Adsorption of Inorganic Salt by Granular Activated Carbon and Related Prediction Models

Kai-Lin Hsu, Jie-Chung Lou and Jia-Yun Han

Abstract—In recent years, the underground water sources in southern Taiwan have become salinized because of saltwater intrusions. This study explores the adsorption characteristics of activated carbon on salinizing inorganic salts using isothermal adsorption experiments and provides a model analysis. The temperature range for the isothermal adsorption experiments ranged between 5 to 45 ℃, and the amount adsorbed varied between 28.21 to 33.87 mg/g. All experimental data of adsorption can be fitted to both the Langmuir and the Freundlich models. The thermodynamic parameters for per chlorate onto granular activated carbon were calculated as -0.99 to -1.11 kcal/mol for $\Delta G°$, -0.6 kcal/mol for $\Delta H°$, and 1.21 to 1.84 kcal/mol for $\Delta S°$. This shows that the adsorption process of granular activated carbon is spontaneously exothermic. The observation of adsorption behaviors under low ionic strength, low pH values, and low temperatures is beneficial to the adsorption removal of perchlorate with granular activated carbon.

Keywords—Water Treatment, Per Chlorate, Adsorption, Granular Activated Carbon

I. INTRODUCTION

GLOBAL warming and climate change in recent years has caused abnormal weather throughout the globe. For example, melting icebergs in Earth's polar regions caused sea levels to rise and substantial rainfall from typhoons and hurricanes resulted in saltwater intrusion in coastal areas, exposing underground water to the danger of salinization from seawater.

Granular activated carbon is made of multiple materials containing carbon; among them coal and coconut shells are the most common. The production of granular activated carbon is divided into two steps. The first step includes dehydration and carbonization. The second involves the activation of carbon through heating to the appropriate temperature (800 ℃ to 1000 °C) to burn away all degradable substances and create a richly porous structure with a large specific surface ratio, resulting in substantial adsorption capability. [1], [2] The adsorbent is a porous material with adsorptive capability that can adsorb one or multiple substances into a solid surface. The characteristics include large adsorption capacity, chemically stability, insolubility to water, nontoxic material, and a porous structure. [3] Adsorption is very effective in removing pollutants, which makes the development of adsorption methods the common goal for both industries and academics.

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Among the inorganic salts, perchlorates are a significant irritant that trigger coughing after inhalation by irritating the nose and the throat. Ingestion of excessive perchlorates through food or drink inhibit iodide uptake in the thyroid, [4] suppressing thyroxin secretion. The subsequent endocrine disorder can affect metabolism, resulting in deterioration of internal organs and thyroid cancer. Additionally, this may also irreversibly disrupt the mental development of babies exposed to even low thyroxin levels before birth. [5]

This study investigates the adsorption efficiency and mechanism of inorganic salts in water with commercially available activated carbon. We use granular activated carbon as an adsorbent and explore the reaction characteristics and factors influencing the adsorption of inorganic salts in water by granular activated carbon. To enhance understanding of adsorption reaction behavior, this study uses the adsorption model to simulate the adsorption reaction and interprets the adsorption reaction mechanism from a thermodynamic perspective.

II. MATERIALS AND METHODS

A. The models for isothermal adsorptions

At a given temperature, the relationship between the amount of adsorbate on the adsorbent surface and the concentration in gas or solution is called the adsorption isotherm. Freundlich was the first to propose an empirical formula describing the adsorption isotherm. Langmuir later proposed a hypothesis for monolayer molecular adsorption. The adsorption isotherm equations from Freundlich and Langmuir are described below [6], [7].

The Freundlich adsorption isotherm equation is an empirical formula, which assumes that different adsorption sites exist on the solid phase surface with different adsorption energy. This equation is often used on adsorption isotherms for adsorbents with an irregular surface or single solute systems within a specific concentration range. The Freundlich equation is expressed as follows (1).

$$q_e = K_F C_e^{\frac{1}{n}} \tag{1}$$

Where are
C_e: Concentration at adsorption equilibrium (mg/L)
q_e: Quantity adsorbed at adsorption equilibrium (mg/g)
K_F: Freundlich constant
n: Freundlich constant

The experimentally derived n value can help determine whether adsorption is favored. As shown in Fig. 1, n>1 is favorable to adsorption, whereas n=1 characterizes linear adsorption and n<1 describes situations unfavorable to adsorption.

