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## Recovery of catechin and epicatechin from sago waste effluent: Study of kinetic and binary adsorption isotherm studies

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## HIGHLIGHTS

- Recovery of catechin and epicatechin from sago waste effluent.
- Supercritical CO<sub>2</sub> desorption of catechin and epicatechin from activated carbon.
- Adsorption of catechin and epicatechin in binary system.

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## ABSTRACT

The recovery of valuable phenolic compounds (catechin and epicatechin) from sago waste effluent by activated carbon adsorption was studied in this work. Single and binary component of catechin and epicatechin was studied in static mode using synthetic effluent. Langmuir model was applied to evaluate the adsorption equilibrium data in single system. In binary system, the modified extended Langmuir model by inclusion of surface coverage was used to represent the adsorption data. All experimental data were well represented either by Langmuir model or its modified form. For kinetic study, it was found that pseudo-second order model represents the experimental data better than pseudo-first order model. Adsorption study using real sago waste effluent indicated that activated carbon adsorption process is promising for recovery of valuable phenolic compounds. Supercritical CO<sub>2</sub> extraction of phenolic compounds from activated carbon resulted in low recovery. The addition of ethanol as co-solvent significantly enhanced the desorption of catechin and epicatechin from activated carbon.

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## 1. Introduction

Phenolic compounds are universally distributed in plants such as leave, trunk, root, seed, and fruit. They are usually are bounded within plant tissues. Phenolic compounds as antioxidants are believed to contribute to health benefits through several possible mechanisms such as by quenching free radicals, chelating transition metals, reducing peroxides and stimulating antioxidative enzyme defense. Natural antioxidants are known to exhibit a wide range of biological effects including anti-bacterial, antiviral, anti-inflammatory, anti-allergic, antithrombotic and vasodilatory activities [1]. The antioxidant activity of phenolic compounds is mainly attributed to their redox properties, which allow them to act as reducing agents, hydrogen donors and quenchers of singlet oxygen. In addition, they may also possess metal chelating properties. Phenolic compounds possess aromatic structure along with hydroxyl

substituent which enable them to protect human tissues from damages caused by oxygen or free radicals, and consequently reduce the risk of various diseases, and offer beneficial effect against cancer, cardiovascular disease, diabetes, and Alzheimer's disease [2–7].

In starch extraction from sago pith, the sago pith slurry during sedimentation is browning due to the oxidation of phenolic compounds by the polyphenol oxidase (PPO) enzyme [8]. Phenolic compounds are located mainly in vacuoles while the PPO is found in plastids. Browning is initiated with the disruption of cell due to cutting or bruising and the compartmentalization is lost. The primary phenolic compounds related to browning are DL-epicatechin and D-catechin [8,9]. Pei-Lang et al. [9] reported that the content of phenolic compounds in sago pith depends on its growth stages and height; and the amount of phenolic compound extracted is less than 1%.

Recovery of phenolic compounds from the waste effluents is beneficial, but it is a challenging process. Adsorption is efficient for removing organic matter from waste effluents. Activated

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carbons are the most widely used adsorbents due to their high adsorption capacities for organic pollutants which are related to their high surface area, pore volume and porosity. The adsorption capacities also strongly depend on the activation method and the nature of source materials. Activated carbon is an effective adsorbent for organic compounds removal, especially for phenolic compounds [10–15]. However, the utilization of activated carbon as adsorbent in the adsorption of epicatechin and catechin has never been reported.

The focus of this work was to evaluate the adsorption performance of activated carbon for the recovery of epicatechin and catechin in single and binary component systems. The surface area was obtained based on Brunauer, Emmet, and Teller (BET) measurements, while the pore volume and pore diameter of activated carbon were calculated from the adsorption experimental data using density functional theory (DFT). The effect of various variables, such as initial adsorbate concentrations, adsorption time and mass of adsorbent were studied using batch equilibrium technique. Pseudo first and second order kinetic models were used to correlate the adsorption dynamic or kinetic data. The adsorption equilibrium data was evaluated using Langmuir model for single component, while modified extended-Langmuir model with incorporation of solute's selectivity factor was used to study the correlation [16]. The feasibility and adsorption performance of activated carbon in recovering epicatechin and catechin was also tested in real effluent.

## 2. Experimental section

### 2.1. Chemicals

HPLC grade (–)-epicatechin (purity 98 wt.%) and (+)-catechin hydrate (purity  $\geq$  98 wt.%) were obtained from Sigma Aldrich (Singapore) and was used without any further purification. Pellet activated carbon (0.5–1.5) produced by Norit (The Netherland) was used as the adsorbent. Double distilled water was used in adsorption experiments.

