Int. J. Electrochem. Sci., 13 **(2018)** 3935 – 3947, doi: 10.20964/2018.04.62

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Adsorption and Kinetics Properties of TiO_2 photoelecrode using Natural Paprika Oleoresin (*Capsicum annuum L.*) Dye for Dye-Sensitized Solar Cells

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Received: 14 January 2016 / *Accepted:* 11 April 2016 / *Published:* 6 March 2018

The adsorption characteristics of paprika oleoresin (*Capsicum annuum L.*) on TiO_2 thin film for a dye-sensitized solar cell (DSSC) were investigated in terms of temperature. The maximum adsorption amount of paprika oleoresin on TiO_2 thin film was approximately 142 mg/g. The adsorption heterogeneity for the adsorption system of paprika oleoresin on TiO_2 thin film increased with increasing temperature. Kinetic studies showed that the adsorption of paprika oleoresin on TiO_2 thin film followed pseudo-first-order model. The energy conversion efficiency of the TiO_2 electrode with successive adsorptions of paprika oleoresin natural dye was about 0.14%.

Keywords: Adsorption, Dye, Heterogeneity, Kinetics, paprika oleoresin

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) are attracting widespread research areas and commercial interests due to low-cost harvest of solar energy using sustainable and environmentally friendly materials [1]. DSSCs consist of a TiO_2 electrode adsorbed dye, an electrolyte solution, and a platinum counter electrode. Among those, the TiO_2 electrode plays important roles in relation to the loading dyes and in separating and transporting electrons [2,3].

Paprika oleoresin has recently been commercialized and has one of the highest carotenoid pigment concentrations of products derived from natural sources. It is oil with a high amount of carotenoids, commonly used in the food industry as a colorant for sauces, soups, or meat-based meals [4]. Carotenoids are light-harvesting pigments and have important roles in photosynthesis protection [5]. Carotenoid pigments complement chlorophylls through redox reactions. The raw natural dyes are better than those of purified or commercial analogs because of the presence of natural extracts, such as alcohols and organic acids, which assist dye adsorption, prevent electrolyte recombination, and decrease dye accumulation. Hemalatha et al. reported that the conversion efficiency of the *Kerria japonica* carotenoid dye is 0.22% [6]. Carotenoids are compounds consisting of eight isoprenoid units that are wide spread in nature, and have great potential as energy harvesters and sensitizers for DSSCs [7]. Unfortunately, studies on the adsorption properties of natural dye for a dye-sensitized solar cell have so far been very limited**.** In this study, to compare adsorption amounts of paprika oleoresin red color on TiO_2 thin film and activated carbon adsorbent carry out adsorption equilibrium test. The adsorption kinetic data were obtained in a small adsorption chamber and analyzed by proposed models. Also, the energy conversion efficiency (η) of the DSSC using paprika oleoresin red color and N719 was investigated.

2. MATERIALS AND METHODS

2.1. Materials

Paprika oleoresin (*Capsicum annuum L.*) was purchased from MSC Co., LTC (Korea). Paprika oleoresin (also known as paprika extract) is an oil-soluble extract from the fruits of *Capsicum annuum* and is primarily used as a dye. It is composed of capsaicin, the main flavouring compound giving pungency in higher concentrations, and capsanthin and capsorubin, the main colouring compounds among other carotenoids [7]. Activated carbon (F400) was manufactured by Calgon Co. (USA). Particle sizes of the activated carbon was 0.55-0.65 mm, and boiling in deionized water for 2 h, and dried in an oven at 393 K during 24 h. Acetonitrile, used as a solvent agent, was purchased from Merk Co. (Germany). All other chemical reagents used were of analytical grade. A fluorine-doped tin dioxide conducting glass (FTO, Pilkington, TEC-8, 80% transmittance in the visible range) with a size of 3×3 cm^2 was first cleaned in a detergent solution for 15 min using an ultrasonic bath, and then rinsed with water and ethanol, and finally dried in an oven at 373 K for 1 h. A mask, with an open area of 2×2 cm^2 was placed on the FTO glass for photoelectrode deposition. TiO_2 paste (DSL 18NR-T, Dyesol) was placed in the mask opening using the squeeze printing technique, followed by annealing at 723 K for 30 min. TiO_2 film of approximately 10 μ-thick with a size of 4 cm^2 was deposited on the FTO glass substrate. The purpose of measuring the samples before and after the deposition of the TiO_2 thin film is to evaluate the weight of the TiO_2 thin film deposited on each photoelectrode before starting the dye adsorption experiment.

