

学校编码: 10384

分类号\_\_\_\_\_密级\_\_\_\_\_

学号: 22620061152375

UDC \_\_\_\_\_

厦 门 大 学

硕 士 学 位 论 文

改性活性炭对烟气中气态汞的吸附研究

Study on Adsorption of Elemental Mercury in Coal-fired  
Flue Gas by Modified Activated Carbons

罗 锦 英

指导教师姓名: 罗 津 晶 副 教 授

专 业 名 称: 环 境 工 程

论文提交日期: 2009 年 6 月

论文答辩日期: 2009 年 6 月

学位授予日期: 2009 年 月

答辩委员会主席: 欧阳通 教授

评 阅 人: 黄碧纯 副教授

余运波 副研究员

2009 年 6 月

## 厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为( )课题(组)的研究成果,获得( )课题(组)经费或实验室的资助,在( )实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

## 厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

1. 经厦门大学保密委员会审查核定的保密学位论文，  
于 年 月 日解密，解密后适用上述授权。

2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月

厦门大学博硕士学位论文摘要库

# 目 录

|                                    |           |
|------------------------------------|-----------|
| 摘要.....                            | IX        |
| ABSTRACT.....                      | XI        |
| 表索引.....                           | XV        |
| 图索引.....                           | XVII      |
| LIST OF TABLES.....                | XIX       |
| LIST OF FIGURES .....              | XXI       |
| <b>第一章 绪论 .....</b>                | <b>1</b>  |
| <b>1.1 研究背景 .....</b>              | <b>1</b>  |
| <b>1.2 国内外研究现状 .....</b>           | <b>3</b>  |
| 1.2.1 燃煤汞排放控制研究现状.....             | 4         |
| 1.2.2 活性炭吸附剂控制 Hg 排放的研究进展.....     | 6         |
| 1.2.3 现有控制方法和研究的不足.....            | 7         |
| <b>1.3 活性炭吸附的理论基础 .....</b>        | <b>8</b>  |
| 1.3.1 活性炭表面的吸附作用.....              | 8         |
| 1.3.2 吸附热力学.....                   | 9         |
| 1.3.3 基于吸附等温线的吸附理论.....            | 11        |
| 1.3.4 吸附动力学理论.....                 | 13        |
| <b>1.4 本课题研究的目的是、内容和技术路线 .....</b> | <b>15</b> |
| 1.4.1 研究目的.....                    | 15        |
| 1.4.2 研究内容.....                    | 15        |
| 1.4.3 研究技术路线.....                  | 15        |
| <b>1.5 本章小结.....</b>               | <b>16</b> |
| <b>第二章 实验部分 .....</b>              | <b>17</b> |

|   |           |
|---|-----------|
| <b>2.1 实验装置</b>                         | <b>17</b> |
| 2.1.1 流量控制部分                            | 17        |
| 2.1.2 模拟气态汞发生器                          | 17        |
| 2.1.3 石英管路部分                            | 18        |
| 2.1.4 吸附反应部分                            | 18        |
| 2.1.5 汞测试装置                             | 19        |
| 2.1.6 尾气处理单元                            | 21        |
| <b>2.2 实验主要仪器及试剂</b>                    | <b>21</b> |
| 2.2.1 实验主要仪器                            | 21        |
| 2.2.2 实验主要试剂                            | 22        |
| 2.2.3 实验材料                              | 22        |
| <b>2.3 实验方法</b>                         | <b>23</b> |
| 2.3.1 活性炭表面官能团的筛选                       | 23        |
| 2.3.2 改性吸附剂的制备                          | 24        |
| 2.3.3 样品的表征                             | 26        |
| 2.3.4 吸附实验                              | 27        |
| <b>2.4 本章小结</b>                         | <b>28</b> |
| <b>第三章 活性炭改性实验</b>                      | <b>29</b> |
| 3.1 改性样品                                | 29        |
| 3.2 负载量的核算                              | 31        |
| 3.3 样品制备的重复性测试                          | 32        |
| 3.4 样品表征                                | 33        |
| 3.4.1 比表面积及孔径分析                         | 33        |
| 3.4.2 XRD 分析                            | 34        |
| 3.4.3 XPS 分析                            | 34        |
| 3.5 本章小结                                | 35        |
| <b>第四章 常温活性炭固定床吸附 Hg<sup>0</sup> 实验</b> | <b>36</b> |
| 4.1 实验系统的稳定可靠性                          | 36        |
| 4.2 水浴温度与汞进口浓度间的关系                      | 36        |
| 4.3 孔径对 Hg <sup>0</sup> 吸附的影响           | 37        |
| 4.4 高温热处理对样品吸附 Hg <sup>0</sup> 的影响      | 38        |