### 2.2. Characterizations of activated carbon

Since structural heterogeneity of activated carbon plays an important role during adsorption therefore it is crucial to characterize the pore structure of activated carbon. Pore structure of the activated carbon was characterized by nitrogen sorption technique in a Quadrasorb SI at boiling point of nitrogen gas ( $-196^\circ\text{C}$ ). Prior to the nitrogen sorption measurement, the activated carbon was degassed in vacuum condition at  $200^\circ\text{C}$  for 48 h. The measurement of the nitrogen sorption isotherms (adsorption and desorption) were conducted over a relative pressure ( $p/p_0$ ) of 0.001–0.990. The BET surface area of the carbon was determined by standard BET equation at a relative pressure of 0.06–0.3. Total of pore volume of the activated carbon was evaluated at the highest relative pressure (0.990). At this relative pressure all pores within the activated carbon were already completely filled with nitrogen gas. Pore size distribution of the carbon was determined by standard DFT method with medium regularization.

### 2.3. Static adsorption experiments

The adsorbate solution was prepared by mixing a known amount of adsorbate ((–)-epicatechin or (+)-catechin hydrate) with double distilled water to produce the desired initial concentrations (100–150 mg/L). The adsorption was carried out isothermally in static mode at 303.15 K. A fixed amount of activated carbon was added to a series of 250 mL glass-stoppered flasks each

filled with 100 mL diluted solutions. The glass stoppered flasks were then put in a thermostatic shaker bath at 120 rpm for 1 h (the equilibrium condition was achieved in about 40 min). The adsorption isotherm for binary systems of epicatechin and catechin was also obtained isothermally at 303.15 K, using the same procedure as for the single component adsorption.

To study the adsorption kinetics, a series of 250 mL glass-stoppered flasks contained 100 mL of phenolic compound solution with certain initial concentration (100–250 mg/L) were prepared. Subsequently, a known amount of activated carbon (0.2 g) was added into each glass-stopper flask. The glass-stopper flasks were placed in thermostatic water-bath shaker for 150 min at 303.15 K. During kinetic experiments, at intervals of 10 min, one of glass-stopper flask was taken and the concentration of phenolic compound was analyzed.

The adsorption of phenolic compounds from waste effluent was carried out using waste water from sago starch extraction. Briefly, sago pith was pulverized into coarse powder and soaked in water (1 h), and then filtered using Buchner funnel to obtain the waste effluent. One gram of activated carbon was added to 250 mL glass-stopper flasks each filled with 100 mL waste effluent. The glass stopper flask was placed in a thermostatic shaker bath at 120 rpm for 1 h.

The initial and equilibrium concentrations of the single and binary solutions and waste effluent were analyzed using a HPLC (Jasco HPLC PU-2089 plus) with a UV-vis detector (UV-2077 plus) set at 280 nm. Separations were achieved in an Enduro C18,  $5\ \mu\text{m}$ ,  $250 \times 4.6\ \text{mm}$ . The flow rate was 0.8 ml/min. The mobile phase used was isocratic elution comprised of 3% acetic acid in double distilled water (60%) and acetonitrile (40%) for a total running time of 10 min. The contents of epicatechin and catechin were determined using calibration curves.

The effect of pH on the adsorption of epicatechin and catechin was investigated in single component systems. It was found that as the initial solution pH was reduced to pH 3, the solution concentration decreased up to 50% of the initial concentration. When the initial solution pH was increased to pH 10, the solution concentration also decreased up to 60–70% of the initial concentration. This is due to oxidation of the phenolic compounds. Therefore, the adsorption of epicatechin and catechin in single and binary component were carried out at pH 7, which is similar to the waste effluent pH.

### 2.4. Calculations

The amounts of epicatechin and catechin adsorbed onto activated carbon in single component system were calculated using the following equation:

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

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration of phenolic compounds in the liquid phase (mg/L), respectively,  $V$  is the volume of phenolic compounds solution (L),  $q_e$  is the amount of metal ions adsorbed per unit of biosorbent mass (mg/g), and  $m$  is the mass of activated carbon (g). The equilibrium concentration of phenolic compound  $i$  species ( $C_{e,i}$ ) in binary mixture was calculated by the same manner using following mass balance equation:

$$q_{e,i} = \frac{(C_{0,i} - C_{e,i})}{m} \times V \quad (2)$$

where  $q_{e,i}$  is the equilibrium amount of solute  $i$  in the adsorbed phase (mg/g),  $C_{0,i}$  and  $C_{e,i}$  are the initial and equilibrium concentration of solute  $i$  in the liquid phase (mg/L), respectively. All data are the average results of triplicates experiments.

### 3. Results and discussion

#### 3.1. Activated carbon characterization

Analysis of nitrogen sorption isotherms and DFT-pore size distribution of the activated carbon used in this study indicates that the NORIT carbon possess both micropore and mesopore structures with micropore structure more dominant than mesopore as indicated by the rapid filling of pores at low relative pressure and followed by the gradual increase of adsorption at moderate relative pressure (S1). The existence of the mesopores is indicated by the presence of hysteresis loop between adsorption and desorption isotherms, an indication of capillary condensation in the mesopores. The BET surface area, micropore volume, and total pore volume of the activated carbon (NORIT nrs carbon Ea 0.5–1.5) were  $890 \text{ m}^2/\text{g}$ ,  $0.431 \text{ cm}^3/\text{g}$ , and  $0.506 \text{ cm}^3/\text{g}$ , respectively.