2.2. Measurements

Paprika oleoresin solution was dissolved in acetonitrile to the required concentration (10, 25, 50, 100, 200 mg/L). For the adsorption equilibrium experiments, TiO_2 thin film and the dye solutions (20 cm^3) were placed in a 50 cm^3 flask and shaken for 1 day in a shaking incubator at different temperature (288, 298, 308 K). In case of the activated carbon, paprika oleoresin solution (200 mg/L, 200 cm^3) and activated carbon (0.001-0.5 g) were placed in a 300 cm^3 flask and shaken for 1 day in a shaking incubator at 298 K. After reaching the equilibrium state, the samples were filtered through a Whatman glass microfilter. The concentration of the separated solutions was carefully measured using UV-VIS spectrophotometry (UV-1601, Shimadzu) at 415 nm. The amount of adsorption at equilibrium, q_e (mg/g), was obtained as follows:

$$q_e = (c_i - c_e)\, V / W \quad (1)$$

Here, q_e is the equilibrium amount of adsorbed the dyes on the TiO_2 thin film (mg/g), c_i and c_e are the initial and equilibrium concentrations of the dyes (mg/L), respectively, V is the solution volume of the dyes (L), and W is the weight of the TiO_2 thin film and activated carbon (g).

Adsorption kinetic experiments of paprika oleoresin on TiO_2 thin film were conducted for a 200 mg/L concentration of paprika oleoresin. The adsorption amounts of paprika oleoresin on TiO_2 thin film were determined by measuring paprika oleoresin concentrations using a UV spectrophotometer at 415 nm. The photovoltaic properties were investigated by measuring the I-V characteristics under irradiation of white light from a 200W Xenon lamp (McScience, Korea). The incident light intensity and the active cell area were both measured at 100 $mWcm^{-2}$.

3. RESULTS AND DISCUSSION

3.1. Adsorption equilibrium

To calculate the adsorption parameter such as maximum adsorption capacity of paprika oleoresin on TiO_2 thin film, The Langmuir adsorption isotherm model was used. The linearized form of the Langmuir equation is represented as:

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \quad (2)$$

where c_e is the supernatant concentration of paprika oleoresin at equilibrium (mg/L), b is the Langmuir affinity constant (L/mg), and q_m is the maximum adsorption capacity of paprika oleoresin on TiO_2 thin film (mg/g).

The Freundlich isotherm equation was considered to describe the exponential distribution of the active centers, which are the characteristics of the heterogeneous surface and indefinite surface coverage. The equation is represented as

$$q = k\, c_e^{1/n} \tag{3}$$

The linearized form of the equation is

$$\log q = \frac{1}{n} \log c_e + \log k \tag{4}$$

where k is the Freundlich constant related to the adsorption capacity and *1/n* is the adsorption intensity. The value of *1/n* less than 1 indicates favorable adsorption.

The Langmuir and Freundlich adsorption isotherm models were used to correlate our experimental equilibrium data. To find the parameters for the Langmuir and Freundlich adsorption isotherm, the linear least square method and a pattern search algorithm were used. The value of the mean percentage error has been used as a test criterion for the fit of the correlations. The mean percentage deviation between the experimental and predicted values was obtained using equation 5.

$$error(\%) = \frac{100}{N} \sum_{k=1}^{N} \left[\frac{\left| q_{\exp,k} - q_{cal.k} \right|}{q_{\exp,k}} \right] \tag{5}$$

where $q_{cal,\,k}$ is each value of q predicted by the fitted model, $q_{exp,\,k}$ is each value of q measured experimentally and N is the number of experiments performed. The parameters and average percentage differences between the measured and calculated values for the adsorption of paprika oleoresin on TiO_2 thin film in terms of temperature are given in Table 1. Table 1 shows the Langmuir equation gave the best fit of our data.

