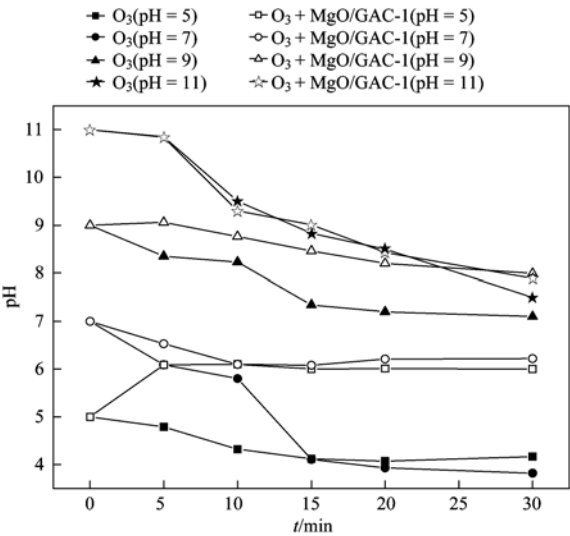


图5 臭氧及MgO/GAC-1催化臭氧化降解敌草隆过程中pH的变化

Fig. 5 Evolution of the pH value of the diuron solution via O₃ and MgO/GAC-1 at different initial pH values

般较高的 pH 值有利于提高臭氧化效率. 降解实验的结果表明(图 6), 加入 MgO/GAC-1 可以明显提高臭氧化的效率, 在不同初始 pH 条件下臭氧化的效率提升幅度为 15% ~ 35%. 吸附实验表明, 当 pH 为 5.0 和 7.0 时, MgO/GAC-1 对敌草隆的吸附去除率只有 1.0%, 当 pH 为 9.0 和 11.0 时, MgO/GAC-1 对敌草隆的吸附效果约为 5.0%, 均明显小于催化臭氧化条件下去除率的提高.

由此可见, 在不同 pH 溶液中, MgO/GAC-1 在一定程度上能提高或减缓了溶液的 pH 变化, 从而提高臭氧化敌草隆的效率.

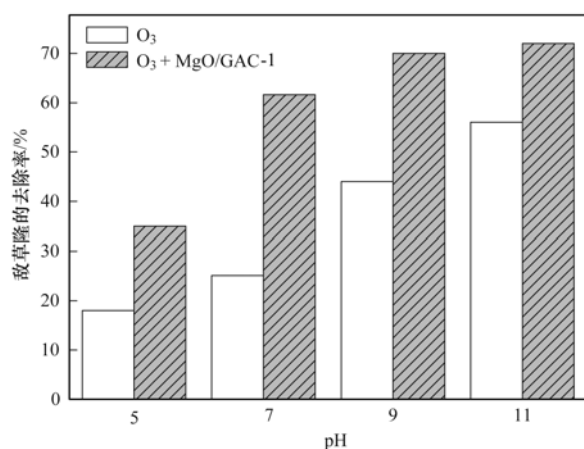


图 6 不同初始 pH 条件下臭氧及 MgO/GAC-1 催化臭氧化敌草隆的效率

Fig. 6 Removal rates of diuron via O₃ and MgO/GAC-1 at different initial pH values

2.3 臭氧化降解乙酸

与敌草隆相比, 乙酸本身是一种小分子有机酸, 其在臭氧化降解的过程中 pH 值不会有较大的变化. 图 7 结果表明, 尽管 pH 的变化幅度有所减缓, 但无论是在酸性条件还是在中碱性条件, MgO/GAC-1 仍然实现了提升溶液 pH 或减缓 pH 下降的目的. 如在 pH 为 5.0 时, 由于乙酸为臭氧惰性物, 故单独臭氧化过程溶液的 pH 几乎不变; 但在 MgO/GAC-1 催化臭氧过程中, 溶液 pH 一直缓慢上升, 30 min 后达到 6.0. 当初始 pH 为 7.0 和 9.0 时, 单独臭氧和催化臭氧化过程均会导致溶液 pH 的下降, 10 min 后 MgO/GAC-1/O₃ 过程溶液 pH 维持在 7.5 左右, 而单独臭氧过程 pH 下降至 7.0 左右. 当 pH 为 11.0 时, 与单独臭氧化相比, MgO/GAC-1/O₃ 过程 pH 下降得慢, 20 min 后两者差 0.5 左右. 图 8 为在不同初始 pH 条件下臭氧与催化臭氧化条件下乙酸的去除率. 除 pH 为 11.0 外, MgO/GAC-1 能使臭氧化的效率提升约 10% ~ 30%.

MgO/GAC-1 的吸附实验表明, 在所有初始 pH 条件下 MgO/GAC-1 对于乙酸的吸附效果约为 6.5% 左右. 在 pH = 11.0 时, 两者对乙酸的去除率几乎相同, 这可能是由于在较高 pH 条件下单独臭氧就能产生较多的羟基自由基, 因此 MgO/GAC-1 的加入作用不明显^[30~32].

