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# Adsorption thermodynamic characteristics of *Chlorella vulgaris* with organic polymer adsorbent cationic starch: Effect of temperature on adsorption capacity and rate

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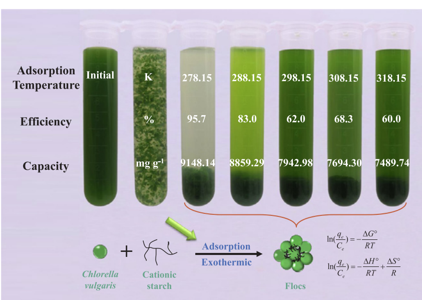
## GRAPHICAL ABSTRACT

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## ABSTRACT

Aiming at optimizing the adsorption process of *Chlorella vulgaris* and cationic starch, the adsorption thermodynamic characteristics were evaluated. Different from inorganic calcium salt adsorbent, the adsorption nature of organic polymer cationic starch is exothermic ($\Delta H^\circ < 0$) and spontaneous ($\Delta G^\circ < 0$). Besides, the adsorption capacity and rate can be well described by Langmiur isotherm and pseudo second kinetic models. As results of exothermic nature and great driving force of lower temperature, the adsorption capacity and rate declined with the rising temperature. The maximal values of them were obtained at 278.15 K, which were 9148.14 mg microalgae (g cationic starch)$^{-1}$ and $8.74 \times 10^{-6}$ mg g$^{-1}$ min$^{-1}$. Additionally, with insufficient adsorbent, the highest adsorption efficiency (96.37%) was achieved at 278.15 K for stirring 150 min. For 288.15, 298.15, 308.15 and 318.15 K, the adsorption efficiency decreased to 93.77%, 86.75%, 83.32% and 81.57% and the time consumed were at least 40 min longer.

## 1. Introduction

As one of the main reasons for global warming, global energy related carbon emissions grew 1.7% in 2018 and reached a historic high of 33.1 Gt (IEA, 2019). Due to the advantage of biomass accumulation for energy utilization, carbon biological fixation received much more attention (Sepehri & Sarrafzadeh, 2019). Among the carbon biological fixation methods, photosynthetic microorganism microalgae is promising as each acre microalgae can fix 3–5 times more $CO_2$ than the terrestrial plants (Liu et al., 2013; Sun et al., 2018). Simultaneously, microalgae can also mitigate the problem of energy shortage as the high lipid content of microalgae (Chen et al., 2018). Whereas, the

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microalgae biomass concentration cultivated under photoautotrophic condition is too low to direct utilize for oil extraction, which makes the microalgae harvesting process necessary before utilization (Christenson and Sims, 2011). Up to now, the high energy consumption of microalgae harvesting procedure (20–30% of the entire cost) impedes the microalgae commercialization process (Wei et al., 2017). Therefore, an efficient and low cost harvesting approach is necessary to reduce the cost of biofuel production.

Among the traditional microalgae harvesting methods of flotation, filtration, centrifugation and flocculation, flocculation is a comparative low cost method at large scale (Vandamme et al., 2013). As a derivative of natural starch, cationic starch has the advantages of both low cost and no poison to the microalgae later utilization (Vandamme et al., 2010). Earlier studies have researched the harvesting performance of cationic starch. Leteliergordo et al. (2014) used cationic starch (Greenfloc 120) to flocculate fresh water microalgae *Chlorella protothecoides* with harvesting efficiency of 98%. Peng et al. (2017) used cationic starch synthesized with different sources to harvest microalgae of *Chlorella pyrenoidosa* and *Botryococcus braunii* and the efficiency can be as high as 90–96%. These studies point out that cationic starch is an efficient floccuant that can harvest microalgae with high efficiency.

In the microalgae flocculation process with cationic starch, it began with the adsorption of microalgae cells by cationic starch and then the settlement of the flocs. Among the flocculation mechanisms of charge neutralization, bridging and sweep, charge neutralization and bridging are mainly related to the adsorption process. On the other hand, sweep is mainly in connection with the settlement process. Additionally, the flocculation influence coefficients of charge neutralization and bridging were about twice greater than the one of sweep (Li et al., 2006). Thus, it can be draw that the adsorption process was the main factor that influenced the final harvesting efficiency and the flocs settle time was mostly affected by the sedimentation process (Volesky, 2007). Additionally, temperature is one of the key factors that influence the adsorption reaction (Chen et al., 2015). Thus, for well understanding the adsorption process, it is indispensable to investigate the adsorption thermodynamic characteristics of microalgae cells with cationic starch. The adsorption thermodynamic characteristics includes the adsorption feasibility, capacity and rate and these indices can be represented by the parameters of thermodynamic, equilibrium and kinetic, respectively (Kothari et al., 2017).

The adsorption thermodynamic parameters are focus on evaluating the adsorption nature that the adsorption process of microalgae with cationic starch is physical or chemical, favorable or unfavorable (Wibowo et al., 2017). The changes in Gibbs free energy ($\Delta G^{\circ}$), entropy ($\Delta S^{\circ}$) and enthalpy ($\Delta H^{\circ}$) can also be determined based on the experiments of temperature dependent microalgae adsorption equilibrium. The $\Delta G^{\circ}$ shows the adsorption process is whether spontaneous process or not, the $\Delta H^{\circ}$ reveals the adsorption process endothermic or exothermic, the $\Delta S^{\circ}$ discloses the disorder degree of the adsorption (Wan Ngah and Hanafiah, 2008).