Table 1. Adsorption equilibrium constants of paprika oleoresin on TiO_2 thin film.

Isotherm type	Parameters	Temperature		
		288 K	298 K	308 K
Langmuir	q_m	2.24	58.24	141.94
	b	0.049	0.057	0.023
	error(%)	3.28	4.73	2.49
Freundlich	k	2.907	9.137	12.92
	n	2.654	2.642	2.31
	error(%)	7.018	8.783	8.730

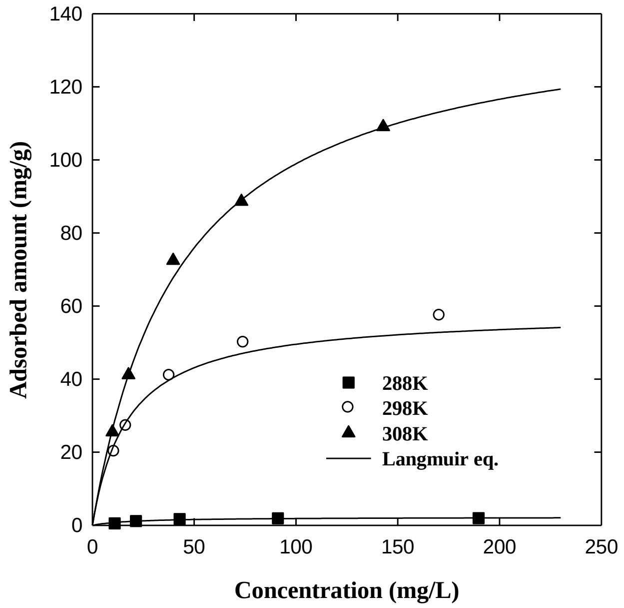

Figure 1. Adsorption equilibrium isotherms of paprika oleoresin on TiO_2 thin film at different temperatures.

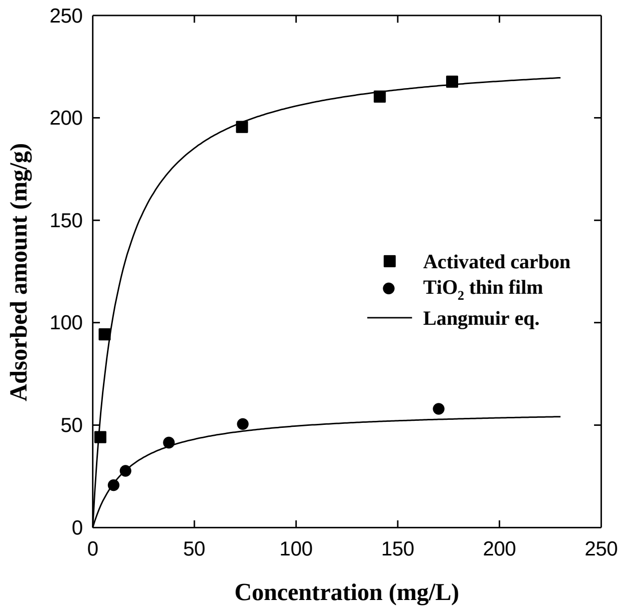

Figure 2. Adsorption isotherms of paprika oleoresin on TiO_2 thin film and activated carbon at 298 K.

Temperature is an important parameter in the adsorption process. All experiments were carried out with optimized parameters at natural pH. Fig. 1 shows the adsorption capacities of the paprika oleoresin on TiO_2 thin film at different temperatures. The amounts of paprika oleoresin adsorbed on TiO_2 thin film increased with increasing solution temperature. This phenomenon suggests that the adsorption of dyes onto vermiculite was an endothermic process [8-10]. Kim and Park [11, 12] studied the adsorption of natural dyes on TiO_2 thin film, and found the adsorption increased with increasing temperature. Fig. 2 shows the adsorption amount of paprika oleoresin on TiO_2 thin film and activated carbon at 298 K. The adsorption capacity of paprika oleoresin on activated carbon was greater than that on the TiO_2 thin film [13]. This result is because activated carbon has highly porous materials and large surface areas compared to TiO_2 thin film [14]. The adsorption equilibrium isotherms of paprika oleoresin on TiO_2 thin film and activated carbon could be represented by the Langmuir equation.