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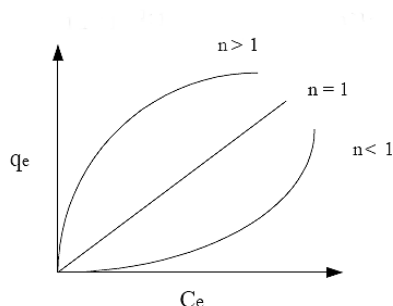Vol:6, No:5, 2012

Fig. 1 Freundlich equation of isotherm adsorption for various n value

For Langmuir adsorption isotherm model, [8], [9] in 1916, Langmuir proposed his model of isothermal adsorption, which was the first adsorption isotherm with a theoretical basis. This adsorption isotherm model is based on the following assumptions:

1. The Adsorbent is a uniform material.
2. The adsorption sites on the adsorbent surface are limited, and only one molecule may adsorb to a single site.
3. Only a monolayer is formed during adsorption. The maximum amount to be adsorbed on the surface is the saturation capacity.
4. Adsorbate molecules occupy separate sites on the adsorbent surface and do not interact with each other.
5. Adsorbed particles do not desorb.
6. Adsorbate molecules are equal in affinity.

According to Langmuir's theory, adsorption is a dynamic balance. The adsorption reaction achieves equilibrium when the adsorption rate equals the desorption rate. From the preceding assumptions and the thermodynamic principles, the Langmuir isotherm equation may be inferred as follows. The Langmuir isotherm adsorption curve may also be drawn as shown in Fig. 2.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

(2)

Where are
C_e: Equilibrium adsorbate concentration (mg/L)
Q_e: Adsorbed quantity at adsorption equilibrium (mg/g)
q_m: Adsorption capacity (mg/g)
K_L: Langmuir adsorption constant

B. The effect of temperature difference

The isothermal adsorption equilibrium experiment investigates the changes in the adsorption quantity of carbon nanotubes under different temperatures. Another aim of this experiment was to identify the related thermodynamic constants.

The experiment was conducted as follows:

1. A series of solutions with perchlorate and HNO_3 concentrations based on the experiment design were prepared and diluted to 1 L with deionized water.

2. 100 mL of each solution was poured into a series of 125 mL brown flasks, and adjusted to the desired pH with 0.1 M H_2SO_4 and 0.1 M NaOH.
3. 0.05 g of granular activated carbon was inserted into each flask. The brown flasks were placed in a temperature-controlled reciprocal shaker. The samples were shaken for 8 hr under 300 rpm (with reference to thermodynamic adsorption equilibrium time).
4. 20 mL of the solution was extracted and filtered through Advantec filter paper with 0.2-μm-sized pores. The remaining perchloric acid concentration was determined using ion chromatography.
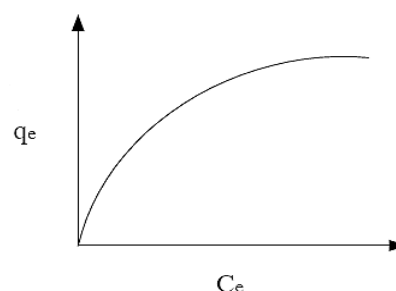

Fig. 2 Langmuir equation of isotherm adsorption

C. Steps for modeling simulation

This study uses the Kaleida Graph graphing software to analyze the experimental data and its fit to nonlinear regression simulation. After determining the best-fit solution, we use the parameters to predict the simulated adsorption reactions.
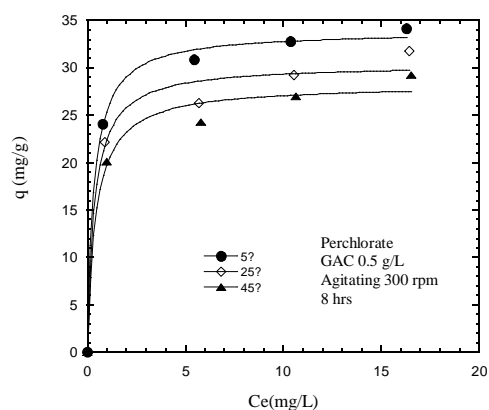
III. RESULTS AND DISCUSSION

A. The effects of temperature difference

To investigate the effects of temperature differences, a series of perchlorate solutions were prepared. Next, 0.5g/L of granular activated carbon was inserted into each sample. The pH value was controlled at 3.0±0.1 and the temperature was regulated at 5 ℃, 25 ℃, and 45 ℃. The experimental results were analyzed using Langmuir and Freundlich adsorption models. The adsorption isotherm for granular activated carbon on perchlorates is shown in Fig. 3. The parameters for the model simulation in Figure 3 are listed in Table 1.

The Langmuir model analysis showed that the maximum adsorption capacity gradually declines with increases in temperature. The maximum adsorption capacity (q_m) of perchlorate by granular activated carbon at 5 ℃, 25 ℃, and 45 ℃ was 33.87, 30.38, and 28.21 mg/g, respectively. The decreases of both the K_L and n values with increases in temperature indicate that the adsorption affinity is higher between perchlorate and granular activated carbon at lower temperatures.

