ADSORPTION ISOTHERM OF VAPOR-PHASE MERCURY CHLORIDE ONTO SPHERICAL ACTIVATED CARBONS VIA THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

This study investigated the adsorptive capacity and isotherm of $HgCl_2$ onto spherical activated carbons (SAC) via thermogravimetric analysis (TGA). Activated carbon injection (ACI) is thought as the best available control technology (BACT) for mercury removal from flue gas. There are two major forms of vapor-phase mercury, Hg^o and Hg^{2+}, of which $HgCl_2$ accounts for 60-95% of total mercury. Mercury emitted from the incineration of municipal solid wastes (MSW) could cause severely adverse effects on human health and ecosystem since it exists mainly in vapor phase due to high vapor pressure. Although the adsorptive capacity of $HgCl_2$ onto activated carbon has been studied in previous adsorption column tests, only a few studies have thoroughly investigated the adsorption isotherms of $HgCl_2$ onto SAC. In this study, TGA was applied to obtain the adsorptive capacity of $HgCl_2$ onto SAC with adsorption temperature (30~150^{o}C) and influent $HgCl_2$ concentration (50~1,000$\mu g/m^3$). Experimental results indicated that the adsorptive capacity of $HgCl_2$ onto SAC was 2.79 and 0.18 mg/gC at 30 and 150^{o}C, respectively. Further comparing experimental data with four adsorption isotherms showed that Freundlich isotherm demonstrated the best fitting on the adsorption of $HgCl_2$ onto SAC.

Key Words: Spherical activated carbon, mercury chloride, adsorptive capacity, adsorption isotherm, thermogravimetric analysis (TGA)

INTRODUCTION

Incineration has been extensively developed and increasingly adopted by many countries for the treatment of municipal solid waste (MSW) in view of energetic vaporization of materials and reduction of hazardousness, mass, and volume, before final disposal [1-3]. MSW is an extremely heterogeneous material and almost all of these constituents contain some quantity of heavy metals, which could be further vaporized in flue gas and/or contained in particulate matter (PM) during the incineration of MSW [4-6]. Most of trace metallic species could be efficiently removed by properly operated particulate removal systems. However, mercury is present mainly in vapor form and can not be captured effectively by existing particulate removal systems [7]. Mercury concentrations from MSW incineration range from 200 to 1000$\mu g/m^3$ and can be classified as elemental (Hg^o) and oxidized (Hg^{2+}) forms [7, 8]. Furthermore, in the flue gas of MSW incinerators, mercury is mainly existed as $HgCl_2$, due to relatively high concentration of HCl [9]. At the present, the most mature retrofit technology available for the removal of mercury is the injection of sorbents such as powdered activated carbon (PAC) into the flue gas at the upstream of air pollution control devices (APCD). The gas-phase mercury contacts the injected sorbent and attaches onto its surface.

Existing APCD, either an electrostatic precipitator (ESP) or a fabric filter, collects the sorbent with attached mercury along with fly ashes [9-11].

Equilibrium and kinetic studies are important towards obtaining a better understanding of mercury adsorption. Many investigations have addressed the relationship between sorption kinetics and equilibrium for different adsorbent/adsorbate combinations [12-15]. For the removal of vapor-phase mercury, several bench-,pilot-, and full-scale tests have be proceeded to examine the influence of carbon types, carbon structures, carbon surface characteristics, injection methods (dry or wet), amount of carbon injected, and flue gas temperature on mercury removal [7, 9-11, 16]. In addition, the dynamics of granular activated carbon (GAC) adsorbers for the uptake of gas-phase mercury was evaluated as a function of temperature, influent concentration of mercury, and empty-bed residence time [17]. However, only a few studies investigated the adsorption isotherms of $HgCl_2$ onto activated carbons.