3.2. Thermodynamic study

The effect of temperature on the adsorption of paprika oleoresin on TiO_2 thin film is shown in Fig. 1. It was found that an increase in temperature resulted in an increase in the adsorption of paprika oleoresin. This indicates that the adsorption on TiO_2 thin film is an endothermic process. The free energy change ΔG° was evaluated using the Van't Hoff equation:

$$\log \frac{q_e}{C_e} = -\frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R} \quad (6)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (7)$$

where, *ΔG°* is the Gibbs free energy (J/mol), *ΔH°* is the enthalpy (J/mol), *ΔS°* is the entropy (J/mol K), R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). The relationship between *ΔH°* and *ΔS°* was determined from the slope and intercept of the Van't Hoff plots of log q_e/c_e versus *1/T*. Table 2 presents the thermodynamic parameters at various temperatures. At these temperatures, the negative values of *ΔG°* confirm the feasibility of the process and the spontaneous nature of the adsorption [15, 16]. The greater number of negative values of *ΔG°* implies a greater driving force to the adsorption process. Additionally, the positive value of *ΔH°* reveals the endothermic nature of the adsorption process, while the positive value of *ΔS°* suggests its increased randomness and can be connected with the affinity of studied complexes towards adsorbates [17]. The enthalpy and entropy implied by the temperature dependence for paprika oleoresin on TiO_2 thin film were found to be 176.75 kcal/mol and 0.678 kcal/mol, respectively.

Table 2. Thermodynamic parameters of paprika oleoresin on TiO_2 thin film at different temperatures.

Temperature [K]	Thermodynamic parameters		
	ΔG° [kcal/mol]	ΔH° [kcal/mol]	ΔS° [kcal/mol]
288	-18.51	176.75	0.678
298	-25.29		
308	-32.07		

3.3. Adsorption energy distribution function

Adsorption energy distributions have been extensively applied for characterizing the numerous adsorption systems and for understanding the surface energy heterogeneities concerned in physico-chemical networks. Experimental adsorption isotherm data, including a theoretical local adsorption isotherm equation and an adsorption energy distribution function, are crucial factors for characterizing the surface energy heterogeneity of an adsorbent. According to the theory of adsorption on heterogeneous surfaces, the total adsorption of the solute can be described as the integral of an energetically homogeneous isotherm $\theta(\alpha)$ multiplied by a site energy distribution U over a range of energies [14, 18, 19]:

$$\theta(\alpha) = \int_0^{\infty} \theta_1(\alpha, U) F(U) du \qquad (8)$$

where $\theta(\alpha)$ is the experimental adsorption isotherm data (here, α = c for liquid phase), U is the difference between the solute and solvent adsorption energies for a given adsorption sites, *F(U)* is the adsorption energy distribution function, and $\theta(\alpha,U)$ is a local adsorption isotherm with an adsorption energy. The minimum and maximum adsorption energies are typically not known a priori, so the limits on the integral are generally assumed for convenience that they range from zero to infinity [20]

The Langmuir–Freundlich equation, an appropriate model for the estimation of monolayer adsorption capacity, was selected as the local adsorption isotherm equation to determine the adsorption energy distribution for the liquid phase adsorption studies. The adsorption energy distribution for the adsorption of single-solute from dilute aqueous solutions can be described from the following fundamental expression of the integral equation.

$$\theta_T(c) = \int_{E12\min}^{E_{12\max}} \frac{\Phi x \exp(E_{12}/RT)}{1 + \Phi x \exp(E_{12}/RT)} F(E_{12}) dE_{12} \qquad (9)$$

where $\theta(c)$ is the total fractional coverage of the solute, E_{12} is the energy difference of components, $\Phi = \Phi(c, \theta_T)$ is a model dependent function (i.e. the molecular interactions between bulk and surface phases), and $F(E_{12})$ is the energy distribution function, $x = c / c_{sol}$, where c_{sol} is the solubility of adsorbate, R is the gas constant, and T is the absolute temperature. The function (Φ) is closely related to the model of the bulk and surface phases, and the surface topography.

