

Thermodynamic parameters of cadmium adsorption onto orange peel calculated from various methods: A comparison study



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ARTICLE INFO

Article history:

Received 3 March 2016

Received in revised form 6 May 2016

Accepted 7 May 2016

Available online 9 May 2016

Keywords:

Equilibrium constant

Thermodynamic parameters

Physical adsorption

Electrostatic attraction

Cadmium

Orange peel

ABSTRACT

Thermodynamic adsorption investigation plays a key role in estimating adsorptive mechanisms (i.e., physical or chemical). Accuracy estimation of the thermodynamic parameters is directly dependent on the equilibrium constant between two phases (K_C ; dimensionless). In this study, the thermodynamic parameters were calculated from the K_C constants derived from the adsorption isotherm constants (i.e., Langmuir, Freundlich, and Henry) and partition coefficient, with and without dimensionality consideration. Results showed that the optimal selection of K_C is strongly dependent on: the adsorption characteristics (i.e., Henry, Freundlich, and Langmuir) where equilibrium data are actually located; and the correlation coefficient of the van't Hoff equation. Both the Langmuir and Freundlich constants (dimensionless) are appropriate to calculate the thermodynamic parameters. The Langmuir constants from its four linear forms can be applied to calculate the thermodynamic parameters without significant difference. The Cd(II) biosorption process onto the orange peel (OP) occurred spontaneously ($-\Delta G^\circ$), in an exothermic nature ($-\Delta H^\circ$), and with increased randomness ($+\Delta S^\circ$). The biosorption process involved physical adsorption with minimal activation energy (E_a) and adsorption energy (E). The biosorption phenomenon reached fast equilibrium and reversibility. The negatively charged carboxylic groups ($-\text{COO}^-$) on the OP's surface play an important role (approximately 90%) in Cd^{2+} biosorption through electrostatic attractions (out-sphere complexes).

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1. Introduction

Isotherms, kinetics, and thermodynamics studies play an important role in thoroughly understanding the adsorption process of organic and inorganic compounds in water solutions. In the three studies, the thermodynamic adsorption is essential in consideration of the types and mechanisms of the adsorption process under variations of the solution temperature. The thermodynamics can effectively exhibit adsorption mechanisms through a series of the adsorptive equilibrium experiments under different temperatures and various initial adsorbate concentrations as well as fixed optimal conditions (i.e., pH of the solution, the adsorbent's particle size, ionic strength, and solid/liquid ratio). When the adsorption phenomenon reaches equilibrium, the thermodynamic parameters can be calculated. These parameters comprise the Gibbs energy change (ΔG°), the enthalpy change

(ΔH°), and the entropy change (ΔS°). It is noticeable that the estimation of ΔG° , ΔH° , and ΔS° is directly affected by the thermodynamic equilibrium constant (K_C ; dimensionless). In adsorption thermodynamics, the equilibrium constant K_C can derive from the constants of various adsorption isotherms (i.e., Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), Henry, Frumkin, Flory-Huggins, and Redlich-Petersone) or the partition coefficient. The different estimation approaches might lead to great variations in the thermodynamic parameters; therefore, the most appropriate approaches should be recommended.

Several researchers presented the thermodynamic parameters of adsorption phenomena by employing the equilibrium constants derived from the constants of various adsorption isotherms or the partition coefficient. For example, Lyubchik et al. [1] compared the thermodynamic parameters of the adsorption process of the metals from liquid phase on activated carbons, estimated from the various equilibrium constants derived from the constants of Henry, Langmuir, Freundlich, and BET isotherms. Roth et al. [2] applied the constants of Langmuir isotherm, distribution (the Henry's constant), and partition for computing the thermodynamic parameters of cadmium accumulation process onto different

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granulometric soil fractions. In addition, the comparison of the thermodynamic parameters of ammonium removal from an aqueous solution by using clinoptilolite was also investigated by Tosun [3]. These parameters were calculated based on the constants of the Langmuir and Tempkin models, and partition.

Unfortunately, the important role of dimensionality of the thermodynamic equilibrium constant K_C is often neglected. As a result, both sign and magnitude of the thermodynamic parameters— ΔG° , ΔH° , and ΔS° —usually indicate a confused representation. Noticeably, the Langmuir constant has been widely applied to compute of the thermodynamic parameters in the literature. However, there is a limitation in the comparison of the thermodynamic parameters derived from four linearized forms of the Langmuir model. Therefore, it is necessary to clarify the difference in estimation methods.

The objectives of this study are to (1) compare the thermodynamic parameters calculated from various equilibrium constants (K_C) that were derived from the isotherm constants of Langmuir, Freundlich, Henry, and the partition coefficient with and without considerations of the K_C dimensionality; and (2) consider the difference among the thermodynamic parameters calculated from the four linearized forms of the Langmuir model. In addition, dominate adsorption mechanisms were also discussed based on the thermodynamic parameters, adsorption rates, activation energy, adsorption energy, and reversibility.