Langmuir, Freundlich, Langmuir-Freundlich (or slips model), and Redlich-Peterson models are often used by researchers in the modeling of adsorption isotherms of metallic ions [18]. Among them, Langmuir and Freundlich isotherms are most popular empirical models, which have been widely applied since they are simple and only two parameters are required for the calculations. Furthermore, thermogravimetric analysis (TGA) has been commonly used to investigate the differential variation of tested material's mass with duration at either constant temperature or varying temperature environments. For instance, TGA has been used to determine reaction rate and to investigate kinetic modeling during the pyrolysis of waste tires as well as the adsorption rate and the kinetic modeling of volatile organic compounds (VOCs) by GAC. However, the application of TGA on the investigation of heavy metals adsorbed by AC is seldom. Therefore, the objectives of this study were to determine the adsorptive capacity of $HgCl_2$ by spherical activated carbons (SAC), to investigate the adsorption isotherms of $HgCl_2$ via TGA, and to evaluate the influence of adsorption temperature on the adsorptive capacity of SAC.

EXPERIMENTAL METHODS

Activated Carbon

Spherical activated carbons (X-7000) tested in this study were provided by the Veterans Affairs Commission at Yunlin County. The physical and chemical properties of the virgin SAC are analyzed and listed in Table 1. The virgin SAC was initially rinsed with deionized water (D.I. H_2O) and then dried at 104℃ for 48 hours. Furthermore, the SAC was heated in a tubular oven at 900℃ for 4 hours to remove the residual impurities of SAC. Finally, the SAC was stored in desiccators prior to conduct the adsorption isotherm tests.

Table 1. Physical and chemical properties of virgin X-7000 spherical activated carbon.

Physical properties	Unit	Values
Specific surface area	m^2/g	950~1150
Diameter	mm	1~1.5
Bulk density	g/cm^3	0.44~0.49
Mass mean diameter	nm	1.3~1.6
Uniform coefficient	-	< 1.5

Hardness	%, JIS	> 90
pH	-	10~12
Molasses number	mg/g	180~200

Adsorption Isotherm Tests

The adsorption isotherm experiments of SAC on vapor-phase $HgCl_2$ was conducted in a self-designed adsorption isotherm system. The schematic diagram of experimental setup is shown in Figure 1. This system consisted of a $HgCl_2$ generation assembly and a thermogravimetric analysis assembly. A permeation tube manufactured by VICI Metronics Inc. was used to produce vapor-phase $HgCl_2$ by using nitrogen gas as carrier gas. A wide range of mercury concentration was generated by varying the tube temperature and the flow rate of nitrogen gas. The mercury vapor (reactive gas) flows at about 10 ml/min through Telfon lines to the TGA reaction chamber (0.8 cm ID) containing 20-30 mg of SAC to be studied. The temperature of TGA reaction chamber could be controlled by TGA software. The protective gas (nitrogen gas) flow was controlled at 10 ml/min. The purge gas instead of the reactive gas was purged to remove the residual mercury vapor remained in the TGA reaction chamber at the end of experiments. The adsorption temperatures and $HgCl_2$ concentrations investigated in the adsorption isotherm experiments were 30~150^{o}C and 50~1,000μg/m^{3}, respectively.