In this study, the surface heterogeneities of the prepared TiO_2 thin film was analyzed based on the liquid phase adsorption experimental results. The Langmuir-Freundich local adsorption isotherm equations were utilized for determining the adsorption energy distribution for the liquid (paprika oleoresin) phase adsorptions. The generalized regularization method was applied to obtain the reliable and stable adsorption energy distribution [21, 22].

Fig. 3 shows that general trend of the adsorption energy distribution functions of paprika oleoresin on TiO_2 thin film and activated carbon. The adsorption energy distribution curves of paprika oleoresin for the adsorbents have a single peak. The peaks of the energy distribution curves indicated that its corresponding site energies are the main adsorption sites. The highest adsorption energy peaks for TiO_2 thin film and activated carbon were found to be around 7.56 and 8.91 kJ/mol, respectively. When at low energy sites, the energy distribution of TiO_2 thin film increased sharply, and high binding energy sites decreased rapidly with the increase of site energy, there were little sorption sites in the region of 12-16 kJ/mol. In general, the heterogeneity of adsorbent surface increased with decreasing energy peak height and increasing energy peak width [14, 23].

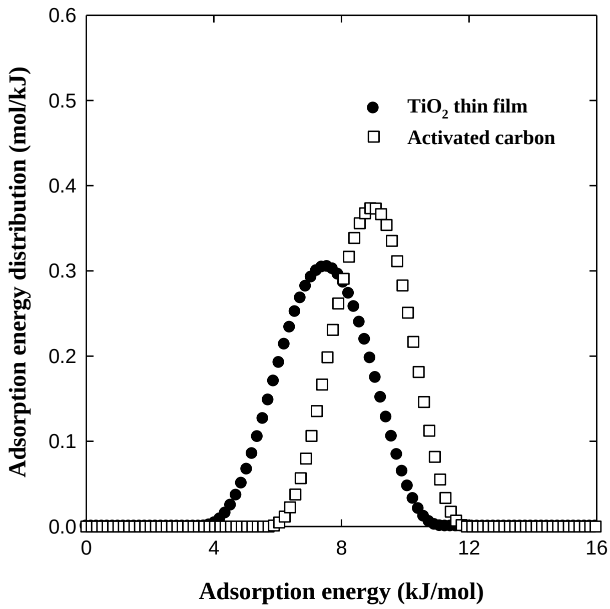

Figure 3. Adsorption energy distributions of paprika oleoresin on TiO_2 thin film and activated carbon at different temperatures.

As can be seen in this figure, with the increasing temperature of the adsorption system, the adsorption energy maximum peak gradually moves to a higher energy and extends, lowering the peak height and width. From the above results, the adsorption heterogeneity for the adsorption system of paprika oleoresin on TiO_2 thin film increased with increasing temperature [21].

3.4 Kinetic studies

It is important to provide sufficient contact time to the adsorption system to achieve equilibrium and to estimate the accurate adsorbent capacity of paprika oleoresin on TiO_2 thin film. In this study, pseudo-first-order and pseudo-second-order models were used to fit our experimental data. The Lagergren pseudo-first-order kinetic model equation is given as follows [24, 25]:

$$\log\left(q_{eq} - q_t\right) = \log q_{eq} - \frac{k_1}{2.303}t \qquad (10)$$

where q_{eq} and q_t are the amounts (mg/g) of adsorbed paprika oleoresin on TiO_2 thin film at equilibrium and at time t, and k_1 is the rate constant of the pseudo-first order-sorption process (1/min).

Fig. 4 shows the experimental data and the Lagergren pseudo-first-order kinetic plot for paprika oleoresin on TiO_2 thin film at different temperatures in a batch adsorber, where the first-order rate constant, $k_{1,}$ and theoretical q_{eq} values were calculated from the slope and intercept, respectively (Table 3).