2. Materials and methods

2.1. Biosorbent preparation

Orange peel (OP) was collected from a local market near Chung Yuan Christian University, Taiwan. The collected OP was then washed with water at least three times and with deionized distilled (DD) water to remove any adhering dirt and impurity. They were then placed in a drying oven at 85 °C for 24 h. The dried OP was sieved into particles ranging from 0.106 to 0.25 mm, which was used as a green biosorbent without any further treatment. The basic characteristics of orange peel (i.e., textural, physicochemical, ultimate, and proximate) are shown in Table 1. The surface chemistry of OP identified by using Fourier transform infrared spectroscopy (FTIR; FT/IR-6600 JASCO) and the pH value of OP at

Table 1
Basic characteristics of pristine orange peel.

	Orange peel
1. Textural parameters	
BET surface area (m ² /g)	19.01
Langmuir surface area (m ² /g)	23.83
Total pore volume (cm ³ /g)	0.021
2. Physicochemical properties	
Hardness (%)	39.7 ± 1.15
Bulk density (g/cm ³)	0.61 ± 0.05
pH _{1:20}	4.69 ± 0.18
pH _{pzc}	5.18 ± 0.07
3. Ultimate analysis	
C (wt%)	44.34
H (wt%)	5.91
N (wt%)	1.14
O (wt%) ^a	48.61
4. Proximate analysis	
Moisture (wt%)	8.54 ± 1.98
Total ash (wt%)	3.49 ± 0.99
Volatile (wt%)	74.34 ± 2.95
Fixed carbon (wt%) ^a	13.62 ± 2.18

^a Calculated by difference.

the point of zero charge (pH_{pzc}), are shown in Figs. S1 and S2, respectively. The results of FTIR indicated that the OP particles possess abundant carboxylic (–COOH) and phenolic (–OH) groups on their surface. The morphology and superficial element composition of OP before and after adsorption were also examined using scanning electron microscopy (SEM; JSM-7600F, JEOL) at 15 kV and energy dispersive X-ray spectroscopy (EDX), respectively.

2.2. Batch adsorption experiment

All Cd solutions were diluted from stock solutions of Cd (1,000 mg/L), which were prepared by dissolving cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O; Alfa Aesar) in DD water.

Experimental procedure followed our previous research [4]. Adsorption isotherm studies were conducted with five initial Cd²⁺ concentrations (i.e., 50, 100, 200, 400 and 600 mg/L) and in fixed other environmental parameters (i.e., an initial pH value of 7.0 ± 0.2 and a solid/liquid ratio of 0.1 g/50 mL). The flask containing the Cd–OP mixture was placed on a stirrer with hotplate (Corning PC-420D, Fisher Scientific) for 24 h with a rotating speed of 600 rpm under predetermined temperatures 20–50 °C (Fig. 1). After agitating 24 h, the mixture of solid and liquid was separated using glass fiber filters. The liquid was filtered through a 0.45-μm syringe filter. The Cd concentration in the solutions was determined using atomic absorption spectrometry (Avanta/AAS, GBC). The amount of Cd uptake at equilibrium, q_e (mg/g), was calculated using the mass balance equation, as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 (mg/L) is the initial Cd(II) concentration in the solution, C_e (mg/L) is the Cd(II) concentration in the solution at equilibrium, m (g) is the dried mass of used OP, and V (L) is the volume of the Cd(II) solution.

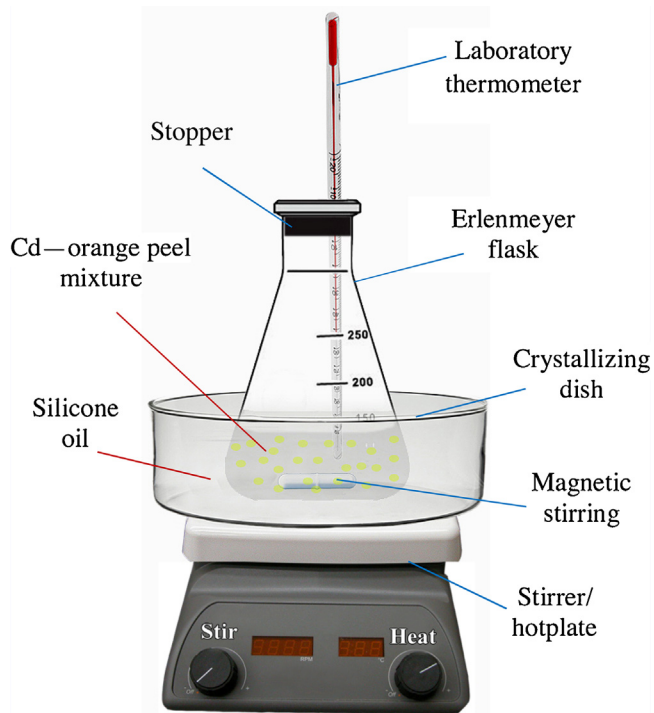


Fig. 1. Experimental set-up of adsorption process of Cd²⁺ ions onto orange peel. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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