|   |           |
|---|-----------|
| 4.5 酚羟基对 $\text{Hg}^0$ 吸附的影响 .....                      | 40        |
| 4.6 羧基对 $\text{Hg}^0$ 吸附的影响 .....                       | 40        |
| 4.7 水分对 $\text{Hg}^0$ 吸附的影响 .....                       | 42        |
| 4.8 本章小结 .....  | 44        |
| <b>第五章 高温活性炭固定床吸附 <math>\text{Hg}^0</math> 实验 .....</b> | <b>45</b> |
| 5.1 实验系统的稳定可靠性 .....                                    | 45        |
| 5.2 吸附剂的筛选和性能评价 .....                                   | 45        |
| 5.2.1 高温热处理对 $\text{Hg}^0$ 吸附的影响 .....                  | 45        |
| 5.2.2 酚羟基对 $\text{Hg}^0$ 吸附的影响 .....                    | 46        |
| 5.2.3 羧基对 $\text{Hg}^0$ 吸附的影响 .....                     | 48        |
| 5.3 温度对 $\text{Hg}^0$ 吸附的影响 .....                       | 49        |
| 5.4 进口汞浓度对 $\text{Hg}^0$ 吸附的影响 .....                    | 51        |
| 5.5 本章小结 .....  | 52        |
| <b>第六章 活性炭吸附 <math>\text{Hg}^0</math> 的数学模型 .....</b>   | <b>54</b> |
| 6.1 吸附等温线模型 .....                                       | 54        |
| 6.2 吸附动力学模型 .....                                       | 59        |
| 6.3 吸附活化能与指前因子的计算 .....                                 | 63        |
| 6.4 本章小结 .....  | 64        |
| <b>第七章 总结 .....</b>                                     | <b>66</b> |
| 7.1 全文总结 .....  | 66        |
| 7.2 主要创新点 .....   | 68        |
| 7.3 不足之处 .....  | 68        |
| 7.4 进一步的工作及建议 .....                                     | 68        |
| <b>参考文献.....</b>  | <b>69</b> |
| <b>攻读硕士学位期间发表的论文 .....</b>                              | <b>73</b> |
| <b>致谢.....</b>  | <b>74</b> |

厦门大学博硕士学位论文摘要库



## Table of Contents

|   |            |
|---|------------|
| <b>ABSTRACT(in Chinese)</b> .....   | <b>IX</b>  |
| <b>ABSTRACT(in English)</b> .....   | <b>XI</b>  |
| <b>LIST OF TABLES</b> .....   | <b>XIX</b> |
| <b>LIST OF FIGURES</b> .....  | <b>XXI</b> |
| <b>CHAPTER 1 PREFACE</b> .....  | <b>1</b>   |
| <b>1.1 Research background</b> .....  | <b>1</b>   |
| <b>1.2 Literature review</b> .....  | <b>3</b>   |
| 1.2.1 Mercury removal technologies for coal-fired power plants.....                   | 4          |
| 1.2.2 Research development of mercury removal technologies by activated carbons ..... | 6          |
| 1.2.3 Disadvantages of current mercury removal technologies and researches .....      | 7          |
| <b>1.3 Theoretical foundation of mercury adsorption by activated carbons</b> .....    | <b>8</b>   |
| 1.3.1 Adsorption mechanism on the surface of activated carbons .....                  | 8          |
| 1.3.2 Adsorption thermodynamics .....   | 9          |
| 1.3.3 Theories based on adsorption isotherm.....                                      | 11         |
| 1.3.4 Theories of adsorption kinetics .....   | 13         |
| <b>1.4 Objectives、 contents and technical approach of this research</b> .....         | <b>15</b>  |
| 1.4.1 Objectives .....  | 15         |
| 1.4.2 Contents .....  | 15         |
| 1.4.3 Technical approach .....  | 16         |
| <b>1.5 Conclusions</b> .....  | <b>16</b>  |
| <b>CHAPTER 2 EXPERIMENTS</b> .....  | <b>17</b>  |
| <b>2.1 Experimental devices</b> .....   | <b>17</b>  |
| 2.1.1 Flux control system.....  | 17         |