The equilibrium and kinetic parameters were concentrated on the determination of the adsorption capacity and rate of microalgae with cationic starch. The equilibrium parameters were determined by the adsorption isotherms which reflected the surface properties and affinity of the cationic starch in aqueous solutions (Ghaemi et al., 2011). There are many studies heading for describing adsorption isotherms, and Langmuir and Freundlich are two classical models that are very popular in liquid phase systems (Azizian et al., 2018). On the other hand, kinetic parameters were used to describe the interaction between cationic starch and microalgae cells under certain conditions, such as mixing intensity, time and temperature. The common kinetic model are pseudo first and pseudo second models that based on pseudo adsorption equilibrium capacity of the solid phase (Liu et al., 2016).

Various studies have conducted to evaluate the adsorption process using these models. Zheng et al. (2017) reported that the adsorption process of p-nitrophenols with microalgae biochars can be well depicted by pseudo second order and Freundlich model. Yin et al. (2018) directed the research of heavy metal Pb (II) adsorption by melamine modified metal–organic frameworks and reported that the nature of adsorption process was spontaneous and exothermic since the value of $\Delta G^{\circ}$ and $\Delta H^{\circ}$ were both negative. As for the adsorption of microalgae, Kothari et al. (2017) directed the research of *Chlorella* sp. adsorption with egg shell based adsorbent (calcium salt). They found that the microalgae adsorption nature with the inorganic calcium adsorbent was spontaneous and endothermic as the values of $\Delta G^{\circ}$ and $\Delta H^{\circ}$ were negative and positive, respectively. However, the sweet potato based cationic starch is different from egg shell which is mainly consist of calcium carbonate i.e. 95%. The great difference of surface properties between cationic starch and calcium carbonate will lead to a wide gap for the affinity of microalgae cells in suspension. Although lots of studies have researched the adsorption characteristics of many systems, the adsorption characteristics for particular field of microalgae harvesting is very few. As for the organic polymer adsorbents, no studies have been reported yet. Meanwhile, the evaluation of adsorption characteristics of microalgae with cationic starch hopefully provide the vision of the adsorption mechanism for further modifying and optimizing the adsorption process.

Hence, this study aims to explore the adsorption thermodynamics of microalgae with cationic starch. To fulfill this purpose, the effect of temperature, initial microalgae biomass concentration and cationic starch dosage were studied. Besides, Langmiur, Freundlich isotherm equation models and thermodynamic analysis were applied to study the microalgae adsorption process. Moreover, the pseudo first and second kinetic models were applied to analyze the adsorption of microalgae by cationic starch with various conditions of temperature, mixing time and intensity.

## 2. Materials and methods

### 2.1. Microalgae species and cationic starch preparation

The photoautotroph microalgae used in this study were freshwater *Chlorella vulgaris* (*C. vulgaris*) FACHB-31 that obtained from the Institute of Hydrobiology in Wuhan, Chinese Academy of Sciences. The medium of Blue-Green (BG11) (Wei et al., 2017) was used to sustain the grow of microalgae with 24 h illumination of 90 μmol $m^{-2} s^{-1}$, 0.1 vvm (5% $CO_2$ air gas volume per broth volume per min) bubbling and stable temperature of 298.15 ± 1 K. The microalgae were cultivated 8 days with the biomass concentration of 3.51 g $L^{-1}$, and the average growth rate was 0.44 g $L^{-1} d^{-1}$.

The preparation of cationic starch was depicted in previous study (Huang et al., 2018), which prepared the cationic starch with (3-chloro-2-hydroxypropyl) Trimethyl ammonium chloride (CHPTAC) as the cationic etherifying agent. Briefly, NaOH, CHPTAC (60% mass concentration) and deionized water were stirred for 10 min at 277.15 K. Then, the starch was added to the flask and mixed for 5 min, and then, the flask contained the mixture was put in the water bath for 4 h at 353.15 K. After that, the obtained cationic starch was washed with 80% ethanol and dried in a vacuum oven at 323.15 K for 6 h.

### 2.2. Adsorption thermodynamic characteristics of microalgae with cationic starch

#### 2.2.1. Adsorption equilibrium parameters of microalgae with cationic starch

The adsorption equilibrium parameters (i.e. adsorption isotherms) indicate the association between the adsorbed microalgae quantity and their corresponding concentration in the suspension with specific temperature. The adsorption isotherm denotes the cationic starch adsorption ability and it is helpful to illuminate the mechanism of the adsorption process. The models of Langmuir and Freundlich were used to analyze the adsorption of cationic starch. Langmuir model assumes that the adsorption is monolayer and there is no interaction among the microalgae cells (Yao et al., 2010). The Langmuir model represents as Eq. (1):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_l q_m} \tag{1}$$

where $C_e$ denotes the final equilibrium microalgae concentration ($mg\,L^{-1}$), $q_e$ represents the adsorbed microalgae biomass per gram cationic starch at final equilibrium ($mg\,g^{-1}$), $q_m$ represents the Langmuir parameter related to the greatest adsorption quantity of microalgae and $k_l$ represents the Langmuir parameter associated to the microalgae adsorption rate. $C_e$ and $q_e$ can be calculated as Eqs. (2) and (3)

