氧化锰/凹土复合材料的制备与应用

冀巍　(江苏省淮安市环境科学研究所,江苏淮安 223001)

摘要　[目的]研究氧化锰/凹土复合材料对硝基苯废水的处理效果。[方法]利用液相沉淀法制备氧化锰/凹土复合材料,用于对硝基苯废水的处理,同时测定处理前后废水的硝基苯含量变化。[结果]氧化锰/凹土复合材料对硝基苯废水处理效果较好,在投加量为1.5 g,pH为4~5的条件下,复合材料处理后的废水硝基苯去除率为100%左右。[结论]氧化锰/凹土复合材料可用于硝基苯废水的处理。

关键词　凹土;氧化锰;硝基苯废水
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Preparation and Application of Manganese Oxide/Attapulgite Composite Material

JI Wei　(Huaian Science Institute of Environment, Huaian, Jiangsu 223001)

Abstract　[Objective] The research aimed to study the effects of manganese oxide/attapulgite composite material on the treatment of wastewater containing with nitrobenzene. [Method] Manganese oxide/attapulgite composite material was prepared though liquid precipitation method and was utilized in the treatment of wastewater containing with nitrobenzene. Meantime, the content of nitrobenzene of wastewater before and after treatment was determined. [Result] The results showed that the composite material had ideal effects on the treatment of wastewater containing with nitrobenzene. The removal rate of nitrobenzene was close to 100% with the dosage of composite material of 1.5 g, pH of 4 - 5. [Conclusion] The new composite material of manganese oxide/attapulgite could be used for the removal of nitrobenzene from wastewater.

Key words　Attapulgite; Manganese oxide; Nitrobenzene wastewater

硝基苯废水是一种典型的高盐、高毒、难生物降解有机废水,造成的水体污染持续时间长,使用常规的废水处理方法处理难度大,许多国家都将其列为优先控制的污染物。硝基甲苯化合物化学性质比较稳定,苯环容易发生亲电取代,但不易发生氧化反应,因而在一般情况下,利用氧使芳环破裂而达到硝基甲苯化合物分子裂解是不容易的,所以硝基苯生产废水非常难降解,因此对含硝基苯废水高效处理技术研发具有重要意义。

凹土又名坡缕石,是一种层链状结构的含水富镁铝硅酸盐粘土矿物。其理想分子式为:$(Mg,Al,Fe)_5Si_8O_{20}(HO)_2(OH_2)_4 \cdot 4H_2O$,比表面积大,具有优良的吸附性,且在我国矿藏集中、丰富、价格低,是一种良好的水处理材料。由于凹土有独特的晶体结构,类似沸石的大通道,且具有较大的比表面积等特殊的晶体结构和性质,所以具有许多特殊的物化及工艺性能,凹土在环境保护中的应用开发成为国内外研究的热点[1-5]。同时,有研究表明,二氧化锰能被腐殖酸及其他与腐殖酸结构相似的小分子有机物还原溶解,因此推测二氧化锰可能是某些环境中有机物降解的重要途径。二氧化锰在水处理中的应用研究目前涉及以下几个方面:作为氧化剂氧化一些有机物和具有还原性的无机离子;作为吸附剂吸附水中的有机物和无机离子;作为催化剂催化某些氧化还原反应[6-7]。为此,笔者选用凹土作为载体,通过氯化锰和NaOH之间的液相沉淀法来制备氧化锰/凹土复合材料,以硝基苯废水为目标污染物,验证氧化锰/凹土复合材料对硝基苯废水的处理能力,为硝基苯废水处理研究提供新的材料选择。

1　材料与方法

1.1　试验药品　凹土购自江苏盱眙玖川科技有限公司;其他化学试剂均为分析纯,购自国药集团化学试剂有限公司,购买后直接使用。

1.2　氧化锰/凹土复合材料的制备方法

1.2.1　反应原理。选用氯化锰和氢氧化钠之间的液相沉淀法来实现凹土的MnO_2改性。其反应方程式为:

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$$

$$Mn(OH)_2 \rightarrow Mn_2O_3 \cdot xH_2O \rightarrow MnO_2 \cdot yH_2O$$

1.2.2　制备方法。取15 g未经处理的凹土原料加入到50 ml、6 mol/L的NaOH溶液中;在80 ℃下浸泡2 h后,除去上层溶液,接着加入100 ml浓度为2.5 mol/L的$MnCl_2$溶液(pH用HCl调至1~2以防止锰的析出)中浸泡10 h以上;除去上层溶液,室温条件下又在6 mol/L的NaOH溶液中浸泡10 h以生成;除去上层溶液,使样品在空气中充分氧化(生成MnO或MnO_2),接着水洗数次,100 ℃左右烘干,研磨,制得样品。

1.3　材料SEM表征　采用日立S-3000N扫描电镜观察载体的结构与形貌。

1.4　硝基苯废水处理试验　废水样品取自淮安市某化工厂,水质参数中pH为9.87,COD_{Cr}、苯胺含量、硝基苯含量分别为1 290.167、1.499 2、15.575 8 mg/L。

硝基苯测定方法:还原-偶氮光度法;苯胺的测定方法:N-(1-萘基)乙二胺偶氮分光光度法。

2　结果与分析

2.1　氧化锰/凹土复合材料的电镜分析结果　通过复合材料的电镜照片(图1)可以看出,凹土是一维纳米棒晶结构,氧化锰包覆凹土表面,在形成的氧化锰/凹土材料的表面有凹土的棒晶镶嵌。

2.2　复合材料对硝基苯废水的处理效果

2.2.1　硝基苯含量变化。由图2可见,氧化锰/凹土复合材料处理硝基苯废水,随着反应时间的延长,处理后的硝基苯

作者简介　冀巍(1979 -),男,江苏淮安人,工程师,从事环境规划、环境影响评价研究。
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废水硝基苯浓度先降低后升高,40 ~ 80 min 时硝基苯去除率相对比较高,此时处理后硝基苯废水苯胺浓度最高,硝基苯浓度相对较低。

2.2.2 pH 对去除硝基苯的影响。分别取 1 g 凹土和 1 g 氧化锰/凹土复合材料于 100 ml 原水中,用盐酸调节 pH,分别为酸性(pH = 5)、中性(pH = 7)、碱性(pH = 9.87)。振荡 80 min,过滤后,测定其 COD_{Cr}、苯胺浓度和硝基苯浓度,结果见图 3。由图 3 可见,在 pH 为 9.87 时,复合材料对硝基苯的去除效果最好。