The pore distribution of activated carbon represents a model of carbon internal structure which represents non-interacting of regularly shape model pores and complex void spaces within the carbon. The pore size distribution of the carbon is one of its most important characteristics of the carbon in studying adsorption equilibrium and kinetic. The pore size distribution of the activated carbon confirms that the carbon possesses both micropore and mesopore structure (S2).

#### 3.2. Adsorption isotherms

The isotherm shape can be used as quasi-qualitative information on the nature of the solute-surface interaction. In the case of adsorption of phenolic compounds from water, it is characterized by initial region (high uptake at low concentration); and Langmuir model is best fitted for this case [17,18]. Based on the classification proposed by Giles et al. [17,18], the curve shape in Fig. 1 is class L2 according to the Giles classification suggests that the aromatic ring adsorbed is parallel to the surface and no strong competition exists between the adsorbate and the solvent to occupy the adsorption sites [12]. Langmuir isotherm is characterized by a plateau curve which indicates that equilibrium has been achieved. The Langmuir isotherm was originally developed for describing gas adsorption phenomena but it has been extensively used for the correlation of adsorption equilibrium data of various solute-sorbent interactions in liquid phase [19–21]. The Langmuir isotherm model is given as follows:

$$q_e = q_m \frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3)$$

where  $q_m$  is the maximum adsorption capacity of the solid (mg/g) corresponding to monolayer surface coverage and  $K_L$  is Langmuir constants of adsorption affinity (L/mg).

Fig. 1 shows that the adsorption equilibrium data of phenolic compounds are well fitted by the Langmuir isotherm model and the correlation coefficients for epicatechin and catechin are 0.97 and 0.94, respectively. The maximum adsorption capacity ( $q_m$ ) of catechin (73.56 mg/g) obtained by fitting calculation using Sigma-Plot 12.0 is higher than that of epicatechin (29.04 mg/g). The adsorption affinity parameter ( $K_L$ ) of catechin and epicatechin obtained are 0.1257 L/mg and 0.041 L/mg, respectively. Higher adsorption affinity parameter of catechin than epicatechin indicates that catechin is easier adsorbed onto the surface interior of the carbon.

Industrial Adsorption process usually involves multi-component, therefore, information on adsorption equilibria in multi-component system is required for engineering design of the adsorption process. Compare to the single component adsorption, reliable experimental multi-component adsorption isotherm data are more

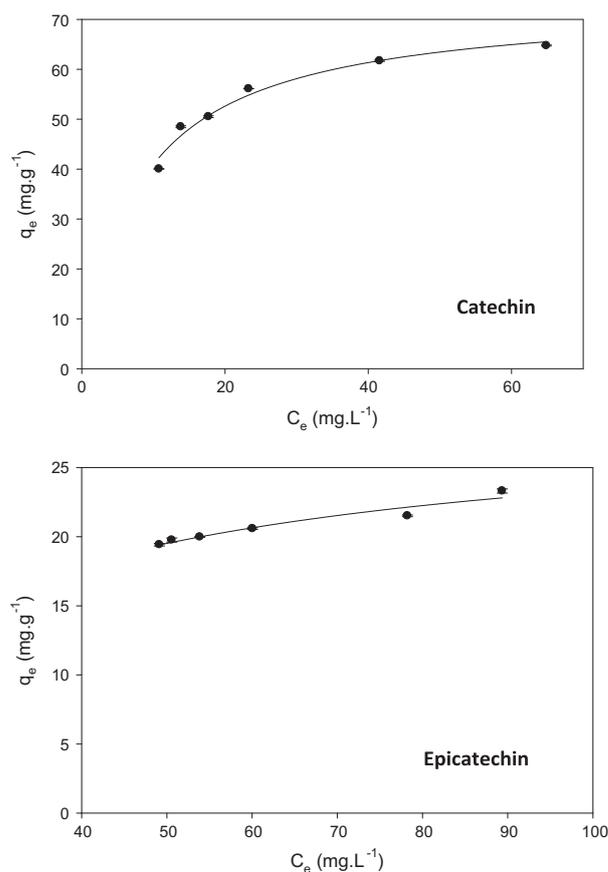


Fig. 1. Adsorption isotherm of catechin and epicatechin onto activated carbon NORIT nrs carbon Ea 0.5–1.5 and Langmuir isotherm model (solid lines).

time consuming and much more difficult to obtain. Therefore it will be convenient if the multi-component isotherm can be constructed based on single adsorption isotherms. Various models have been developed for this purpose and one of the most widely used is the extended Langmuir and its modified forms [16,22,23]. The extended Langmuir model for a two-component system can be expressed as:

$$q_{e,1} = \frac{q_{m,1}K_{L,1}C_{e,1}}{1 + K_{L,1}C_{e,1} + K_{L,2}C_{e,2}} \quad (4)$$

$$q_{e,2} = \frac{q_{m,2}K_{L,2}C_{e,2}}{1 + K_{L,1}C_{e,1} + K_{L,2}C_{e,2}} \quad (5)$$

where  $q_{m,i}$  and  $C_{e,i}$  are the amount adsorbed and equilibrium concentration of component  $i$ , respectively. The parameters  $q_{m,i}$  and  $K_{L,i}$  are the adsorption capacity of component  $i$  in the adsorbent and adsorption affinity of component  $i$ , respectively. All these parameters are obtained from single adsorption isotherms.