$$C_e = C_i \frac{OD_f}{OD_i} \tag{2}$$

$$q_e = \frac{C_i(OD_i - OD_f) \times V}{OD_i \times m} = \frac{(C_i - C_e) \times V}{m} \tag{3}$$

where $C_i$ denotes initial microalgae biomass concentration ($mg\,L^{-1}$) abstained gravimetrically, $V$ denotes the suspension volume of the mixture of microalgae and cationic starch suspension (L), $m$ denotes the dry weight of cationic starch (g), $OD_i$ and $OD_f$ are the initial optical density ($OD$) of microalgae suspension and final mixture solution optical density of the microalgae and cationic starch at absorbance of 680 nm.

The Freundlich model could applied to depict both monolayer and multilayer adsorption as it's effective for heterogeneous surfaces (Zheng et al., 2017). The Freundlich model can be determined as Eq. (4):

$$\ln(q_e) = \frac{1}{\mathrm{n}} \ln(C_e) + \ln(k_f) \tag{4}$$

where n represents an indication of the adsorption favorability of cationic starch and $k_f$ denotes the adsorption capacity of microalgae with the cationic starch.

### 2.2.2. Adsorption thermodynamic parameters of microalgae with cationic starch

In order to understand the adsorption nature of microalgae with cationic starch better, the basic thermodynamic characteristics of enthalpy change, entropy change and Gibbs free energy change during the adsorption were calculated by Eqs. (5), and (6) (Barka et al., 2013):

$$\ln\left(\frac{q_e}{C_e}\right) = -\frac{\Delta G^\circ}{RT} \tag{5}$$

$$\ln\left(\frac{q_e}{C_e}\right) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

where $R$ is the gas constant ($8.314\,J\,K^{-1}\,mol^{-1}$) and $T$ is the microalgae adsorption temperature in Kelvin. The values of $\Delta H^\circ$ and $\Delta S^\circ$ can be attained from the slope and intercept of the plot of $\ln(q_e/c_e)$ as a function of $T^{-1}$.

### 2.2.3. Adsorption kinetic parameters of microalgae with cationic starch

The pseudo first and pseudo second kinetic models (Liu et al., 2016) based on pseudo adsorption equilibrium capacity of the solid phase were used to fit the evolution of the adsorbed mass of microalgae with cationic starch. The pseudo first kinetic model proposed by Lagergreen (Yuh-Shan, 2004) can be expressed as Eq. (7):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

where $k_1$ represent the adsorption rate constant of microalgae for pseudo first kinetic model ($g\,mg^{-1}\,min^{-1}$), $q_t$ is the adsorbed amount of microalgae biomass with per gram cationic starch at time $t$ ($mg\,g^{-1}$) and it was determined as:

$$q_t = \frac{C_i(OD_i - OD_t) \times V}{OD_i \times m} \tag{8}$$

where $OD_t$ is the mixture solution optical density measured at time t.

With the consideration of $q_t = 0$ when $t = 0$, the equation becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{9}$$

The pseudo second kinetic model proposed by Ho and McKay (Ho and McKay, 1998) can be expressed as Eqs. (10) and (11):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

$$\frac{\mathrm{t}}{q_t} = \frac{1}{k_2 q_e^2} + \frac{\mathrm{t}}{q_e} \tag{11}$$

where $k_2$ represents the adsorption rate constant of microalgae for pseudo second kinetic model ($g\,mg^{-1}\,min^{-1}$).

### 2.2.4. Adsorption experiment of microalgae with cationic starch

To obtain the thermodynamic characteristics parameters, the temperature dependent microalgae adsorption experiments with cationic starch were conducted in neutral condition. Initially, the prepared cationic starch was allowed to swell in 353.15 K hot deionized water with 300 revolutions per minute (rpm) stirring for half of an hour. After that, the cationic starch solution was cooled to 298.15 K and the value of pH was 8.21 due to the residual NaOH. The adsorption procedure of microalgae was directed with the addition of certain amount cationic starch solution into the microalgae suspension (pH value of 7.19) with various temperature (278.15 K–318.15 K) and initial biomass concentration ($350.63\,mg\,L^{-1}$–$3506.25\,mg\,L^{-1}$). After that, the mixture of microalgae and cationic starch was allowed to mix at 500 rpm for 20 min, during which the pH held at 7.28 steadily. And then, the mixture was allowed to settle down for 5 min. Then, 3.5 mL clarified supernatant were sampled to measure the $OD$ at absorbance of 680 nm by the UV-Visible spectrophotometer (T6 New century, Persee, China). The adsorption efficiency was determined as Eq. (12) (Huang et al., 2018):

$$AE = \frac{OD_i - OD_f}{OD_i} \tag{12}$$

The microalgae biomass concentration was measured gravimetrically. To be brief, 8 mL microalgae suspension after cultivation was sampled and centrifuged at 8000 rpm for 10 min and dried at 358.15 K to constant weight. The microalgae suspensions with different biomass concentration were attained by quantifiably adding the clarified supernatant of the centrifuged microalgae suspension or deionized water on the basis of the biomass concentration measured and then mixing the suspension well. The microalgae adsorption temperature was sustained by the thermostatic bath. The microalgae adsorption experiments were repeated twice to remove the single influence and the experiment data represented in the figures were the mean values with standard deviations.