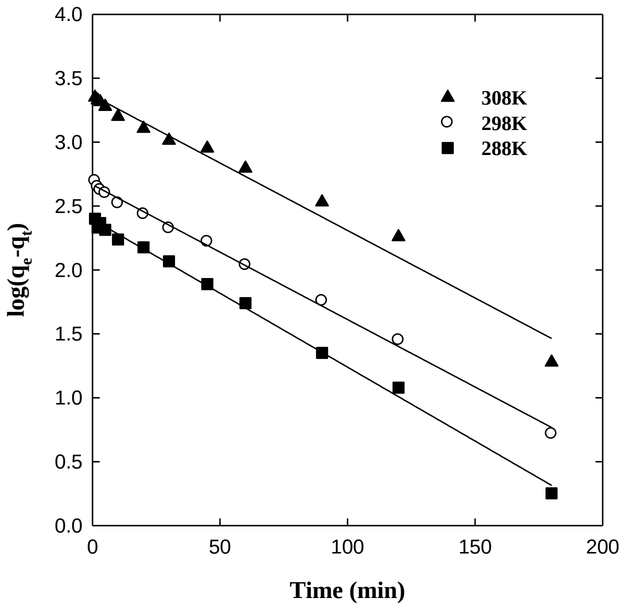

Figure 4. Linearized pseudo-first-order kinetic model of paprika oleoresin on TiO_2 thin film at different temperatures.

Table 3. Kinetic parameters for the removal of paprika oleoresin on TiO_2 thin film.

Temp. [K]	Pseudo-first order			Pseudo-second order			Measured q_e [mg/g]
	$k_1 \times 10^{-1}$ [min]	q_{eq} [mg/g]	R^2	$k_2 \times 10^{-2}$ [g/mg min]	q_{eq} [mg/g]	R^2	
288	0.11	28.94	0.98	0.02	38.91	0.97	27.12
298	0.11	14.41	0.99	0.08	17.78	0.97	13.91
308	0.12	10.98	0.99	0.08	14.12	0.96	10.34

The determined rate constants of $k_{1,}$ and theoretical q_{eq} values were in the range of 0.011 - 0.012 min^{-1} and 28.94 - 10.98 mg/g, respectively. It can be seen that the R^2 value for the pseudo-first-order model is close to 1. The values of k_1 increased with increasing temperature, presumably due to the swelling effect within the internal structure of TiO_2 thin film, the pores open, which enable large paprika oleoresin molecules to penetrate deeply. The calculated equilibrium adsorption capacity of paprika oleoresin on TiO_2 thin film is consistent with the experimental data.

The pseudo-second-order model equation is given as follows [26]:

$$\frac{t}{q_t} = \frac{1}{k_{2,ad} q^2_{eq}} + \frac{1}{q_{eq}} t \tag{11}$$

where k_2 is the rate constant of the pseudo- second-order kinetic model (g/mg min).

The rate parameters k_2 and q_{eq} can be directly obtained from the intercept and slope of a plot of t/q_t versus t, as shown in Fig. 5.

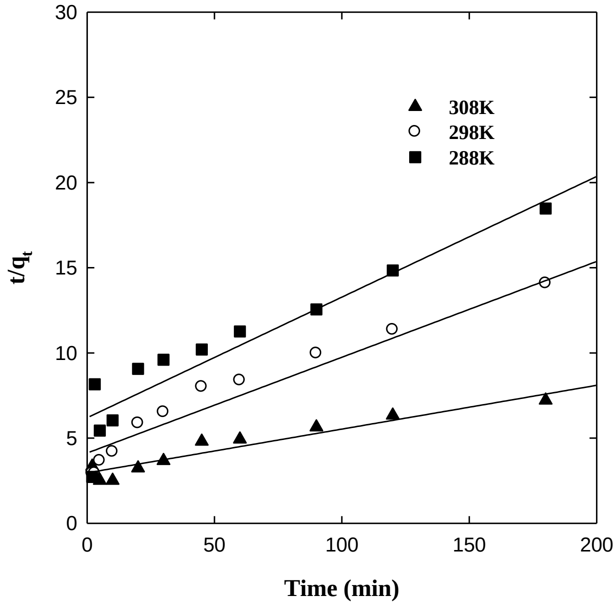

Figure 5. Linearized pseudo-second-order kinetic model of paprika oleoresin on TiO_2 thin film at different temperatures.

