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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

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摘 要

汞是煤中的痕量元素之一，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Hg^0吸附的影响，并建立了活性炭固定床吸附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Hg^0实验

在常温下考察活性炭的物理化学性质对Hg^0吸附的影响。结果表明，在常温下，活性炭对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Hg^0吸附影响实验证实：相对于中孔来说，微孔更有利于Hg^0的吸附。酚羟基和羧基改性样品对Hg^0吸附实验表明，酚羟基对Hg^0的吸附不起促进作用，而羧基有利于其对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Hg^0实验

在140 ℃下考察改性样品对Hg^0的吸附性能，在此基础上，筛选出对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Hg^0的吸附起抑制作用，而羧

基对Hg^0的吸附起促进作用，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。随着反应温度的升高，羧基改性样品对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 μg/m^3时，其对Hg^0的吸附能力达到最佳，而对于羧基负载量为28.89 mg/g样品(BPL-s4)，当进口汞浓度为60 μg/m^3时，其对Hg^0的吸附能力达到最佳。

(4) 活性炭吸附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Hg^0的吸附。燃煤烟气中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 KJ/mol，指前因子为22.16 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 arosed 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 ℃). 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 ℃). 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 ℃, 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 weaken, 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 mecury 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 μg/m^3, the mercury adsorption capacity for BPL samples reaches the best result. While mercury inlet concentration is 60 μg/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.