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(a) Langmuir simulation results

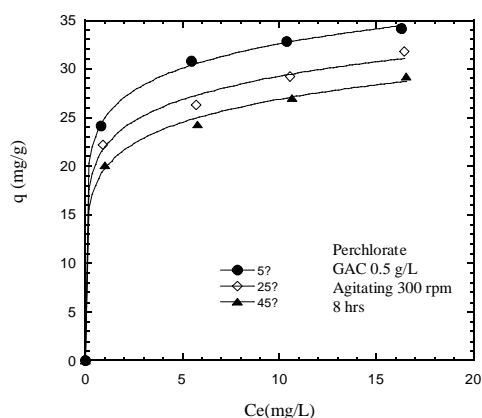

(b) Freundlich simulation results

Fig. 3 The adsorption isotherm for simulating two models of
perchlorates onto granular activated carbon

TABLE I
LANGMUIR AND FREUNDLICH PARAMETERS FOR PERCHLORATE ADSORPTION
BY GRANULAR ACTIVATED CARBON

Temp. (℃)	Langmuir Model			Freundlich Model		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
5	33.87	3.02	0.997	24.98	8.68	0.999
25	30.38	2.813	0.985	21.99	8.09	0.997
45	28.21	2.33	0.987	19.78	7.51	0.998

Regarding the Freundlich constant (K_F), the KF value also declines with increases in temperature. The q_m and KF values of these two commonly used adsorption isotherms are obviously correlated. We infer from the experimental data and adsorption isotherm curve that temperature increases may influence the characteristics of the adsorbent surface and accelerate desorption from the granular activated carbon surface, leading to reduced adsorption capacity. The R^2 value and the simulation curves reveal that the Langmuir and Freundlich isotherm are highly correlated, meaning that both these models are suitable for describing the adsorption behavior in this study.

B. The thermodynamics of adsorption

Below we present a calculation of thermodynamic constants, including the free energy change (ΔGo), the enthalpy change (ΔHo), and the entropy change (ΔSo). After K0 is derived, ln K0 and 1/T are graphed, as shown in Fig. 4 and table 2. Generally, the ΔGo values for physical adsorptions range between 0 and -4.7 kcal/mol, whereas chemical adsorptions range between -19 and -95 kcal/mol. [10]

The ΔG° values in this study range between -0.99 and -1.11kcal/mol, within the range of physical adsorption. Values of both ΔG° and ΔH° are negative, which indicates that the process of adsorbing perchlorate by granular activated carbon is spontaneously exothermic within 5 to 45 ℃.
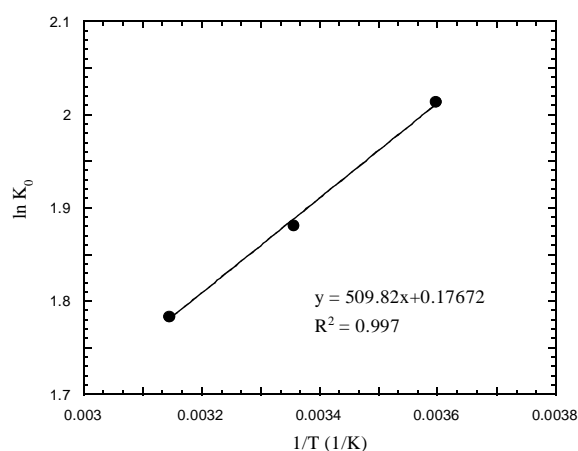

Fig. 4 The effect of ln K_0 at different temperature on perchlorate adsorption by granular activated carbons

IV. CONCLUSION

TABLE II
THE THERMODYNAMIC CONSTANTS FOR PERCHLORATE ADSORPTION BY
GRANULAR ACTIVATED CARBON

Temp. (℃)	K_0	ΔG° (kcal/mol)	ΔH° (kcal/mol)	ΔS° (cal/mol-k)
5	7.49	-1.11	-0.6	1.84
25	6.56	-1.04	-0.6	1.47
45	5.95	-0.99	-0.6	1.21

Both the Langmuir and Freundlich models are acceptable for describing the adsorption isotherm of perchlorate. The adsorption capacity and affinity increase with temperature reductions.

Perchlorate adsorption by granular activated carbon is facilitated under conditions of low ionic strength, low pH levels, and low temperatures.

The thermodynamic constant values reveal that the adsorption process of perchlorate by granular activated carbon is spontaneous and exothermic.

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