## 3. Results and discussions

### 3.1. Effect of temperature on the adsorption efficiency and capacity of microalgae with cationic starch

The adsorption efficiency of *C. vulgaris* with cationic starch over variable temperature (278.15, 288.15, 298.15, 308.15 and 318.15 K) were investigated to get more critical findings about thermodynamic characteristics of the adsorption process (Fig. 1a). As indicated, with insufficient cationic starch added to the microalgae suspension (the dry weight ratio of cationic starch to microalgae was 1:10.13), the highest adsorption efficiency was achieved (96.37%) at the temperature of 278.15 K for stirring 150 min with the speed of 500 rpm. When the

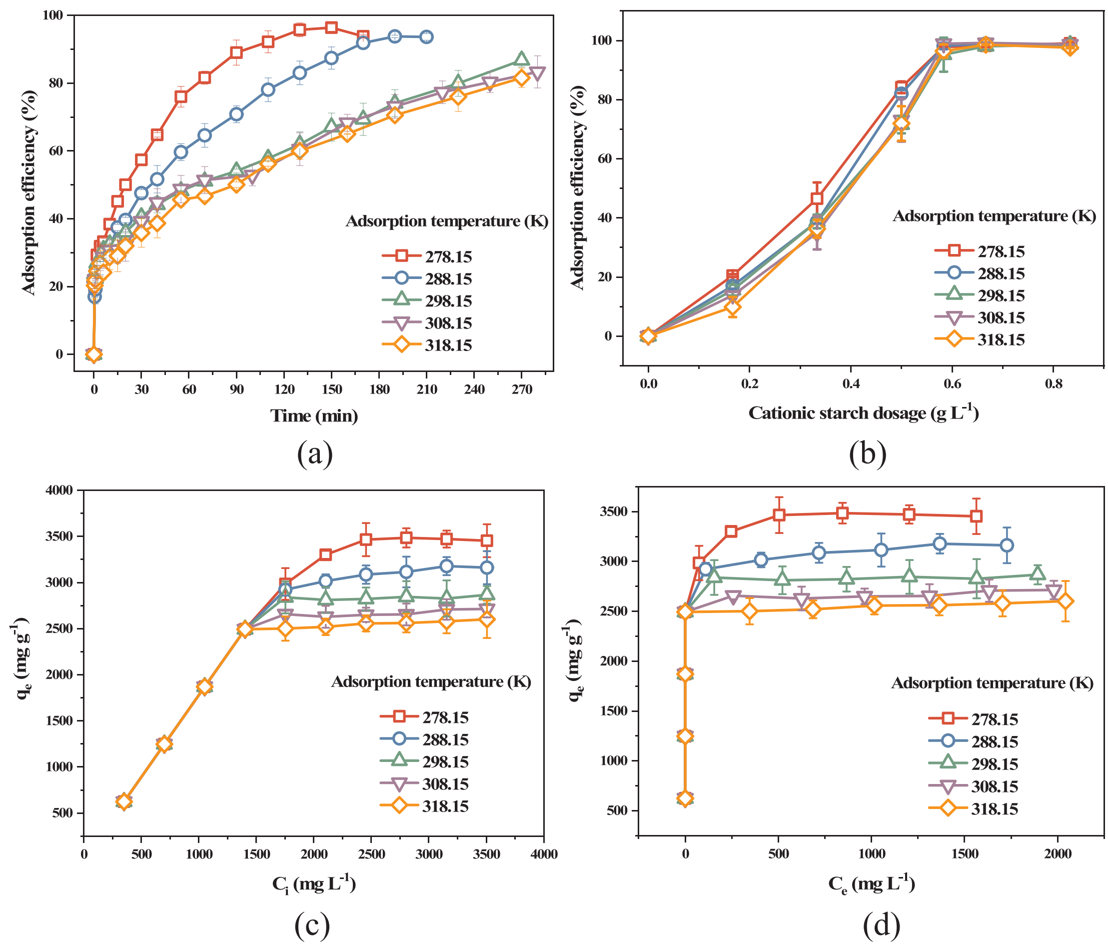


**Fig. 1.** The adsorption efficiency of microalgae by cationic starch with variable time (a) and cationic starch dosage (b) at different temperature; The equilibrium adsorption biomass with various initial microalgae concentration (c) and final microalgae concentration (d) at different temperature.

temperature rose to 288.15 K, the adsorption efficiency of cationic starch decreased to 93.77% and the time consumed was 40 min longer than the one of 278.15 K. As for 298.15, 308.15 and 318.15 K, the adsorption efficiency was 86.75%, 83.32% and 81.57%, respectively. Besides, the time needed to achieve the highest adsorption efficiency were much longer. In addition, the disparities of adsorption performance among 298.15, 308.15 and 318.15 K were little. It could be decided that cationic starch presented a better adsorption performance at lower temperature and cool water would be conducive for the adsorption of *C. vulgaris* with cationic starch. This meant that the adsorption of *C. vulgaris* with cationic starch was exothermic (You et al., 2009) and the following thermodynamic parameters part would give the reason.