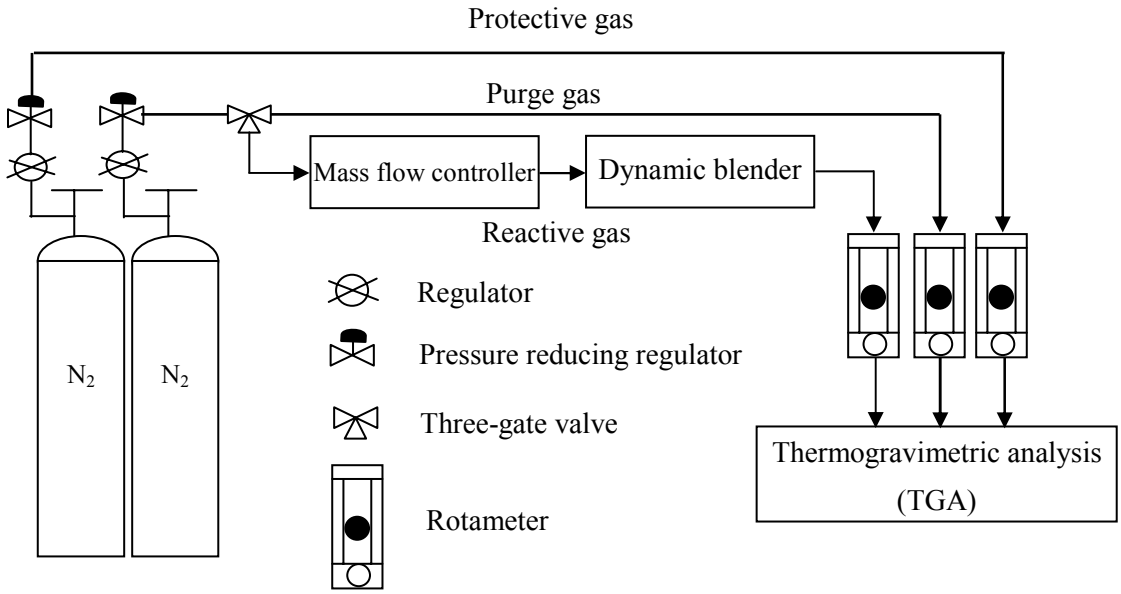

Figure 1. Schematic diagram of the isotherm adsorption system.

Table 2. Description of Langmuir and Freundlich isotherms.

Isotherms	Equations	Parameter definition

Langmuir	$q = \frac{q_m k_L C}{1 + k_L C}$	q: amount of chemical adsorbed by carbon (mg/g) q_m: maximum amount of chemical adsorbed by carbon (mg/g) k_L: adsorption coefficient (-) C: equilibrium concentration of chemical (mg/l)
Freundlich	$q = AC^{n}$	q: amount of chemical adsorbed by carbon (mg/g) A: adsorption constant (-) n: Freundlich adsorption coefficient (-) C: equilibrium concentration of chemical (mg/L)

Two adsorption isotherms including the Langmuir isotherm and Freundlich isotherm were evaluated to determine the most proper adsorption isotherm by comparing experimental results with model simulations. The definitions of parameters for the above two mentioned isotherms were tabulated in Table 2.

RESULTS AND DISCUSSION

In probing into the adsorptive capacity of spherical activated carbon on $HgCl_2$ vapor, the experiments were proceeded at the adsorption temperatures of 30 and 150℃. The influences of adsorption temperature on the adsorptive capacity of SAC are illustrated in Figures 2 and 3. Furthermore, the parameters of adsorption isotherms and the deviation between experimental data and model simulations are listed in Table 3. The experimental results showed that the maximum adsorptive capacities of SAC were 2.79 and 0.18 mg/g at 30 and 150℃, respectively. In addition, the values of k_L were 13.050 and 21.833 at 30 and 150℃, respectively. The value of k_L decreased with the increase of the adsorption temperature.

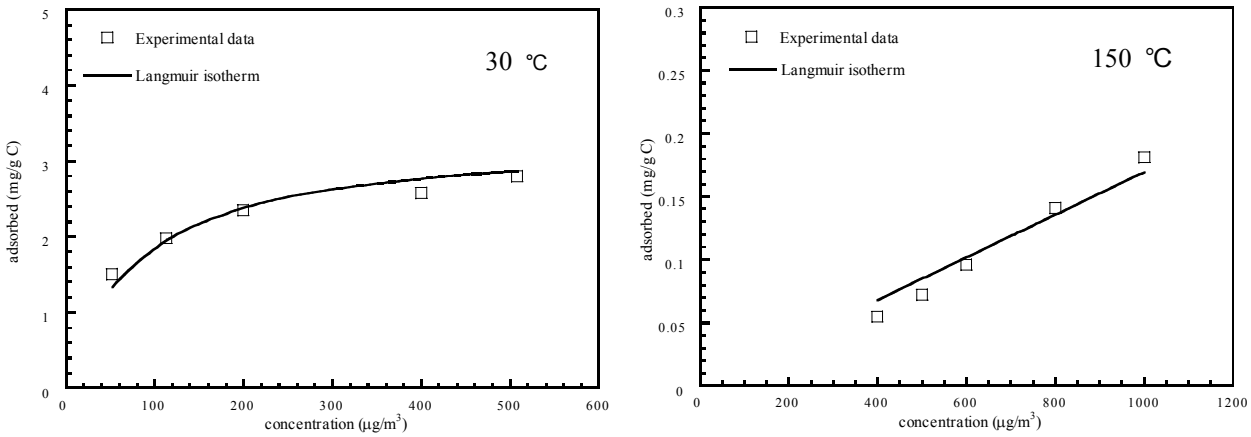

Figure 2. The influence of adsorption temperature on the adsorptive capacity of SAC. (Langmuir isotherm)