In a multi-component system, competition for vacant adsorption sites in the surface of adsorbent occurs not only between the same molecules but also between different adsorbate species. This competition may act as the controlling factor for the adsorption process [16,23] and such phenomenon is not captured by original extended Langmuir model. Recently, Kurniawan et al. [23] and Soetaredjo et al. [16] modified the extended Langmuir model by including fractional surface loading or coverage [23] and selectivity factor [16]. Since both epicatechin and catechin are organic compounds, the fractional surface loading approach by Kurniawan et al. [23] is more suitable to represent the binary adsorption data of this study.

Since competition between catechin and epicatechin molecules for vacant adsorption sites in the activated carbon occurred during the adsorption process, catechin and epicatechin were adsorbed in certain amount, and the adsorption capacity of the activated for both adsorbates (binary) can be written as

$$q_{m,bin} = q_{m,1}\theta_1 + q_{m,2}\theta_2 \quad (6)$$

Here  $\theta_1$  and  $\theta_2$  are the fractional loading of catechin and epicatechin, respectively, and  $\theta_1 + \theta_2 = 1$ . The adsorption affinity parameter in Langmuir equation represents how strong an adsorbate molecule is attracted onto the surface of the adsorbent. In a binary system, the competition between different molecules weakens the adsorption potential of the adsorbate toward the surface of adsorbent, therefore, the affinity parameter of binary compounds can be written as:

$$K_{L,1(bin)} = K_{L,1} \exp\left(-\frac{\theta_2}{\theta_1}\right) \quad (7)$$

$$K_{L,2(bin)} = K_{L,2} \exp\left(-\frac{\theta_1}{\theta_2}\right) \quad (8)$$

where  $K_{L,1(bin)}$  and  $K_{L,2(bin)}$  are the affinity parameter of catechin and epicatechin in binary system, respectively. The final expressions of extended Langmuir model with inclusion of fractional loading concept are

$$q_{e,1} = \frac{q_{m,bin}K_{L,1(bin)}C_{e,1}}{1 + K_{L,1(bin)}C_{e,1} + K_{L,2(bin)}C_{e,2}} \quad (9)$$

$$q_{e,2} = \frac{q_{m,bin}K_{L,2(bin)}C_{e,2}}{1 + K_{L,1(bin)}C_{e,1} + K_{L,2(bin)}C_{e,2}} \quad (10)$$

The applicability of the modified extended Langmuir model was tested against the liquid phase binary adsorption data of catechin and epicatechin. The parameter  $\hat{e}_1$  and  $\hat{e}_2$  were obtained by the simultaneously fitting of Eqs. (9) and (10) using nonlinear least square method by minimizing the following objective function

$$SSE = \left[ \frac{\sum (q_{exp} - q_{cal})^2}{n} \right]^{0.5} \quad (11)$$

where  $q_{exp}$  and  $q_{cal}$  are the actual amount and the calculated values of catechin and epicatechin adsorbed by activated carbon, respectively;  $n$  is the total number of experimental data used in the fitting procedure.

Fig. 2 shows the 3D plots of binary adsorption of catechin and epicatechin at various initial concentrations and the model calculated by Eqs. (9) and (10). The fitted parameters  $\theta_1$  and  $\theta_2$  with calculate values of  $q_{m(bin)}$ ,  $K_{L,1(bin)}$ , and  $K_{L,2(bin)}$  are summarized in Table 1. In this work an improvement was made in the fitting procedure of modified extended Langmuir model by Kurniawan et al. [23]. Both Eqs. (9) and (10) were simultaneously fitted by nonlinear least square method with  $\theta_1$  and  $\theta_2$  as the fitted parameters, with boundary condition of the fitting procedure as  $\theta_1 + \theta_2 = 1$ . It is obvious that this fitting procedure improved the applicability of the modified extended Langmuir model in correlating the binary experimental data of catechin and epicatechin as indicated in Fig. 2.

The maximum amount of adsorbates adsorbed in binary system ( $q_{m(bin)}$ ) was lower than in single system ( $q_m$ ) due to the effect of molecular competition between both adsorbate molecules. This competition was accommodated in the modified extended Langmuir by taking into account of fractional loading coverage. The fractional coverage of catechin ( $\theta_1$ ) and the maximum amount adsorbates adsorbed ( $q_{m(bin)}$ ) decreased with increasing initial epicatechin concentration as shown in Table 1. This result is consis-