When the mixing time was fixed to 20 min (Fig. 1b), similar results could be reached that the microalgae adsorption efficiency of cationic starch decreased with rising temperature and the disparities of 298.15, 308.15 and 318.15 K were little. These findings was in keeping with the studies directed by You et al. (2009) and Mpofu et al. (2004) that used bio-adsorbents to harvest microalgae and kaolinite, respectively. Thus, temperature is important to enhance the adsorption capacity and rate of cationic starch and the winter season would benefit the adsorption process for the low temperature.

In order to explore the microalgae adsorption properties of cationic starch and evaluate the effect of adsorption temperature, microalgae adsorption experiments by quantitative cationic starch with different initial biomass concentration (350.63–3506.25 mg $L^{-1}$) and temperature (278.15–318.15 K) were conducted (Fig. 1c). Apparently, when the initial biomass concentration was low (0–1402.5 mg $L^{-1}$), the add cationic starch was excess. The $q_e$ were the same for all of the adsorption temperature and it increased linearly with the increasing biomass concentration. When the initial biomass concentration was above 1402.5 mg $L^{-1}$, the gap of $q_e$ with various adsorption temperature appeared and enlarged with the increasing biomass concentration. In addition, the equilibrium adsorption capacity of high temperature always found the balance before the low temperature did. This meant that the $q_e$ of higher temperature would find the balance earlier. Moreover, the corresponding $q_e$ values decreased from 3484.99 to 2601.64 mg $g^{-1}$ with the temperature rising from 278.15 to 318.15 K, which suggested that the adsorption capacity of cationic starch at low temperature was greater than that at high temperature. The drop of $q_e$ with rising temperature might reveal the exothermic nature of organic polymer cationic starch, which was different from inorganic calcium salt adsorbent and it will be verified in the part of thermodynamic parameters. Fig. 1 (d) was the corresponding equilibrium biomass concentration of the microalgae suspension after mixing for 20 min and it can directly point out that there were no microalgae left in the suspension when the initial biomass concentration was lower than 1402.5 mg $L^{-1}$.

### 3.2. Adsorption equilibrium parameters of microalgae with cationic starch

The microalgae adsorption isotherm experiments data of Fig. 1 (c and d) were applied to the linear form of two classical empirical models Langmiur and Freundlich isotherm (Fig. 2). It was obvious that the linearity of empirical Langmuir isotherm model (Fig. 2a) was much greater than that of Freundlich isotherm model, which suggested that

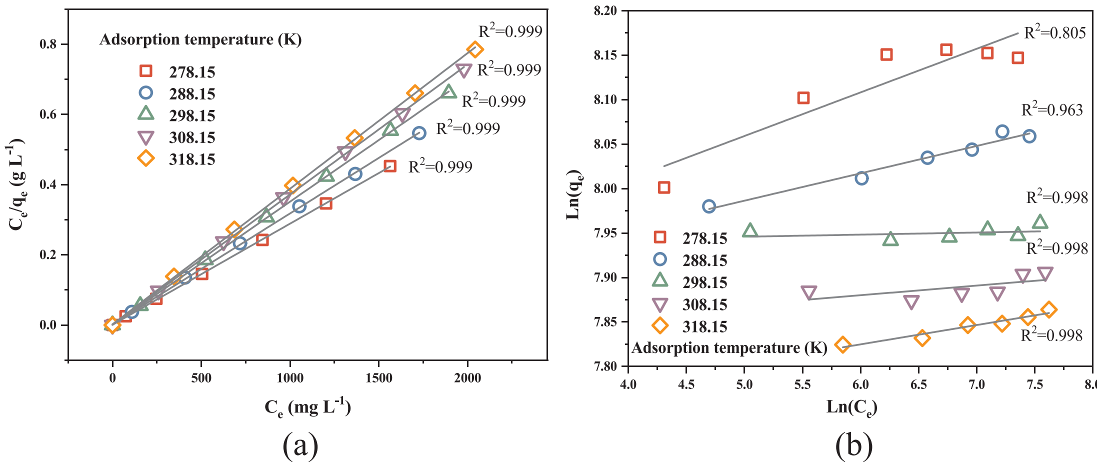


**Fig. 2.** The *C. vulgaris* adsorption isotherms fitting of linear Langmuir model (a) and Freundlich model (b) with cationic starch at different temperature.

**Table 1**
Langmuir and Freundlich isotherm model constants for the adsorption of microalgae with cationic starch.

| Adsorption temperature | Langmuir model | | | Freundlich model | | |
|---|---|---|---|---|---|---|
| | $q_m$ | $k_l$ | $R^2$ | n | $k_f$ | $R^2$ |
| (K) | (mg g$^{-1}$) | (L mg$^{-1}$) | | | (mg g$^{-1}$) | |
| 278.15 | 3470.46 | 0.507 | 0.999 | 20.38 | 2474.59 | 0.805 |
| 288.15 | 3162.57 | 0.342 | 0.998 | 32.48 | 2521.17 | 0.963 |
| 298.15 | 2849.84 | 0.208 | 0.999 | 421.94 | 2790.73 | 0.126 |
| 308.15 | 2700.21 | 0.188 | 0.998 | 92.34 | 2477.74 | 0.254 |
| 318.15 | 2588.43 | 0.177 | 0.999 | 46.04 | 2196.28 | 0.934 |

$q_m$: The Langmuir constant related to the maximum adsorption capacity.
$k_l$: The Langmuir constant related to the rate of adsorption.
$R^2$: Determination coefficients.
n: The Freundlich isotherm constant related to the degree of system heterogeneity.
$k_f$: The Freundlich isotherm constant related to the rate of adsorption.