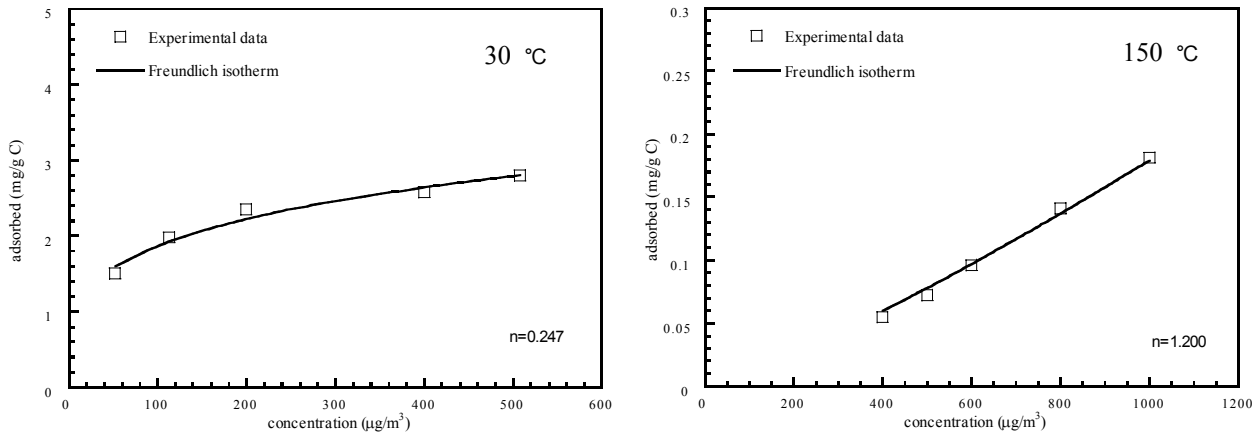

Figure 3. The influence of adsorption temperature on the adsorptive capacity of SAC. (Freundlich isotherm)

Table 3. Values of parameters for applied adsorption isotherms and deviation of simulation results from experimental results for the adsorption of mercury chloride at 30 and 150℃.

Adsorption isotherm	Adsorption model	Simulation parameter values			Deviation of simulation results from experimental results	
		Parameters	30℃	150℃	30℃	150℃
Langmuir	$q = \frac{q_m k_L C}{1 + k_L C}$	q_m	3.300	8.623	5%	12%
		k_L	13.050	21.833		
Freundlich	$q = AC^n$	A	18.288	32.443	3%	4%
		n	0.247	1.200		

Furthermore, the adsorption results could be simulated with Freundlich isotherm. The parameter, n, could be used to determine whether the adsorption was favorable or unfavorable equilibrium. According to previous published literatures [19], the adsorptive capacity of activated carbon increased with the increase of adsorbate concentration ($n > 1$). The results indicated that the adsorption of activated carbon was unfavorable equilibrium to measure the maximum equilibrium adsorptive capacity. In addition, the adsorptive capacity of activated carbon could reach a constant as the adsorbate concentration increased continually ($n < 1$). As shown in Table 3, the parameter n was 0.247 (< 1) at the adsorption temperature of 30℃. While, the parameter n was 1.200 at the adsorption temperature of 150℃. The results suggested that the adsorption of $HgCl_2$ vapor onto SAC was favorable equilibrium at 30℃ and unfavorable equilibrium at 150℃, respectively. In comparison of experimental data with two common isotherms, Freundlich isotherm fitted the experimental results better than Langmuir isotherm.

CONCLUSIONS

This study investigated the adsorptive capacity of $HgCl_2$ vapor onto SAC via TGA analysis. Experimental results indicated that the adsorptive capacity of SAC decreased with the increase of the adsorption temperature. Furthermore, the results suggested that that the

adsorption of SAC on $HgCl_2$ vapor was favorable equilibrium at 30℃ and unfavorable equilibrium at 150℃. In comparison of the experimental data with isotherm equations, Freundlich isotherm fitted the experimental results better than Langmuir isotherm.

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