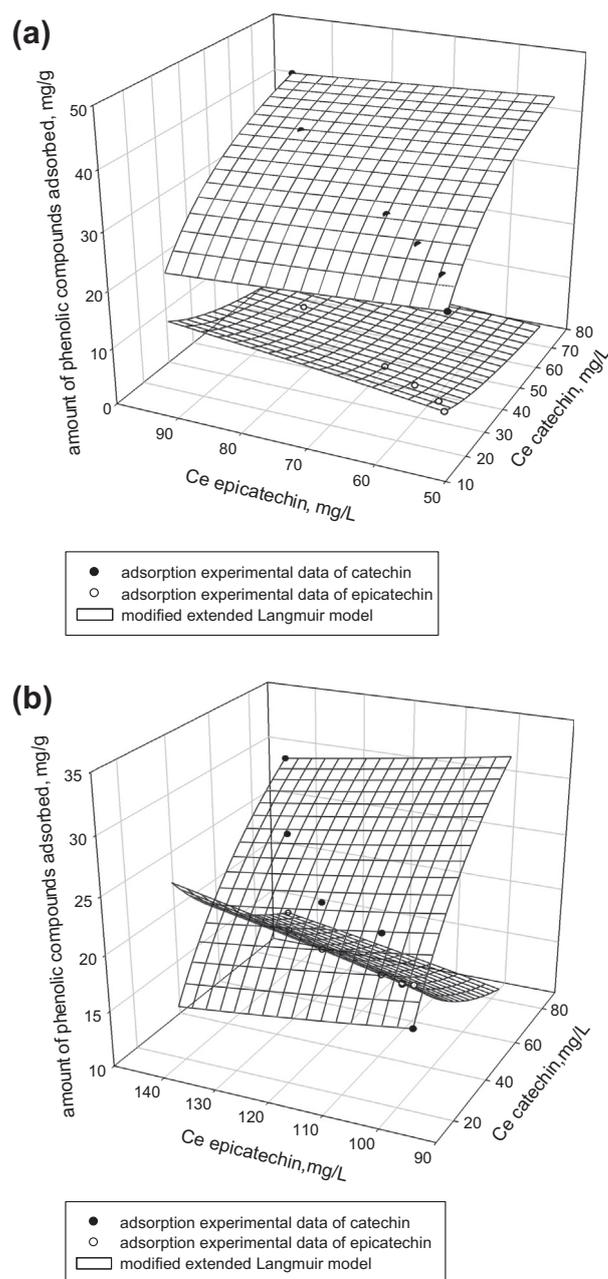


Fig. 2. 3D plot of binary adsorption data and modified extended Langmuir model. (a) Catechin 100 mg/L + epicatechin 100 mg/L, (b) catechin 100 mg/L + epicatechin 150 mg/L.

tent with adsorption characteristics in single adsorption system that the adsorption capacity of epicatechin is less than that of catechin, therefore increasing the concentration of epicatechin in binary system caused the interaction of adsorbate molecules to become even higher and reduce the value of  $q_{m(bin)}$ .

### 3.3. Adsorption kinetics

The effective design of an adsorption system requires information about the rate at which the organic compounds removal takes place in a given sorbent/solution system. Several adsorption kinetic models have been developed to describe the adsorption kinetics in liquid phase. The development of adsorption kinetic models mostly is based on fundamental approach to interfacial kinetics and its modifications [24]. Several models which have been developed

**Table 1**  
Fitted and calculated parameters for catechin and epicatechin adsorption at several initial concentrations.

Phenolic compounds mixture	Fitted parameter		Calculate parameter			$R^2$
	$\theta_1$	$\theta_2$	$q_{m,(bin)},$ mg/g	$K_{L,1(bin)},$ L/mg	$K_{L,2(bin)},$ L/mg	
Catechin 100 mg/ L + Epicatechin 100 mg/L	0.632	0.368	57.1	0.0699	0.0075	0.998
Catechin 100 mg/ L + Epicatechin 150 mg/L	0.524	0.476	52.2	0.0499	0.0139	0.997

based on this approach are Langmuir kinetics, first and second order, reversible first and second order, and irreversible reactions [24]. Another approach which is used to develop the kinetic models is based on assuming that surface reaction is the rate controlling step in sorption. Many simple and compact models have been proposed based on this approach and the famous and widely used models are pseudo-first (Lagergren) and pseudo-second order [24].

Pseudo-first order model which is also known as Lagergren equation is the earliest empirical model describing the rate of adsorption in a liquid phase system [25]. The differential form of this model is

$$\frac{dq(t)}{dt} = k_1(q_e - q(t)) \quad (12)$$

The integration of Eq. (12) with initial conditions:  $q(t) = 0$  at  $t = 0$  gives

$$q(t) = q_e(1 - \exp(-k_1t)) \quad (13)$$

where  $q(t)$  is the amount of adsorbate adsorbed at time  $t$  (mg/g), and  $k_1$  is the rate constant (1/min).