Langmuir model provided a much better fitting with the adsorption performance of cationic starch. The regression analysis of the linear form of Langmuir isotherm (Fig. 2a) and Freundlich isotherm (Fig. 2b) by the slope and the intercept gave the adsorption constants of $q_m$, $k_1$, n, $k_f$ and correlation coefficients ($R^2$). The fitting constants of the Langmuir and Freundlich isotherm with variable temperature were shown in Table 1. On the basis of $R^2$, the Langmuir model were the uppermost which were higher than 0.998 for all of the adsorption temperature and the $R^2$ of the Freundlich model fluctuated widely from 0.126 to 0.963. Hence, compared with Freundlich model, Langmuir model was best choice for describing the microalgae adsorption with cationic starch. Additionally, the Langmuir constants of $q_m$ declined from 3470.46 to 2588.43 mg g$^{-1}$ when the temperature increased from 278.15 to 318.15 K. Similarly, The Langmuir constants $k_l$ decreased from 0.51 to 0.18 L mg$^{-1}$ with the rising temperature from 278.15 to 318.15 K. It was obvious that the value of both $q_m$ and $k_l$ declined with the growing adsorption temperature which suggested that both of the adsorption capacity and rate of the cationic starch would decrease with the growing temperature and these results were coincident well with that of Fig. 1. And the underlying reason might be the intense molecular thermal motion at high temperature strongly impeded the microalgae adsorption with cationic starch.

### *3.3. Adsorption thermodynamic parameters of microalgae with cationic starch*

Thermodynamic parameters are benefit to explore the adsorption

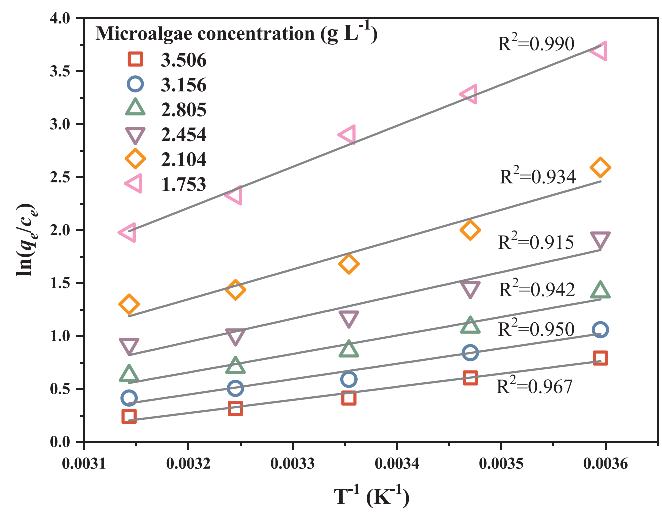


**Fig. 3.** The linear dependence of $\ln(q_e/c_e)$ on $T^{-1}$ based on the adsorption thermodynamic at different temperature.

process as they can directly characterize the reaction as a spontaneous process or not by the value of $\Delta G^{\circ}$ (Wan Ngah & Hanafiah, 2008). The plot of $\ln(q_e/c_e)$ as a function of $T^{-1}$ was shown in Fig. 3 and it suggested that the fitness of the microalgae adsorption experiment data with cationic starch at various initial biomass concentration in linear model were all great. The values of $\Delta H^{\circ}$ and $\Delta S^{\circ}$ can be attained from the slope and intercept of the straight lines and the corresponding thermodynamic parameters were shown in Table 2. The experiment data showed that the $\Delta G^{\circ}$ values were negative at all conditions which proved the thermodynamic feasibility and spontaneity of the *C. vulgaris* adsorption with cationic starch. When the initial biomass concentration was fixed, lower temperature conducted larger $\Delta G^{\circ}$ negative values and it indicated that greater adsorption driving power was generated at low temperature. This would give the reason why the microalgae adsorption time needed with low temperature was shorter than that of high temperature as the driving force at low temperature was greater. In addition, when the adsorption temperature was fixed, higher $\Delta G^{\circ}$ negative values were reached at lower initial microalgae biomass concentration and the result was in agreement with the work carried out by Nuhoglu and Malkoc's report (2009). The reason behind this phenomenon might be related to the insufficient cationic starch since the initial biomass concentration was all above 1402.5 mg L$^{-1}$.