|   |           |
|---|-----------|
| 2.1.2 Permeation device arising vapor-phase mercury .....                                     | 17        |
| 2.1.3 Quartz plumbing and valves .....  | 18        |
| 2.1.4 Mercury adsorption reactor .....  | 18        |
| 2.1.5 Detector for mercury vapor .....  | 19        |
| 2.1.6 Residual gas disposing system .....   | 21        |
| <b>2.2 Experimental instruments and reagents .....</b>  | <b>21</b> |
| 2.2.1 Instruments .....   | 21        |
| 2.2.2 Reagents .....  | 22        |
| 2.2.3 Materials .....   | 22        |
| <b>2.3 Experimental method .....</b>  | <b>23</b> |
| 2.3.1 Sieving of surface functional groups on activated carbons .....                         | 23        |
| 2.3.2 Preparation of modified activated carbons .....   | 23        |
| 2.3.3 Samples characterization .....  | 24        |
| 2.3.4 Mercury adsorption experiment .....   | 26        |
| <b>2.4 Conclusions .....</b>  | <b>28</b> |
| <br>  |           |
| <b>CHAPTER 3 PREPARATION OF MODIFIED ACTIVATED</b>  |           |
| <b>CARBONS .....</b>  | <b>29</b> |
| <br>  |           |
| <b>3.1 Modified samples .....</b>   | <b>29</b> |
| <b>3.2 Calculation of the amounts of surface functional groups loaded .....</b>               | <b>31</b> |
| <b>3.3 Repeative tests for preparation of modified samples .....</b>                          | <b>32</b> |
| <b>3.4 Characterisation of the activated carbons .....</b>                                    | <b>33</b> |
| 3.4.1 BET and pore structure analysis .....   | 33        |
| 3.4.2 XRD analysis .....  | 34        |
| 3.4.3 XPS analysis .....  | 34        |
| <b>3.5 Conclusions .....</b>  | <b>35</b> |
| <br>  |           |
| <b>CHAPTER 4 Hg<sup>0</sup> ADSORPTION ON FIXED-BED ACTIVATED</b>                             |           |
| <b>CARBON SYSTEM AT ROOM TEMPERATURE .....</b>  | <b>36</b> |
| <br>  |           |
| <b>4.1 Stability and reliability of Hg<sup>0</sup> adsorption system .....</b>                | <b>36</b> |
| <b>4.2 Relationship between water bath temperature and Hg<sup>0</sup> inlet concentration</b> |           |
| <b>.....</b>  | <b>36</b> |

|  |           |
|--|-----------|
| 4.3 Effect of pore structure on Hg <sup>0</sup> adsorption .....   | 37        |
| 4.4 Effect of heat-treated samples on Hg <sup>0</sup> adsorption .....                                       | 38        |
| 4.5 Effect of phenol groups on Hg <sup>0</sup> adsorption .....  | 40        |
| 4.6 Effect of carboxyl groups on Hg <sup>0</sup> adsorption.....   | 40        |
| 4.7 Effect of moisture on Hg <sup>0</sup> adsorption .....   | 42        |
| 4.8 Conclusions .....  | 44        |
| <b>CHAPTER 5 Hg<sup>0</sup> ADSORPTION ON FIXED-BED ACTIVATED<br/>CARBON SYSTEM AT HIGH TEMPERATURE.....</b> | <b>45</b> |
| 5.1 Stability and reliability of Hg <sup>0</sup> adsorption system .....                                     | 45        |
| 5.2 Screening and adsorption capacity evaluation of activated carbons.....                                   | 45        |
| 5.2.1 Effect of heat-treated samples on Hg <sup>0</sup> adsorption.....                                      | 45        |
| 5.2.2 Effect of phenol groups on Hg <sup>0</sup> adsorption.....   | 46        |
| 5.2.3 Effect of carboxyl groups on Hg <sup>0</sup> adsorption.....   | 48        |
| 5.3 Effect of temperature on Hg <sup>0</sup> adsorption .....  | 49        |
| 5.4 Effect of elemental mercury inlet concentration on Hg <sup>0</sup> adsorption .....                      | 51        |
| 5.5 Conclusions .....  | 52        |
| <b>CHAPTER 6 KINETIC MODELS FOR Hg<sup>0</sup> ADSORPTION ON<br/>MODIFIED ACTIVATED CARBONS.....</b>         | <b>54</b> |
| 6.1 Models of adsorption isotherms .....   | 54        |
| 6.2 Models of adsorption kinetics.....   | 59        |
| 6.3 Calculation of adsorption activation energy and kinetic constant.....                                    | 63        |
| 6.4 Conclusions .....  | 64        |
| <b>CHAPTER 7 SUMMARY .....</b>   | <b>66</b> |
| 7.1 General conclusions.....   | 66        |
| 7.2 Innovation .....   | 68        |
| 7.3 Disadvantages of this research .....   | 68        |
| 7.4 Future work and suggestions.....   | 68        |
| <b>REFERENCE.....</b>  | <b>69</b> |