The pseudo-second-order parameters calculated on TiO_2 thin film for an initial paprika oleoresin concentration of 200 mg/L is presented in Table 3. The results in Table 3 show that the correlation coefficients (R^2) for the second-order kinetic model were close to 0.97. Although the R^2 values can be reasonably high, the calculated q_{eq} values obtained from this kinetic model gave unreasonable values (Table 3), which were too high compared with those obtained experimentally. This suggested that the adsorption process of paprika oleoresin on TiO_2 thin film does not follow the Lagergren expression for pseudo-second-order adsorption.

Fig. 6 presents the experimental data and model prediction for the adsorption of paprika oleoresin at different temperatures in a batch adsorber. The adsorption rate of paprika oleoresin on TiO_2 thin film increased with increasing temperature. The differences in the rates of adsorption of paprika oleoresin on the TiO_2 thin film were primarily attributable to the differences in the equilibrium adsorption capacities of the adsorbent in terms of temperature (shown in Fig. 1). At higher temperatures, the mobility of ions increases. Increasing the number of moieties may also provide sufficient energy, which allows the paprika oleoresin ions to interact with active sites present on the surface of TiO_2 thin film. The pseudo-first-order model shows satisfactory prediction of the concentration decay curves.

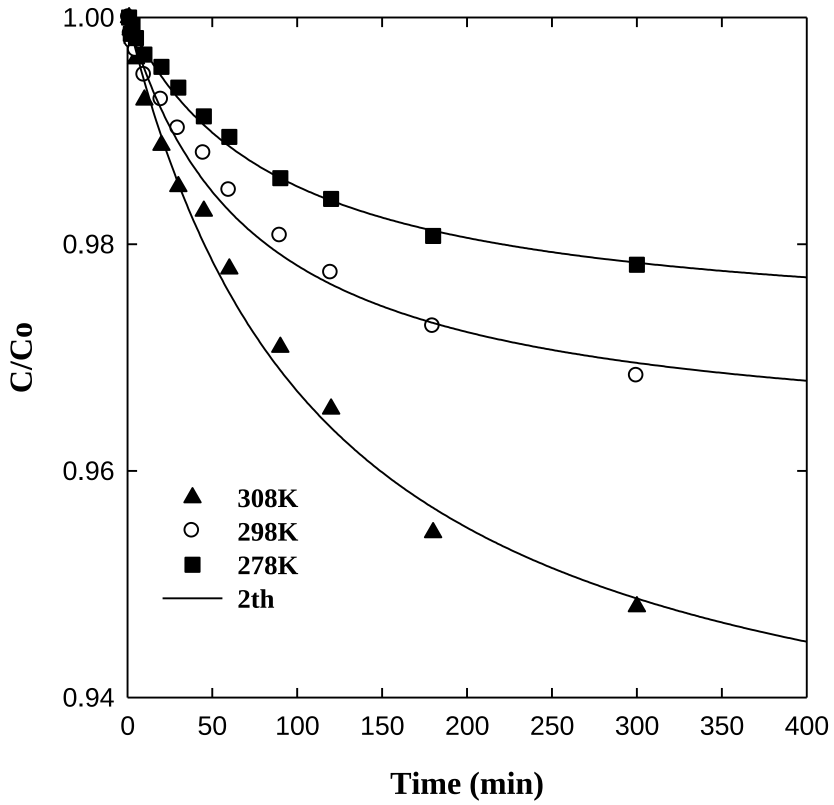

Figure 6. Concentration decay curves of paprika oleoresin on TiO_2 thin film at different temperatures.

3.5. Photovoltaic performance of DSSC

For determining photovoltaic properties of DSSCs using paprika oleoresin and N-719 dyes as sensitizers, photocurrent-voltage (I-V) measurements were performed by a solar simulator under AM1.5 and 100 mW/cm cm^2 illumination. The I-V curves of paprika oleoresin and N-719 dye solar cell under illumination are shown in Fig. 7. After determining the characteristics such as short-circuit current (I_{SC}) and open-circuit voltage (V_{OC}) from Fig. 7, the values of fill factor (FF) and overall conversion efficiency (η_{eff}) of the DSSCs can be determined by following equations:

$$FF = \frac{I_{\max} \times V_{\max}}{I_{SC} \times V_{OC}} \quad (12)$$

$$\eta(\%) = \frac{P_{out}}{P_{in}} \times 100 = \frac{I_{\max} \times V_{\max}}{P_{in}} \times 100 = \frac{I_{SC} \times V_{OC} \times FF}{P_{in}} \times 100 \quad (13)$$