The exothermic nature of the microalgae adsorption process with cationic starch was further illustrated by negative values of $\Delta H^{\circ}$, which were all less than 40 kJ mol$^{-1}$. In addition, the information about the

**Table 2**
The thermodynamic parameters for the adsorption of microalgae with cationic starch.

| Initial biomass concentration | T = 278.15 K | 288.15 K | 298.15 K | 308.15 K | 318.15 K | ΔH° | ΔS° | $R^2$ |
|---|---|---|---|---|---|---|---|---|
| ($g\ L^{-1}$) | ΔG° ($kJ\ mol^{-1}$) | | | | | ($kJ\ mol^{-1}$) | ($kJ\ mol^{-1}\cdot K^{-1}$) | |
| 3.506 | −1.76 | −1.46 | −1.15 | −0.84 | −0.54 | −10.30 | −0.031 | 0.967 |
| 3.156 | −2.36 | −2.02 | −1.67 | −1.32 | −0.97 | −12.07 | −0.035 | 0.950 |
| 2.805 | −3.12 | −2.71 | −2.30 | −1.89 | −1.48 | −14.52 | −0.041 | 0.943 |
| 2.454 | −4.19 | −3.69 | −3.18 | −2.68 | −2.17 | −18.25 | −0.051 | 0.915 |
| 2.104 | −5.69 | −5.05 | −4.41 | −3.78 | −3.14 | –23.40 | −0.064 | 0.934 |
| 1.753 | −8.65 | −7.81 | −6.96 | −6.11 | −5.27 | –32.21 | −0.085 | 0.990 |

ΔG°: The free energy change during the adsorption process.
ΔH°: The enthalpy change during the adsorption process.
ΔS°: The entropy change during the adsorption process.
$R^2$: Determination coefficients.

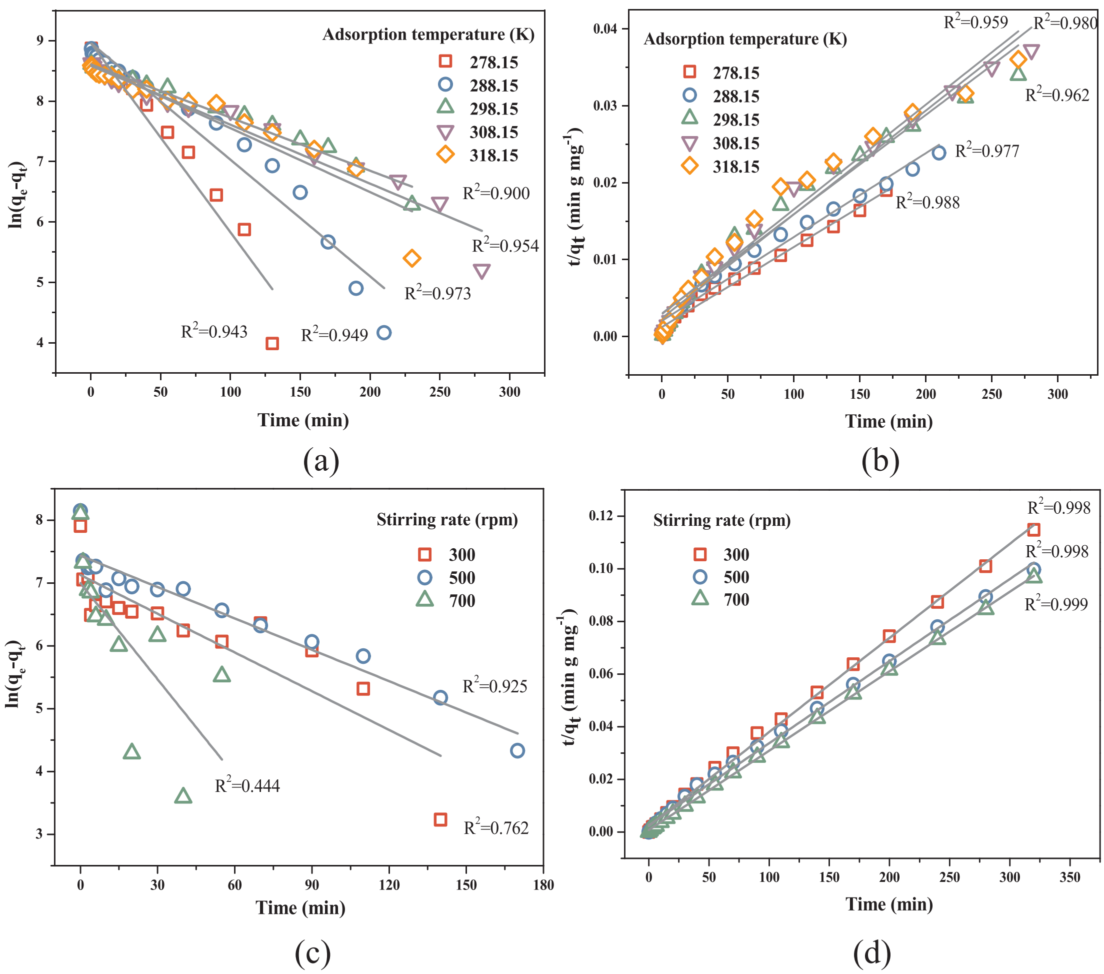


**Fig. 4.** The *C. vulgaris* adsorption kinetic fitting of linear pseudo first (a) and pseudo second (b) models at different temperature with 500 rpm stirring rate; and fitting of linear pseudo first (c) and pseudo second (d) models at 298.15 K with different stirring rate.

forces related to the adsorption process was available from the magnitude of ΔH°. According to Kumar and Barakat (2013), the energy associated with physical forces was usually less than 40 $kJ\ mol^{-1}$ and it was greater than 60 $kJ\ mol^{-1}$ for chemical forces. For the adsorption of microalgae with cationic starch, the driving forces was physical forces since the ΔH° values were all less than 40 $kJ\ mol^{-1}$. As for ΔS°, the negative value revealed that there was a decrease in randomness at the surface and the decrease was no significant as the values were small (Nuhoglu & Malkoc, 2009). Additionally, the negative values of the ΔG°, ΔH° and ΔS° were also reported by other studies such as methyl orange adsorption with chitosan-$Al_2O_3$-magnetite nanoparticles (Tanhaei et al., 2015) and adsorption of heavy metal Pb (II) with melamine modified metal–organic frameworks (Yin et al., 2018). Moreover, both of the two organic adsorbent were exothermic and physical adsorption as the values of ΔH° of the two adsorbents were −11.99 and −10.69 $kJ\ mol^{-1}\ K^{-1}$, respectively.