Pseudo-second order was first proposed by Blanchard et al. [26]. This model assumes that direct adsorption/desorption (seen as chemical reaction) is the rate controlling step in the overall sorption kinetics [24], and has the differential form as

$$\frac{dq(t)}{dt} = k_2(q_e - q(t))^2 \quad (14)$$

Here  $k_2$  is rate constant of pseudo-second order (g/mg min). Integration of Eq. (14) gives the following result

$$q(t) = q_e \left( \frac{k_2 q_e t}{1 + k_2 q_e t} \right) \quad (15)$$

To obtain the parameters of pseudo-first and pseudo-second order equations, non-linear least square method was employed by fitting the kinetic experimental data with Eqs. (13) and (15) and the results are summarized in Table 2. Figs. 3 and 4 present the plots of catechin and epicatechin uptake as the function of time, respectively. The symbols represent the kinetic experimental data while the solid lines represent the pseudo-first and pseudo-second order kinetic models. As shown in Table 2, the values of  $R^2$  obtained from the fitting of kinetic experimental data using both models were similar, however the pseudo-second order kinetic model represents kinetic experimental data better than the pseudo-first order since the predicted amount of adsorbate adsorbed in equilibrium condition was closer to that of the measured one. This is confirmed by the fact that from the values of fitting parameter  $q_e$  of pseudo-second order model agree with the values of  $q_e$  from kinetic experimental data. As mentioned by Plazinski et al. [24] that one of the potential advantages of using pseudo-second order kinetic model to correlate the adsorption kinetic experimental data is its small sensitivity to the influence of the random experimental error, especially for the fitting parameter  $q_e$ . Another advantage of using the pseudo-second order is that the value of fitted parameter  $q_e$  can be obtained from the independent plot of kinetic adsorption experimental data [24,27].

In many adsorption kinetic studies [24,27–29], failure of the pseudo-first order in correlating adsorption kinetic experimental data is due to the theoretical interpretations of this equation. In pseudo-first order it is based on the common assumption that the overall sorption process is controlled by the rate of adsorption/desorption processes which is seen as a chemical reaction on the surface of adsorbent [24]. However in many cases, the rate of diffusion of solute into interior of the adsorbent also controls the adsorption mechanism and this phenomenon is not captured by the pseudo-first order model.

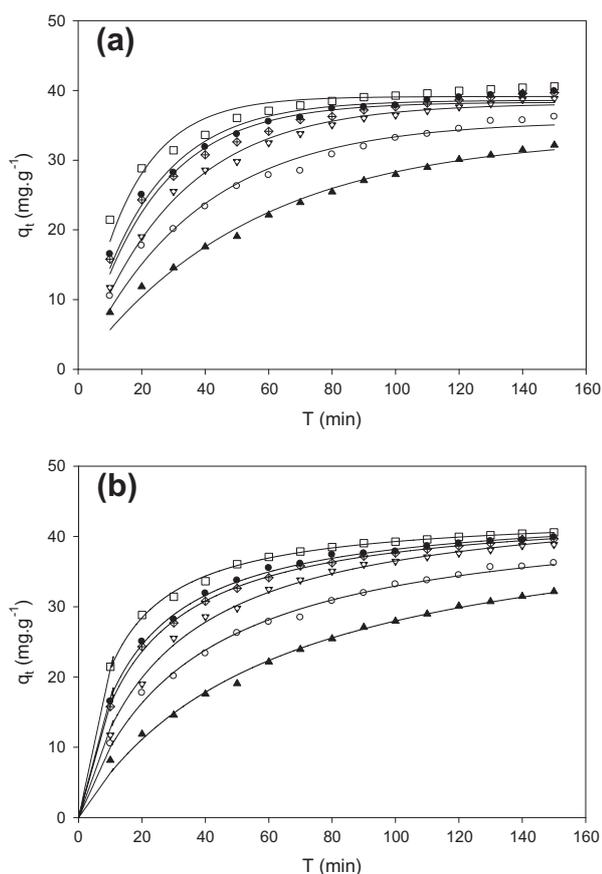
Table 2, Figs. 3 and 4 clearly indicate that the parameter  $k_2$  plays a role as time scaling factor. At high  $k_2$ , shorter time is required to reach equilibrium. As can be seen in Table 2,  $k_2$  decreased with increasing initial concentration. A simple correlation between of  $k_2$  and initial concentration of the adsorbate ( $C_0$ ) is given as follows:

$$k_2 = k_{2,0} + a \exp(-bC_0) \quad (16)$$

where  $k_{2,0}$ ,  $a$  and  $b$  are empirical constants. Plots of  $C_0$  versus  $k_2$  are given in Fig. 5. The fitted empirical constants for catechin are  $k_{2,0} = 0.0013$  g/mg min,  $a = 0.0194$  g/mg min, and  $b = 0.0092$  L/mg, while for epicatechin are  $k_{2,0} = 0.0004$  g/mg min,  $a = 0.0147$  g/mg min, and  $b = 0.0207$  L/mg.

**Table 2**  
Fitted parameters of pseudo-first and pseudo-second order of catechin and epicatechin adsorption onto activated carbon NORIT nrs carbon Ea 0.5–1.5.