**MANUSCRIPTS DURING GRADUATE STUDY.....73**

**ACKNOWLEDGEMENTS .....74**

厦门大学博硕士论文摘要库

## 摘要

汞是煤中的微量元素之一，其随着煤的燃烧释放到大气中。由于汞污染物具有较强的生理毒性和生物累积性，所以其污染控制受到了人们的普遍关注。我国作为以煤为主要能源结构的国家，对燃煤电站汞的排放控制研究刻不容缓。

本研究以目前燃煤烟气汞污染控制的主流吸附剂——活性炭为对象，从活性炭表面官能团出发，采用高温惰性氛围加热法去除活性炭表面所有酸性含氧官能团，继而通过化学浸渍法制备改性样品。通过吸附实验，研究改性前后样品的物理化学性质对  $\text{Hg}^0$  吸附的影响，并建立了活性炭固定床吸附  $\text{Hg}^0$  的简单数学模型。研究的主要内容和结果如下：

### (1) 改性样品的制备

通过惰性氛围高温热处理去除活性炭表面的官能团，在此基础上采用化学浸渍法制备了不同负载量的酚羟基和羧基改性样品。为了考察活性炭表面水分对气态汞吸附的影响，对原材料(BPL)进行加湿处理，得到表面含有不同水分的样品。

### (2) 常温活性炭固定床吸附 $\text{Hg}^0$ 实验

在常温下考察活性炭的物理化学性质对  $\text{Hg}^0$  吸附的影响。结果表明，在常温下，活性炭对  $\text{Hg}^0$  的吸附是物理和化学作用的结果。在吸附过程的最初阶段，物理吸附比化学吸附更具竞争力。孔径对  $\text{Hg}^0$  吸附影响实验证实：相对于中孔来说，微孔更有利于  $\text{Hg}^0$  的吸附。酚羟基和羧基改性样品对  $\text{Hg}^0$  吸附实验表明，酚羟基对  $\text{Hg}^0$  的吸附不起促进作用，而羧基有利于其对  $\text{Hg}^0$  的吸附，且当羧基负载量为 28.89 mg/g 时，活性炭的吸附性能达到最佳。活性炭表面存在适量水分有利于  $\text{Hg}^0$  的吸附。在本研究中，当活性炭表面含水率为 14.49% 时，样品吸附性能达到最佳。

### (3) 高温活性炭固定床吸附 $\text{Hg}^0$ 实验

在 140 °C 下考察改性样品对  $\text{Hg}^0$  的吸附性能，在此基础上，筛选出对  $\text{Hg}^0$  有较好吸附效果的样品，继而考察温度和进口汞浓度等因素对其吸附性能的影响。结果表明，活性炭对  $\text{Hg}^0$  的吸附过程既有物理作用也有化学作用，随着吸附温度的升高，物理作用减弱，而化学作用增强。酚羟基对  $\text{Hg}^0$  的吸附起抑制作用，而羧

基对 $\text{Hg}^0$ 的吸附起促进作用,且当羧基负载量为 $28.89 \text{ mg/g}$ 时,活性炭的吸附性能达到最佳。随着反应温度的升高,羧基改性样品对 $\text{Hg}^0$ 的吸附量降低,而且反应温度越高,下降的幅度越大。在一定范围内,进口汞浓度对羧基改性样品吸附 $\text{Hg}^0$ 具有正效应,但过大的进口汞浓度,其负效应远大于正效应。对于BPL样品,当进口汞浓度为 $48 \text{ }\mu\text{g/m}^3$ 时,其对 $\text{Hg}^0$ 的吸附能力达到最佳,而对于羧基负载量为 $28.89 \text{ mg/g}$ 样品(BPL-s4),当进口汞浓度为 $60 \text{ }\mu\text{g/m}^3$ 时,其对 $\text{Hg}^0$ 的吸附能力达到最佳。

