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厦门大学

硕士学位论文

# 石墨烯/二氧化钛/沸石复合材料对环氧四环素的光降解研究

# Study on the Photocatalytic Degradation of Oxytetracycline by Graphene/$TiO_2$/Zeolite compounds

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# 摘 要

环氧四环素(Oxytetracycline, OTC)又称土霉素，属于四环素类广谱抗生素，作为抗菌剂和饲料添加剂被广泛地应用于人类和动物，具有潜在的生态毒性，目前尚未找到一种理想而有效的处理方法。本研究采用光催化氧化法对其进行光催化降解实验。$TiO_2$以其化学稳定性、无毒性、价格低廉、光催化活性高等优异性能被广泛研究。但因其颗粒过小，易团聚，不易与水分离，吸附能力差，需紫外光激发而受到限制。

本研究以具有大表面、高吸附性能的沸石为载体，以具有优异的导电性能、较高的比表面积、可最大限度地拓展光催化剂对可见光的响应范围的石墨烯掺杂，采用固态分散法制备石墨烯/二氧化钛/沸石(Graphene/$TiO_2$/ZSM-5)复合光催化材料。首次尝试使用三角形混合实验设计及响应曲面分析方法，来确定石墨烯、二氧化钛、沸石这三种组分的最佳混合质量比，并借助 X 射线衍射(X-ray Diffractometer System, XRD)、紫外-可见分光光度法(Ultraviolet-Visible Spectrophotometry, UV-Vis)、透射电镜-衍射能谱(Transmission Electron Microscope-Energy Dispersive Spectroscopy, TEM-EDS)、傅里叶-红外光谱(Fourier Transform Infrared Spectroscopy, FTIR)、氮气等温吸附/脱附仪($N_2$ Adsorption/Desorption analyzer) 与比表面积测试法(Brunauer-Emmett-Teller, BET)等分析方法对复合材料进行了性能分析，考查了pH、原水浓度、温度对Graphene/$TiO_2$/ZSM-5复合材料光催化降解环氧四环素(OTC)的影响。同时，本研究对光降解过程中模拟OTC废水的生物毒性效力变化进行了评估，对可能的反应机理进行了探讨。取得如下研究成果：

(1) 通过固态分散法制备了 Graphene/$TiO_2$/ZSM-5 复合材料，并通过三角形混合实验设计及响应曲面分析方法，确定了 Graphene/$TiO_2$/ZSM-5 复合材料降解环氧四环素的最佳混合质量比，即 Graphene: $TiO_2$: ZSM-5 = 1: 8: 1 时，反应速率最佳，可达$5\times10^{-2}$ mg $L^{-1}$ $min^{-1}$，将此复合材料命名为 GTZ(1: 8: 1)。

(2) 通过 XRD、UV-Vis、TEM-EDS、FTIR、BET 等方法对 GTZ(1: 8: 1) 复合材料进行性能分析，XRD 分析结果表明：采用固态分散法制备复合材料并没

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有破坏各组分自身的结构，且复合材料在光催化降解的过程中是稳定的。UV-Vis分析结果表明：GTZ(1: 8: 1)复合材料在紫外光区和可见光区均有较强的吸收，GTZ(1: 8: 1)复合材料具有较低的能带间隙(2.8 eV)，可以拓宽 $TiO_2$ 基材料的光响应范围。TEM-EDS 分析结果表明：GTZ(1: 8: 1)复合材料中三种组分，均匀分散，无团聚现象，$TiO_2$ 分散吸附于 Zeolite 的表面和 Graphene 的单层片状结构上。FTIR 分析结果表明：三种组分的构成微粒之间通过氢键聚集在一起。BET 分析结果表明：GTZ(1: 8: 1)复合材料有较高的比表面积(130.93 $m^2 g^{-1}$)，复合材料呈现出优异的吸附性能。

(3) 采用 GTZ(1: 8: 1)复合材料作为光催化剂对 OTC 进行光降解实验。当 OTC 初始浓度为 10 mg $L^{-1}$，初始 pH 为 7，复合材料催化剂投加量为 0.2 g $L^{-1}$，环境温度为 25℃，在氙灯光源(300 W $m^{-2}$)照射下进行光降解反应，测试溶液的降解率与 TOC 值，经过 180 min 的光催化降解反应后，其降解去除率和矿化率可分别达到 97%和 67%。矿化率明显低于去除率，说明材料对 OTC 光催化降解过程中有中间有机产物的生成。当去除率在光照 180 min 达到基本平稳后，其矿化率仍有提升，说明在反应的后期，材料主要对反应中间产物进行降解。

(4) 分析 GTZ(1: 8: 1)复合材料光催化降解 OTC 的路径。将电子捕获剂(t-buton)和空穴捕获剂(EDTA-2Na)加入到复合材料光降解 OTC 的反应体系，以检测反应系统中主要的氧化基团。结果显示：添加 EDTA-2Na 对光降解速率的抑制作用较为明显，说明在该反应中空穴和羟基自由基是主要的氧化基团。