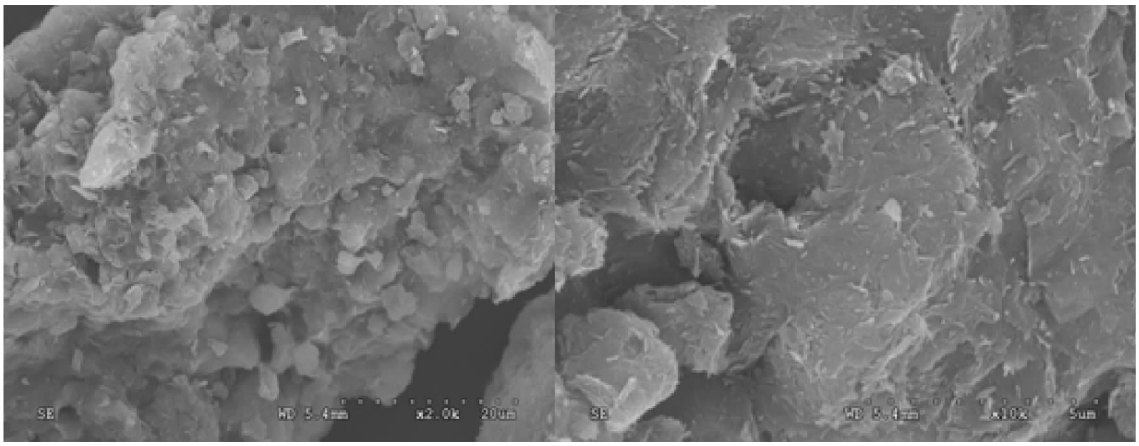

图 1 氧化锰/凹土的电镜照片

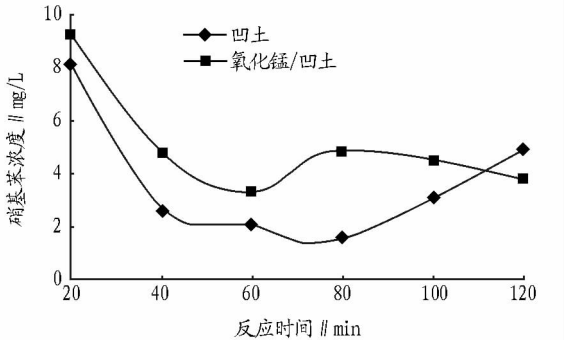

图 2 凹土及氧化锰 - 凹土复合材料处理硝基苯废水的效果比较

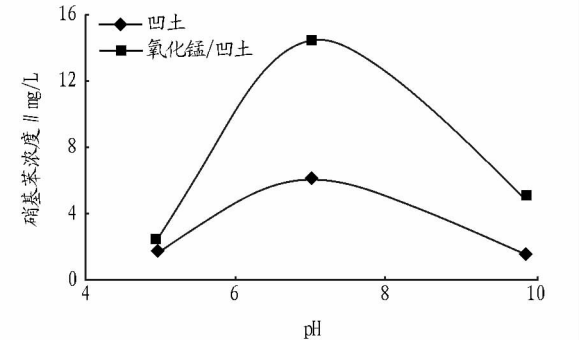

图 3 pH 对复合材料去除硝基苯效果的影响

由图 4 可见,氧化锰/凹土复合材料表面附着的氧化锰消失,这就说明氧化锰的反应为界面吸附氧化还原反应,即有机物先在二氧化锰表面吸附,然后发生电子转移。反应步骤为:①有机物在二氧化锰表面的吸附;②有机物与二氧化锰表面活性位结合生成表面络合物;③二氧化锰与有机物间的电子转移;④有机自由基的生成;⑤自由基相互聚合;⑥还原锰的生成及释放进入溶液;⑦氧化产物的释放。表面化学反应是反应的控速步骤,而且表面吸附及络合反应发生在二氧化锰与有机物的电子转移之前,且随着 pH 降低反应速率加快。

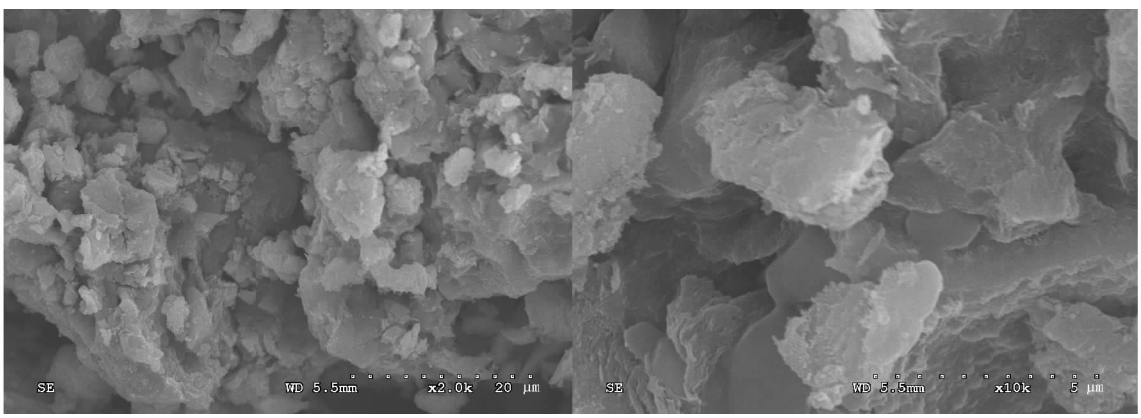

图 4 处理硝基苯废水前后复合材料的电镜照片

3 结论

(1)随着反应时间的增长,氧化锰/凹土复合材料处理硝基苯废水会使废水 COD_{Cr} 逐步降低。

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(2)pH 对氧化锰/凹土复合材料去除硝基苯的效果有很大影响,在 pH 为 9.87 时,处理效果最理想。

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