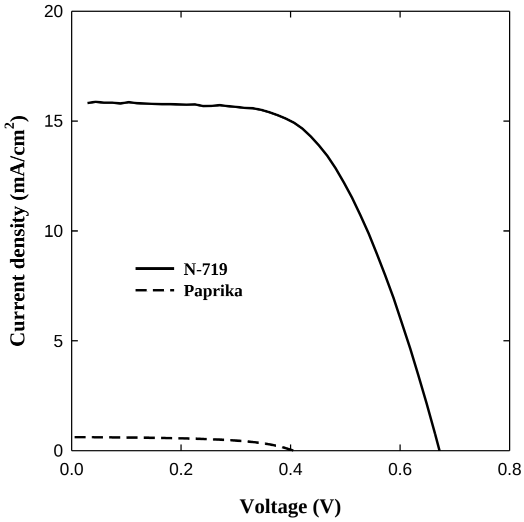

Figure 7. *I-V* curves of paprika oleoresin (dash) and N-719 (line).

where I_{SC} is the short-circuit current density (mA/cm^2), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, and I_{max} (mA/cm^2) and V_{max} (V) are the current density and voltage in the I-V curve at the point of maximum power output, respectively. FF is the ratio of the rectangular area formed by the multiplication of V_{max} and I_{max} to the rectangular area formed by the multiplication of V_{oc} and I_{sc}. Paprika oleoresin dye-sensitized solar cell assembled had an open-circuit voltage and a short-circuit current density of 0.41 V of 0.62 mA/cm^2 respectively. According to previous research, I_{SC} values of solar cell using mallow, henna, strawberry and spinach as sensitizer was 0.69, 0.66, 1.33, 0.55 mA/cm^2 [27]. The power conversion efficiency of paprika oleoresin was 0.14% for an incident light intensity of 100mW/cm^2. Hemalatha et al. reported similar results, in which the conversion efficiency of the carotenoid dye is 0.22% [6]. However, the power conversion efficiency was 7.2% in the DSSC consisting of commercial dye (N719), with an open-circuit voltage of 0.70 V and a short-circuit current density of 17.1 mA/cm^2. The DSSCs sensitized by paprika oleoresin dye did not offer high conversion efficiency compared to N719. This can be explained as due to the lack of available bonds between the dye and TiO_2 molecules which electrons can transport from the excited dye molecules to the TiO_2 film.

4. CONCLUSIONS

The adsorption characteristics of paprika oleoresin (*Capsicum annuum L.*) on TiO_2 photoelectrode for a dye-sensitized solar cell (DSSC) were investigated in terms of temperature. The amount of adsorbed natural dye increased with increasing temperature and the maximum adsorption capacity of paprika oleoresin on TiO_2 thin film was about 141.94 mg/g at 308K. Adsorption heterogeneity for the adsorption system of paprika oleoresin on TiO_2 thin film increased with increasing temperature. The positive values of ΔH^o and ΔS^o indicated the endothermic nature of the adsorption of paprika oleoresin onTiO_2 thin film. The negative values of ΔG° had occurred, indicating a spontaneous process. The kinetics data were better fitted with the pseudo-first-order model than with the pseudo-second-order model. The DSSC fabricated using paprika oleoresin was achieved with a V_{oc} of 0.41 V and an I_{sc} of 0.62 mA/cm^2 and a power conversion efficiency of 0.14%.

ACKNOWLEDGEMENT
This research was supported by the Specialized Local Industry Development Program through the Korea Institute for Advancement of Technology (KIAT) funded by the Ministry of Trade, Industry and Energy, South Korea (1415127923-R0002040). This work was supported by the Human Resource Training Program for Regional Innovation and Creativity through the Ministry of Education and National Research Foundation of Korea (2015H1C1A1035883)

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