Phenolic compound	$C_0$ , mg/L	$q_e$ , mg/g, experiment	Pseudo-first order			Pseudo-second order		
			$k_1$ , 1/min	$q_e$ , mg/g	$R^2$	$k_2$ , g/mg min	$q_e$ , mg/g	$R^2$
Catechin	101.3	43.3	0.0631	39.1	0.996	0.0022	43.4	0.997
	122.5	43.9	0.0471	38.6	0.997	0.0014	44.3	0.998
	139.8	44.5	0.0441	38.3	0.998	0.0013	44.3	0.999
	158.7	44.7	0.0337	38.2	0.998	0.0008	46.1	0.998
	203.6	45.3	0.0275	35.6	0.996	0.0007	44.2	0.997
	251.9	46.1	0.0185	33.6	0.994	0.0004	45.1	0.996
Epicatechin	100.5	21.2	0.1037	19.6	0.993	0.0086	20.9	0.994
	118.4	21.9	0.1096	22.2	0.996	0.0083	23.6	0.998
	141.2	23.2	0.0974	21.1	0.996	0.0069	22.8	0.996
	161.5	25.4	0.0795	22.5	0.995	0.0053	24.5	0.996
	201.7	28.2	0.0708	25.4	0.994	0.0040	27.9	0.997
	252.3	28.9	0.0656	26.5	0.995	0.0034	29.3	0.995

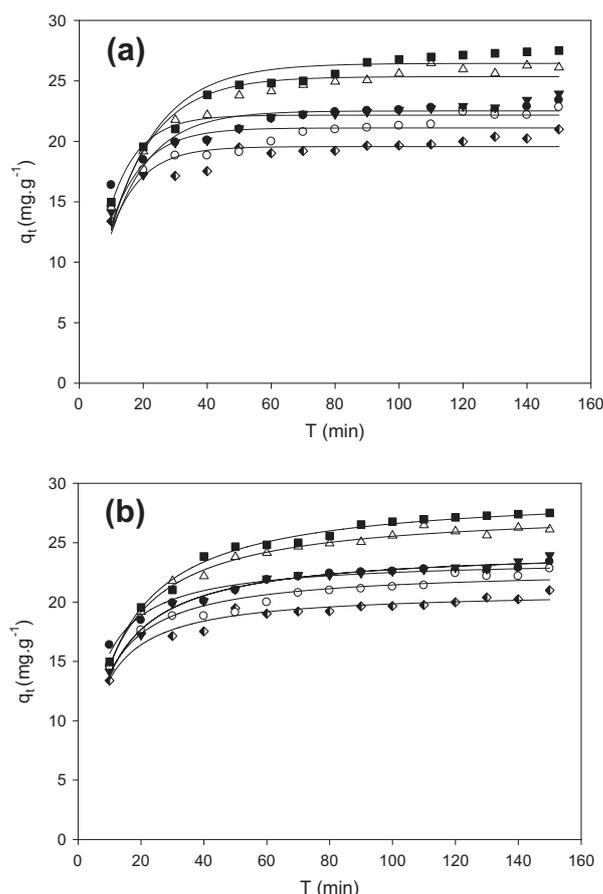


**Fig. 3.** Kinetic adsorption experimental data of catechin onto activated carbon NORIT nrs carbon Ea 0.5–1.5 at various initial concentration and plots of (a) pseudo-first order, and (b) pseudo-second order.

### 3.4. Recover of phenolic compounds in sago waste effluent

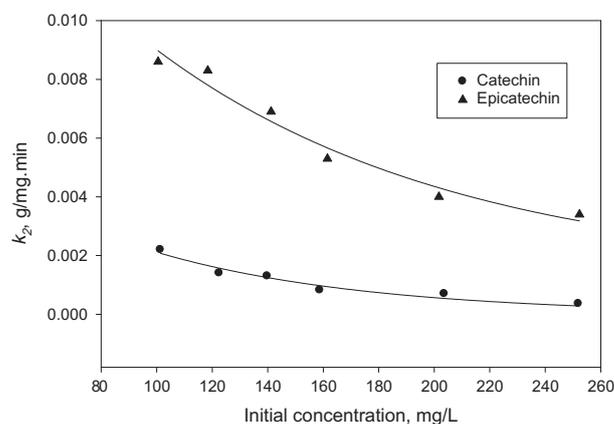
To verify the potential application of recovering phenolic compounds from sago waste effluent by adsorption, adsorption experiments using real sago waste effluent were also conducted. The adsorption of catechin and epicatechin from real sago waste effluent was conducted isothermally at 303.15 K under static condition. Prior to the adsorption experiment, the sago waste effluent was filtered to remove solid particles. The initial concentration of catechin and epicatechin in sago waste effluent was 321.8 mg/L and 158.2 mg/L, respectively. The recovery of catechin and epicatechin in sago waste effluent is given in Table 3. From Table 3 it can be seen that the recovery of both phenolic compounds increases with increasing activated carbon mass due to the increase of adsorption active sites. At an adsorbent dose of 2%, the recovery of catechin and epicatechin from sago waste effluent was 85% and 53%, respectively. It can be seen that the amount of phenolic compounds adsorbed by the activated carbon from real waste sago effluent (Table 3) is less than that of the synthetic one (Fig. 2). In waste sago effluent, in addition to catechin and epicatechin other compounds such as protein and soluble starch are also present which compete for adsorption active sites resulting in the observed decrease of adsorption capacity toward catechin and epicatechin.

