Adsorption of Vanillin using Macroporous Resin H103

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ABSTRACT: Six resins (Amberlite XAD-16, Amberlite XAD-2, Sepabeads SP207, DIAION HP-20, DM11 and H103) were tested for vanillin adsorption in aqueous solution. All of the resins gave more than 95% adsorption rate except for Amberlite XAD-2 and DM11. Resin H103 was selected for the subsequent work due to its high adsorption capacity and low cost. A kinetic analysis revealed that the adsorption process followed pseudo-second-order kinetic model and occurred rapidly. The equilibrium point was reached after 90 minutes of reaction. Adsorption isotherm was also determined at 25 °C and it was fitted to Langmuir and Freundlich equations using linear regression and non-linear regression (sum of squares) methods. The regression shows that the adsorption of vanillin onto resin H103 followed Langmuir model (R^2 = 0.9984) with a maximum capacity of 73.015 mg/g.

1. INTRODUCTION

Vanillin (4-hydroxy-3-methoxybenzaldehyde, $C_8H_8O_3$, 152.15 g/mol) is a compound, that finds a great interest in food and beverages industries. It is a widely used flavour all around the world, in the form of vanilla extract. It is naturally found in the beans of *Vanilla planifolia* (Reineccius 2005). However, only 0.2% of vanillin is extracted from the beans, and their rate varies between \$30/kg and \$120/kg (Priefert *et al*. 2001). This relatively high price of vanilla pods is mainly due to the labour-intensive activities of cultivation, manual pollination, harvesting and curing of vanilla pods to obtain natural vanillin. As a result, presently, vanillin is produced synthetically to meet the market demands, and it has a very low price at about \$12/kg. At the same time, extensive studies are also carried out on the production of vanillin by microbial transformation from different substrates.

In order to recover the vanillin from aqueous solution or fermentation broth, a number of separation techniques could be applied. One of the promising techniques is adsorption using resin. One of the advantages of using adsorption is that it is able to recover solutes from dilute solutions, which in turn reduces the number of purification steps required in the overall recovery process. It also has high selectivity in separation, especially the affinity adsorption type, as well as a relatively simple design of operation and scale up, and low cost. For the past several years, adsorption has gained a lot of interest in separating vanillin, from either aqueous solution or fermentation broth. Polymeric resin SEPABEADS SP206 was characterized for adsorption of synthetic vanillin in both static and dynamic separation modes (Zabkova *et al*. 2006). Meanwhile, HD-8 resin was found to be superior to avoid inhibition of vanillin towards *Bacillus fusiformis* culture (Zhao *et al*. 2006). In a previous report, resins NKA-2, S-8 and H103 (macroporous

adsorbent resins with cross-linked polystyrene) were tested, and H103 resin was found to have the greatest adsorption capacity for vanillin (Zhang *et al*. 2008). To date, the highest vanillin concentration was obtained at 19.2 g/l using resin DM11, which in turn would assist the crystallization step (Hua *et al*. 2007). Another report demonstrated the application of macroporous adsorption resin D101 for the separation of vanillin and syringaldehyde from oxygen delignification spent liquor (Wang *et al*. 2010). Recently, an anisole-modified hyper-cross-linked polystyrene (HJ-108) was characterized and evaluated in the adsorption of vanillin from aqueous solution (Jin and Huang 2012).

A number of resins are available for the recovery of vanillin and their characteristics differ from one resin to another. This work targeted at characterizing the adsorption process of vanillin onto resin H103 in relation to the effect of several parameters such as resin dosage, initial vanillin concentration, contact time, pH and temperature. Kinetics, isotherms, and thermodynamics studies were then carried out to further elucidate the process. In addition, the linear and non-linear regression methods were implemented to fit the experimental data with pseudo-first-order and pseudo-second-order kinetic models, as well as Langmuir and Freundlich isotherms. It is expected that the adsorption process will be further utilized for the separation of biovanillin, which is produced by microbial transformation of ferulic acid obtained from alkaline hydrolysis of oil palm empty fruit bunch.