#### (4) 活性炭吸附 $\text{Hg}^0$ 的数学模型

在参考前人和本人实验结果的基础上,建立了活性炭固定床吸附 $\text{Hg}^0$ 的简单数学模型,研究了汞在BPL-s4样品上的吸附平衡过程和动力学过程。结果表明,活性炭对 $\text{Hg}^0$ 的吸附过程较容易进行,但相对于高温来说,低温更有利于活性炭对 $\text{Hg}^0$ 的吸附。燃煤烟气中 $\text{Hg}^0$ 在BPL-s4样品上的吸附符合一级反应动力学方程,吸附速率常数与反应温度呈正相关,吸附反应的活化能为 $25.86 \text{ KJ/mol}$ ,指前因子为 $22.16 \text{ min}^{-1}$ 。

**关键词:** 活性炭 气态汞 吸附

## ABSTRACT

Mercury is one of trace elements in coal, it is emitted into the atmosphere during the coal combustion process. Mercury control is aroused great attention because of its high physiological toxicity and bioaccumulation. Coal is the major energy source in China, so the control of mercury emission from coal-fired power plants demands immediate actions.

This research is focused on activated carbons which are the major sorbents used for mercury removal in coal-fired power plants currently. The oxygen-containing functional groups on activated carbon surfaces were studied. They could be removed by heating in nitrogen (1000 °C). After heat treatment, carboxyl and phenol groups were added separately to the surface of activated carbons by chemical immersion method. The effect of physical-chemical properties for original activated carbons and modified activated carbons was studied by adsorption experiment, and simple mathematic models were developed to describe mercury adsorption on fixed-bed activated carbon system. The major contents and results of this research were as follow:

### (1) Preparation of modified samples

The oxygen-containing functional groups on activated carbon surfaces were removed by heating in nitrogen (1000 °C). After heat treatment, carboxyl and phenol groups were added separately to the surface of activated carbons by chemical immersion method. The origin materials were sprayed with some deionized water to prepare samples containing different contents of moisture, and then the effect of moisture on mercury adsorption was studied.

### (2) Mercury adsorption experiment on fixed-bed activated carbon system at room temperature

The effect of physical-chemical properties of activated carbons on mercury adsorption was studied at room temperature. The results show that the mechanism of mercury adsorption on activated carbons is a combination of physical and chemical

adsorption. At the first phase of adsorption, physical reaction is more competitive than chemical reaction. Compared to the mesopore structure, micropore structure on the surface of activated carbons is in favor of capturing mercury from carrier gas. The phenol groups may have no effect on mercury adsorption, while the carboxyl groups are beneficial to the mercury adsorption. When the modification ratio is 28.89 mg carboxyl groups per gram activated carbon, the mercury adsorption capacity reaches the best result. The presence of moisture on the surface of activated carbons can enhance their mercury adsorption capacities, and when the moisture content is 14.49%, the adsorption capacity reaches the best result.

### (3) Mercury adsorption experiment on fixed-bed activated carbon system at high temperature

The capacity of modified samples on mercury adsorption was studied at 140 °C, and then samples which show a good adsorption capacity were chosen for studying the effect of temperature and mercury inlet concentration on mercury adsorption. The results show that the mechanism of activated carbons on mercury adsorption is a combination of physical and chemical adsorption. As the adsorption temperature increases, physical adsorption is weakened, while the chemical adsorption is reinforced. The phenol groups inhibit mercury adsorption, while the carboxyl groups are beneficial to the mercury adsorption. When the modification ratio is 28.89 mg carboxyl groups per gram activated carbon, the mercury adsorption capacity reaches the best result. The capacity of mercury adsorption on carboxyl-modified samples decreases as the reaction temperature increases. And the degressive amounts of mercury adsorption are increased as the reaction temperature increases. There is a positive relation between mercury inlet concentration and mercury adsorption capacity in a certain range. When mercury inlet concentration is over the best point, the negative effect is stronger than positive effect. When mercury inlet concentration is 48  $\mu\text{g}/\text{m}^3$ , the mercury adsorption capacity for BPL samples reaches the best result. While mercury inlet concentration is 60  $\mu\text{g}/\text{m}^3$ , the mercury adsorption capacity for BPL-s4 samples (the modification ratio is 28.89 mg carboxyl groups per gram activated carbon) reaches the best result.



Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to [etd@xmu.edu.cn](mailto:etd@xmu.edu.cn) for delivery details.

厦门大学博硕士论文摘要库