(5) 通过 DH5α 型大肠杆菌生长抑制试验，对 OTC 废水光降解过程中所产生生物毒性的变化进行了评估。与不同时间光降解处理的 OTC 模拟废水共培养的 DH5α大肠杆菌的细胞生长速率(μ, unit: $h^{-1}$) 排序为：

$$\mu_{OTC+LB}(0) \le \mu_{OTC(90)+LB}(1.6) \le \mu_{OTC(180)+LB}(2.6) \approx \mu_{LB}(2.7)$$

随着光降解时间的延长，OTC 浓度逐渐降低，DH5α 型大肠杆菌的生物毒性逐渐衰减。180 分钟的光降解处理可使模拟 OTC 废水的微生物毒性消失。

(6) 构建公猪精子模型，以精子存活率、细胞膜的完整性、线粒体的功能性为指标，对模拟 OTC 废水光降解过程中生物毒性的变化进行了评估。研究结果

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表明，随着光降解处理时间的延长，与不同时间光降解处理的 OTC 模拟废水共培养的公猪精子细胞的存活率差异不显著，精子细胞膜的完整性降低，精子细胞线粒体功能性增强。在实验浓度水平下(10 μg $L^{-1}$)，反应体系中 OTC 及 OTC 降解中间产物可以改变公猪精子的形态和功能，但未能杀死他们。

采用固态分散法制备的 GTZ(1: 8: 1) 光催化复合材料兼备了石墨烯、$TiO_2$ 与沸石各自的优异性能，使其产生了协同效应，从而提高了光催化氧化的活性。这为解决目前光催化材料回收困难、吸附能力弱、光响应范围窄等问题提供了一种解决途径。

关键词：环氧四环素；复合材料；光降解；生物毒性；机理

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# Abstract

Oxytetracycline(OTC), an important member of tetracycline and is popularly used in humans and animals, which is reported to be a toxic threat to the ecosystem. It is important to find the treatment method which has high removal efficiency for actual use since OTC are not biodegradable. In this study, the photocatalysis was used to degrade the OTC. $TiO_2$ is a promising photocatalyst which is stable, non-toxic, inexpensive, and high photocatalytic activity. However, post-filtration procedures to separate nanometer-levels of $TiO_2$, agglomeration of photocatalyst, poor adsorption capacity and excitation by UV laser are defects that limit its application.

In this case, a solid dispersion method was proposed to load $TiO_2$ on zeolite and graphene. Zeolite has large surface area and high adsorption performance. Graphene has excellent conductivity, high specific surface area, and it could be used to modify $TiO_2$ surface to maximize the performance of Visible-light-responsive photocatalysts. This first-attempt study used a novel method to design a composite material of graphene, $TiO_2$, and zeolite in optimal weight ratios through an experimental design of simplex lattice mixture for maximum photodegradation. The structural features of the photocatalysts were investigated by X-ray diffraction system(XRD), Ultraviolet-Visible spectrophotometer(UV-Vis), Transmission electron microscopy equipped with energy-dispersive spectroscopy(TEM-EDS), Fourier transform infrared spectroscopy(FTIR) and $N_2$ adsorption/desorption analyzer(BET) methods. The findings revealed the effects of initial pH value, OTC concentration and environmental temperature on the photocatalytic performance. Moreover, the changes in the biotoxicity of simulated OTC-bearing wast water using AOPs were investigated along with the possible mechanism of the photodegradation reaction. The conclusions showed as follows:

(1) This first-attempt study revealed the most promising composite of $TiO_2$ loaded on zeolite and graphene for maximal photocatalytic degradation of OTC. The optimal

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weight ratio of graphene, titanium dioxide, and zeolite was 1:8:1 determined via experimental design of simplex lattice mixture. The reaction rate can achieve $5 \times 10^{-2}$ mg $L^{-1}$ $min^{-1}$. The most promising composite was named as GTZ(1: 8: 1).

(2) The composite material was characterized by XRD, UV-Vis, TEM-EDS, FTIR and BET analysis. The XRD results indicated that GTZ(1: 8: 1) composite was successfully prepared using the solid dispersion method and the crystal structure of GTZ(1: 8: 1) composite was stable during photocatalytic degradation. The UV-Vis spectroscopy results showed that the GTZ(1: 8: 1) composite exhibited a higher energy absorption not only in the UV region but also in the visible region. $TiO_2$ had band gap value of 3.2 eV, while GTZ(1: 8: 1) was ca. 2.8 eV. This simply demonstrated improvement of light absorption capabilities due to the deposition of graphene and zeolite. The TEM and EDS analysis results showed that the composite materials were uniformly dispersed. Moreover, $TiO_2$ was evenly distributed on the surface of the zeolite and across the graphene sheet. The FTIR results indicated that the three components were assembled by hydrogen bonding. The BET results showed that the surface values of GTZ(1: 8: 1) was 130.93 $m^2$ $g^{-1}$ and it has promising adsorption characteristics.