2. EXPERIMENTAL SECTION

2.1. Materials

Six macroporous adsorbent resins were tested. Before the adsorption process, all the resins were soaked in absolute methanol and subsequently washed with distilled water (Lee *et al*. 2009). The properties of resins used are listed in Table 1. The selection of the resins was primarily based on a preliminary study and previously published reports on vanillin adsorption using macroporous

TABLE 1. Properties of the Resins [a] Used

Resin	Matrix	Specific surface area (m^2/g)	Particle size (mm)	Porosity (%)	Average pore diameter (Å)	Reference
Amberlite XAD-16	Styrene–divinylbenzene	900	0.56–0.71	55	100	Krings *et al*. (1993)
Amberlite XAD-2	Styrene–divinylbenzene	335.9	0.62	42	90	Krings *et al*. (1993)
Sepabeads SP207	Brominated styrene–divinylbenzene	650	0.35	–	105	Zabkova *et al*. (2006) [b]
DIAION HP-20	Styrene–divinylbenzene	500	0.25–0.85	–	260	Krings *et al*. (1993)
DM11	–	500	0.3–1.25	–	–	Hua *et al*. (2007)
H103	Styrene–divinylbenzene	900–1100	0.3–1.25	55–59	85–89	Zhang *et al*. (2008)

[a] All resins were purchased from Sigma, except for DM11 and H103, which were from Shanghai Sunny Scientific Collaboration Co. Ltd. All the properties were provided by the respective suppliers.

[b] SEPABEADS SP206 (Mitsubishi Chemical Corporation) is equivalent to Sepabeads SP207.

resin (Zabkova *et al.* 2006; Hua *et al.* 2007; Zhang *et al.* 2008). Synthetic vanillin was obtained from Acros Organics (Belgium).

2.2. Vanillin Separation by Batch Adsorption

All adsorbent resins were tested for their capacity of vanillin separation. Approximately 0.5 g adsorbent resin and 100 ml vanillin solution at 50 mg/l were mixed in a conical flask. Several such samples were prepared in separate conical flasks. Approximately 1-ml sample was withdrawn at a designated interval and the residual vanillin concentration was monitored by UV–visible spectrophotometer at 280 nm (Huesgen 2011). The vanillin adsorbed per unit amount of resin (q_t) and percentage of vanillin adsorbed (%) were calculated by the following equations, respectively:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

$$\% \, \text{Adsorbed} = \frac{(C_0 - C_t)100}{C_t} \tag{2}$$

where q_t is amount of solute adsorbed per unit amount of adsorbent at time t (mg/g), C_0 is initial vanillin concentration (mg/l), C_t is residual vanillin concentration in liquid at time t (mg/l), V is volume of the solution (l) and m is mass of resin (g).

The selected resin was then characterized by manipulating several adsorption parameters. Using the same approach, the amount of resin was varied between 0.5 and 5.0 g, the pH value was varied between 3 and 7, and the temperature was varied from 25 to 55 °C (Krings *et al.* 1993; Zabkova *et al.* 2006; Hua *et al.* 2007; Zhang *et al.* 2008). For the kinetics study, the adsorption process was prolonged up to 300 minutes. Meanwhile for the isotherms study, the initial vanillin concentration was varied up to 800 mg/l.

2.3. Adsorption Kinetics

The adsorption kinetics is normally described by either pseudo-first-order or pseudo-second-order kinetics (Ho 2006b; Liu and Shen 2008). The pseudo-first-order equation is given by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where q_t is the amount of solute adsorbed at time t (mg/g), q_e is the amount of solute adsorbed at equilibrium (mg/g) and k_1 is the pseudo-first-order rate constant (minute^{-1}). The equation can be linearized to

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t \tag{4}$$

and a plot of $\ln(q_e - q_t)$ versus t can be constructed to obtain the rate constant.

The pseudo-second-order equation is given by the following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is the pseudo-second-order rate constant (g/mg.minute) and can be linearized to

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

A plot of t/q_t versus t would provide the pseudo-second-order rate constant.

2.4. Adsorption Isotherm

The most frequently used equations for the adsorption isotherm are the Langmuir and Freundlich isotherms (Ho 2006a). These equations explain the relationship between the solute concentration in both liquid and adsorbent's surface at equilibrium. In this work, the equilibrium data were fitted to both equations. The coefficient of determination (R^2) was used as the fitness indicator.

The following equation represents the Langmuir isotherm:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

where q_e is the solute bound per unit amount of adsorbent (mg/g), q_m is the maximum adsorption capacity, K_L is the affinity constant for Langmuir isotherm (l/mg) and C_e is the equilibrium concentration of solute in liquid or unbound solute (mg/l).