Reusability of adsorbent is crucial in industrial application. The recovery of catechin and epicatechin from activated carbon was performed by supercritical  $\text{CO}_2$  at 313.15 K and 26 MPa under static and dynamic conditions. Details about the supercritical system can be found elsewhere [30]. At static condition, the recovery of catechin from activated carbon was only 1.2% while for epicatechin it was 14.5%. This low recovery is consistent with the solubility



**Fig. 4.** Kinetic adsorption experimental data of epicatechin onto activated carbon NORIT nrs carbon Ea 0.5–1.5 at various initial concentration and plots of (a) pseudo-first order, and (b) pseudo-second order.

data of both phenolic compounds in supercritical  $\text{CO}_2$  under static condition [30,31]. In order to increase the recovery of catechin and epicatechin in supercritical  $\text{CO}_2$ , dynamic extraction experiments were also conducted with flow rates of  $\text{CO}_2$  from 0.1 to 1 kg/h. By increasing  $\text{CO}_2$  flow rate from 0 kg/h (static mode) to 0.1 kg/h, the recovery increased from 1.2% to 2.3% and from 14.5% to 27% for catechin and epicatechin, respectively. Maximum recovery (catechin 9.7% and epicatechin 87.3%) was achieved at a  $\text{CO}_2$  flow rate of 0.7 kg/h. Further increase of  $\text{CO}_2$  flow rate to 1 kg/h had negligible effect on the recovery both compounds.



**Fig. 5.** Correlation between  $C_0$  and  $k_2$ .

**Table 3**  
Adsorption of catechin and epicatechin from sago waste effluent.

$C_{o,1}$ catechin, mg/L	$C_{o,2}$ epicatechin, mg/L	$m$ , mass of activated carbon, g	$C_{e,1}$ , mg/L	$C_{e,2}$ , mg/L	$q_{e,1}$ , mg/g	$q_{e,2}$ , mg/g	% Recovery catechin	% Recovery epicatechin
321.8	158.2	0.112	274.4	143.3	42.3	13.3	14.7	9.4
		0.483	141.2	113.8	37.4	9.2	56.1	28.1
		0.689	110.3	103.8	30.7	7.9	65.7	34.4
		0.921	99.8	100.2	24.1	6.3	68.9	36.7
		1.104	95.5	96.4	20.5	5.6	70.3	39.1
		1.328	85.4	93.1	17.8	4.9	73.5	41.1
		1.573	71.2	87.4	15.9	4.5	77.7	44.7
		1.921	48.3	74.2	14.2	4.3	84.8	52.3

Note: volume of sago waste effluent 100 mL.

Low recovery of phenolic compound, especially catechin is caused by the difference in the polarity between the solute (phenolic compound) and the solvent (supercritical CO<sub>2</sub>). Catechin is highly polar while supercritical CO<sub>2</sub> is non-polar. In order to increase the polarity of supercritical CO<sub>2</sub>, ethanol as co-solvent (5–25%) was used in this study. By adding 5% ethanol at a CO<sub>2</sub> flow rate of 0.7 kg/h, the recovery of catechin increased almost two fold (from 9.7% to 18.2%), and while for epicatechin the recovery reached 95.7%. Increasing the percentage of co-solvent increased the recovery of both compounds. For epicatechin the maximum recovery was 99.2% at 20% of co-solvent. Further increase in co-solvent concentration had negligible effect on the recovery of epicatechin. The un-recovered epicatechin may be strongly bound on carbon surface or epicatechin molecule may be adsorbed inside small or ultra micropore so it could not be desorbed by supercritical CO<sub>2</sub>. At 30% co-solvent, the recovery of catechin was 93.1%. Since further increase of co-solvent concentration changed supercritical condition into subcritical, therefore maceration (303.15 K, 24 h) was used to obtain maximum removal of catechin (97.8%) and epicatechin (99.4%).

#### 4. Conclusion

The recovery of catechin and epicatechin from sago waste effluent by adsorption onto activated carbon followed by supercritical CO<sub>2</sub> desorption was demonstrated in this work. To study the kinetic and equilibria of adsorption, synthetic aqueous catechin and epicatechin solution was used instead of sago waste effluent. The adsorption equilibria and kinetic were obtained isothermally at 303.15 K in static mode condition. The adsorption equilibria of single and binary system were modeled using Langmuir and modified extended Langmuir, respectively. It was found that both of models could represent the experimental data well. In adsorption kinetic experiments, the well-known pseudo-first and pseudo-second models were employed to correlate the experimental data. The pseudo-second model gave better representation of experimental data than the pseudo-first model. The effect of initial concentration on the value of fitting parameters  $k_1$  and  $k_2$  was also studied. The results indicate that  $k_2$  plays a role as time scaling factor, at high  $k_2$ , shorter time is required to reach equilibrium.

Adsorption using real sago waste effluent followed by supercritical CO<sub>2</sub> extraction indicates that this method has potential application in recovery catechin and epicatechin in industrial scale. Ethanol as co-solvent was required to obtain high recovery of catechin from the activated carbon.

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