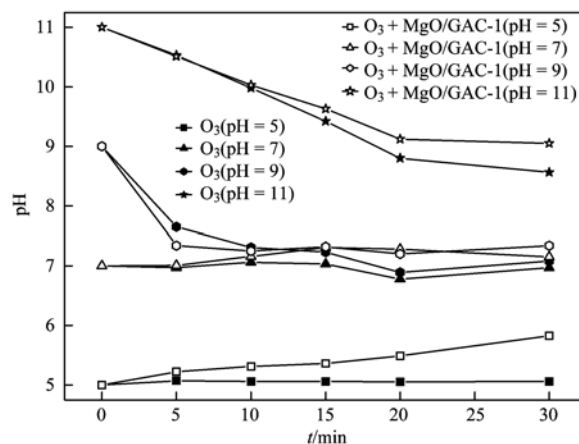


图 7 臭氧及 MgO/GAC-1 催化臭氧化降解乙酸过程中 pH 的变化

Fig. 7 Evolution of the pH values of the acetic acid solution via O₃ and MgO/GAC-1 at different initial pH values

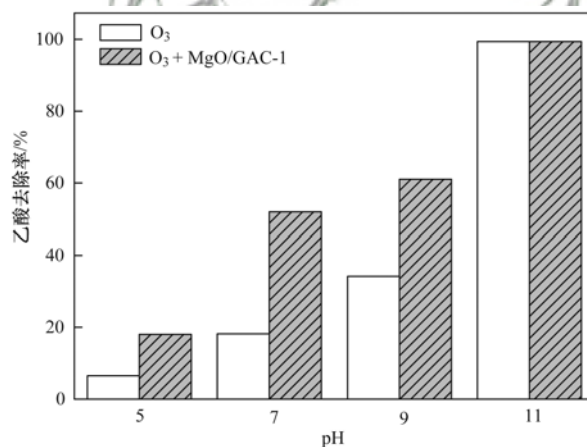


图 8 不同初始 pH 条件下臭氧及 MgO/GAC-1 催化臭氧化乙酸的效率

Fig. 8 Removal rates of acetic via O₃ and MgO/GAC-1 at different initial pH values

以上结果表明, MgO/GAC-1 催化臭氧化降解有机物的本质机制是 MgO/GAC-1 可以有效提升或减缓溶液的 pH 值, 从而保证臭氧化过程在适宜的 pH 值下进行. 这也是 MgO/GAC-1 能有效提高臭氧化效率的主要原因^[33,34]. 在已有氧化镁催化臭氧化有机物的报道中, 作者只是以有机物和 COD 去除率的提高说明 MgO/GAC-2 能催化臭氧产生羟基自由基, 基本没有涉及降解过程溶液 pH 的变化情况,

这显然不利于其作用机制的澄清。

2.4 催化剂稳定性研究

Wang 等^[35]报道了经真空处理的氧化钙和氧化镁对于 1-丁烯异构化反应具有非常高的催化活性, 此研究清楚地指出碱催化剂制备和预处理方法的重要性. 为此工作中对不同方法制备活性炭载氧化镁的活性和稳定性进行了分析. 结果发现(图 9), 利用浸渍法制备的 MgO/GAC-1 在重复使用 10 次后仍然具有较好的催化活性, 乙酸的去除率基本稳定在 45% 左右. 与 MgO/GAC-2 相比, 整个实验过程 MgO/GAC-1 也具有更高的活性和更好的稳定性. 平均而言, MgO/GAC-1/O₃ 对乙酸的去除率要比 MgO/GAC-2/O₃ 高 5.0% 左右. 这主要是因为浸渍法能使盐类充分地进入到孔道里面, 而且沉淀法制备的 MgO/GAC-2 催化剂, MgO 更多的负载在 GAC 的表面, 从而影响催化剂活性和使用寿命^[36].

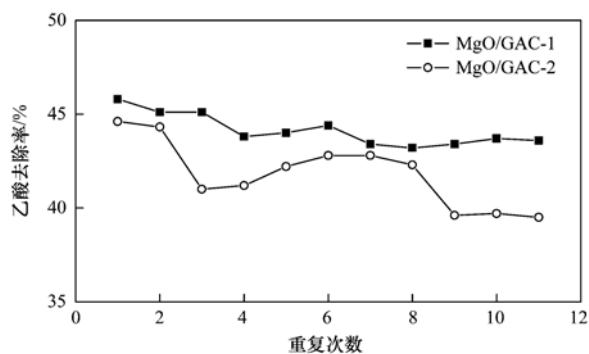


图 9 MgO/GAC-1 和 MgO/GAC-2 稳定性的对比

Fig. 9 Comparison of stability between MgO/GAC-1 and MgO/GAC-2

3 结论

(1) 当溶液初始 pH 为中性或碱性时, MgO/GAC-1 可以有效减缓由于小分子有机酸形成而导致 pH 的下降问题; 当溶液初始 pH 为酸性时, 其在一定程度上可以提升溶液的 pH 值. 结合相应敌草隆和乙酸的降解结果, MgO/GAC-1 对溶液 pH 值的调整作用可能是臭氧氧化效率提高的主要原因.

(2) 在催化臭氧氧化过程中, MgO/GAC-1 比 MgO/GAC-2 稳定性更好.

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