### 3.4. Adsorption kinetic parameters of microalgae with cationic starch

The adsorption kinetics will reflect the microalgae adsorption rate

**Table 3**
Adsorption kinetic parameters of microalgae with cationic starch obtained using Pseudo firs order and Pseudo second order models.

| Adsorption temperature | Adsorption efficiency | $q_e$ | Pseudo first order | | | Pseudo second order | | |
|---|---|---|---|---|---|---|---|---|
| | | | $k_1$ | $q_{e,cal1}$ | $R^2$ | $k_2$ | $q_{e,cal2}$ | $R^2$ |
| (K) | % | (mg $g^{-1}$) | ($\times 10^{-2}$ mg $g^{-1}$ $min^{-1}$) | (mg $g^{-1}$) | | ($\times 10^{-6}$ mg $g^{-1}$ $min^{-1}$) | (mg $g^{-1}$) | |
| 278.15 | 96.37 | 9148.14 | 3.14 | 7839.34 | 0.943 | 8.74 | 9607.44 | 0.988 |
| 288.15 | 95.49 | 8859.29 | 1.93 | 7806.95 | 0.949 | 5.83 | 9170.53 | 0.977 |
| 298.15 | 86.76 | 7942.98 | 0.88 | 5464.51 | 0.972 | 5.54 | 7444.31 | 0.962 |
| 308.15 | 83.35 | 7694.30 | 0.98 | 5359.04 | 0.953 | 7.59 | 7408.83 | 0.980 |
| 318.15 | 81.57 | 7489.74 | 1.09 | 5497.18 | 0.900 | 6.36 | 7340.58 | 0.959 |

$q_e$: The amount of biomass adsorbed at equilibrium (mg $g^{-1}$).
$k$: The rate constant (g $mg^{-1}$ $min^{-1}$).
$q_{e,cal}$: The calculated amount of biomass adsorbed at equilibrium (mg $g^{-1}$).
$R^2$: Determination coefficients.

which in turn regulate the equilibrium time (Dundar et al., 2008). To better study the adsorption rate of cationic starch, pseudo first and second models were used to analyze the adsorbed microalgae biomass with cationic starch at different temperature (Fig. 1a) and the results were shown in Fig. 4(a and b) and Table 3. As can be seen in Fig. 4(a and b), both of the plots shown were linear. However, the $R^2$ of the pseudo second model was larger than the pseudo first model and the $q_{e,cal2}$ was more approximate to the value of $q_e$ than $q_{e,cal1}$. All of these results indicated that the pseudo second kinetic model proved a better suitability for describing the microalgae adsorption process with cationic starch than the pseudo first kinetic model (Ngah & Fatinathan, 2010). The values of $q_e$ and $k_2$ can be attained from the slope and the intercept of the lines, and they were listed in Table 3 for different adsorption temperature. The experiment data shows that $q_e$ and $k$ decreased with the increased temperature, which meant that both of the cationic starch adsorption potential and adsorption rate were less favorable at high temperature. The results agreed well with the uptake results of exothermic nature of the microalgae adsorption process with cationic starch. The maximal adsorption biomass and adsorption rate of cationic starch was obtained at 278.15 K and the values were 9148.14 mg $g^{-1}$ and $8.74 \times 10^{-6}$ mg $g^{-1}$ $min^{-1}$, respectively. The corresponding pseudo second kinetic model equation of microalgae adsorption with cationic starch at 278.15 K was show as follow:

$$q_t = \frac{9607.44\times t}{11.91+t} \tag{13}$$

To further confirm the fitness of pseudo second kinetic model, microalgae harvesting experiments were directed with different stirring rate (300, 500 and 700 rpm) at common room temperature 298.15 K (Fig. 4c and d). The results show that the fitting curves of the pseudo second model were more significant linear regression than the pseudo first model. And the high $R^2$ values (> 0.998) of the pseudo second model supported the adsorption model. Summing up the above, the pseudo second kinetic model can well evaluate the adsorption kinetics of the organic polymer adsorbent cationic starch.

## 4. Conclusions

The adsorption thermodynamic characteristics of *C. vulgaris* with organic polymer adsorbent cationic starch have been investigated based on the temperature dependent equilibrium and kinetic experiments. The microalgae adsorption thermodynamic characteristics fitted well with the Langmuir adsorption isotherm and pseudo second kinetic model. The adsorption process was spontaneous and showed exothermic nature. In addition, cationic starch had better adsorption performance at lower temperature for both of the adsorption efficiency and mixing time needed. This work confirmed that cationic starch flocculation technology provides a great potential for harvesting microalgae with high capacity and rate.

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