(3) OTC was used as model toxicant to evaluate the photodegradation efficiency of the GTZ(1: 8: 1). In optimal operating conditions(i.e., 10 mg $L^{-1}$ Oxytetracycline, 0.2 g $L^{-1}$ GTZ(1: 8: 1) composite, pH = 7, temperature = 25℃, light intensity: 300 W $m^{-2}$), a removal efficiency(ca. 97%) and mineralization efficiency(ca. 67%) were achieved in 180 min, respectively. That indicated that some intermediate organic species were generated during the process. When the removal rate was stable, the mineralization rate was still increased, suggesting that the intermediates were degraded and mineralized in the further step of reaction.

(4) In order to further understand the mechanism during the photocatalytic process, hole scavengers and radical scavengers were added into the reaction for the degradation of OTC with GTZ(1: 8: 1) composites. Both EDTA-2Na and t-BuOH as

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hole and radical scavengers decreased the efficiency of OTC photodegradation. The poorest performance was found by supplementation of EDTA-2Na, which could capture hole to inhibit oxidation, suggesting holes and hydroxyl(·OH) involved in the reaction were the major active oxidant for photodegradation.

(5) The biotoxicity of OTC and its degraded intermediates at various times on cell growth of *Escherichia coli* DH5α was also assayed. The comparison results of the maximal cell growth rate(μ, unit: $h^{-1}$) among the four treatment groups were:

$$\mu_{OTC+LB}(0) \le \mu_{OTC(90)+LB}(1.6) \le \mu_{OTC(180)+LB}(2.6) \approx \mu_{LB}(2.7)$$

The toxicity and the concentration of OTC were continuously decreased over treatment time. After 180 min photocatalytic treatment, OTC solution treated by GTZ(1: 8: 1) showed insignificant biotoxicity to receptor DH5α cells.

(6) The biotoxicity of OTC and its degraded intermediates at various times on a boar-sperm model with the indicators of sperm viability, acrosome integrity, and mitochondrial function was assayed. With increased processing time, the percentage of surviving sperm showed no significant change, the percentage of sperm acrosome integrity decreased, and the percentage of sperm with active mitochondria increased. The biological toxicity of intermediates in coculture samples changed the morphology and function of boar sperm but did not kill them.

Since Graphene/$TiO_2$/zeolite materials combined the advantages of the three components, and even made a synergistic effect. It improves the activity of the photocatalyst in visible light, overcome the shortcomings of hard recycling and weak adsorption ability, which provides a scientific basis on the application of photocatalytic material in industry.

Keywords: Oxytetracycline; Compound material; Photodegradation; Biotoxicity; Mechanism

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# 第 1 章 绪论

## 1.1 环氧四环素(OTC)的潜在风险与处理研究现状

### 1.1.1 抗生素的使用

人们日常生活中大量使用的药品和个人护理品(pharmaceuticals and personal care products, PPCPs)，包括人用、兽用、农用药品，是一类新型化学物质，具有潜在的生态风险效应[1]。PPCPs 中药品的主要分为抗生素、类固醇、消炎止痛药、精神类药、降压药、显影剂、避孕药和减肥药等。个人护理品的主要成份是麝香类化合物、杀菌消毒剂、防晒剂、化妆品等[2-4]。这些药物和日用品从人们开始使用的时候，便开始源源不断地进入环境中，但是一直没有被认为是一类具有潜在危害的环境污染物。自 1999 年 Daughton 等[2]报导 PPCPs 的环境污染问题并将其归纳成“微妙的、潜在的、有累积影响的”环境污染物质以来，PPCPs 及其处理方法越来越得到全世界的广泛关注。

2003 年，我国已是世界上最大的药品生产国，2004 年成为全球最大的药品市场之一。其中，抗生素的使用情况十分广泛，而且存在滥用的现象。在中国医药市场中，抗生素已经连续多年位居销售额第一位。世界卫生组织的资料显示，我国住院患者的抗生素使用率高达 80%，其中广谱抗生素和联合使用抗生素达 58%，远远高于 30%的国际水平[5]。我国自上世纪九十年代初以来,抗生素在畜牧业生产中也得到了广泛应用，近年来动物生产中抗生素年平均消费已达 6000 t，并集中应用于经济发达地区。1997 年德国青霉素产量为 900 t，1998 年丹麦抗生素总产量为 87 t。我国，在 2003 年仅青霉素产量就为 28000 t，占世界总产量的 60%，环氧四环素产量 10000 t，占世界总产量的 65%，多西环素产量也为世界第一[6]。2005 年，我国广州市某城市污水处理厂的出水中，已检测到一定含量的抗生素、多环麝香，其含量在μg $L^{-1}$ 水平[[7-9]。抗生素的残留引起的环境污染日趋严重，但是目前还没有对抗生素残留产生的污染问题引起足够的重视，其处理方法还不够成熟。

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