The Freundlich isotherm is expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{8}$$

where q_e is the solute bound per unit amount of adsorbent (mg/g), K_F is the Freundlich constant (mg/g), C_e is the equilibrium concentration of solute in liquid or unbound solute (mg/l) and $1/n$ is a constant reflecting the solute affinity towards the adsorbent.

Separation factor can also be determined from the Langmuir model (Liu *et al.* 2010). Denoted by R_L, it was calculated by using

$$R_L = \frac{1}{1 + K_L C_0} \tag{9}$$

The value of R_L suggests the nature of the adsorption process with the following criteria: irreversible when $R_L = 0$, favourable when $0 < R_L < 1$, linear when $R_L = 1$ and not favourable when $R_L > 1$.

2.5. Adsorption Thermodynamics

The mechanism of adsorption can be deduced from thermodynamic parameters: Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) (Liu 2009). They can be obtained from

$$\ln K_C = -\frac{\Delta G°}{RT} = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

where K_C, R and T are the concentration ratio between vanillin adsorbed on the adsorbent and in the solution or thermodynamic equilibrium constant, gas constant (8.314 J/mol.K) and temperature (K), respectively.

3. RESULTS AND DISCUSSION

3.1. Preliminary Selection of Resins Based on Adsorption Capacity

Table 2 shows the comparison between all the resins. From the six resins tested, four of them gave substantial vanillin adsorption of more than 95%. One of the main reasons for variation in the amount of adsorption is the surface area of the resin particles. Based on the top two resins, SP207 and H103, the former has a lower surface area (650 m^2/g), and by default, the adsorption capacity would be low as well. However, resin SP207 gave comparable performance (99.04%) as resin H103 (98.58%), which has a surface area of 900–1100 m^2/g, due to a functional group attached to its core structure (brominated styrene–divinylbenzene). The chemically modified resin was proven to modify the interaction strength between solutes and surfaces, thereby enhancing the adsorption capacity, despite the lower surface area. For example, chemically modified Amberlite XAD-2 resins (bromoethylated and chloromethylated) showed great improvement in the adsorption of aspartame (Bautista *et al.* 2003). The chloromethylated Amberlite XAD-2, with a surface area of 143 m^2/g, was capable of adsorbing 25% more aspartame than the unmodified Amberlite XAD-2, with a surface area of 312 m^2/g.

There was also a report on resin H103, which adsorbed approximately 75% of the vanillin from an initial concentration of 1000 mg/l after 150 minutes of reaction period (Zhang *et al.* 2008). Meanwhile, resin DM11, with the surface area of more than 500 m^2/g, was capable of adsorbing 40% of the initial vanillin (10,000 mg/l) on the surface of *Streptomyces* sp. V-1 after 120 minutes

TABLE 2. Amount of Vanillin Adsorbed on Six Adsorbent Resins

Adsorbent resin	Vanillin adsorbed (%)
XAD-16	97.54
XAD-2	87.05
SP207	99.04
HP-20	95.44
DM11	73.25
H103	98.58

Note: The experiment was done in duplicates at 25 °C and 150 rpm (0.5 g resin, 100 ml of vanillin solution at 50 mg/l). The data were taken after 180 minutes of reaction.

of resin addition into the culture suspension (Hua *et al*. 2007). In another work with an initial amount of 80 mg/l, a comparable 95% reduction in vanillin and syringaldehyde concentration was observed after 120 minutes of adsorption using resin D101, which has a surface area value of 400–550 m^2/g (Wang *et al*. 2010). Based on the manufacture's price ($115/kg) and economic viability for scaling-up purpose as compared with other resins, resin H103 was selected for further investigation.

3.2. Effect of pH, Temperature and Resin Dosage on Resin Adsorption Capacity

Table 3 shows no considerable difference in the amount of vanillin adsorbed onto the adsorbent resin H103 within the tested pH range. This might be due to the neutral state of the vanillin molecules within pH 2.0–6.0 (Li *et al*. 1998). Moreover, the current result facilitates the subsequent processes in vanillin separation from fermentation broth, with no additional step to be included to adjust the pH value. It was reported that pH 7.2 was optimal for vanillin production from ferulic acid, which was also the best condition for vanillin recovery by pervaporation (Brazinha *et al*. 2011). In another report, a fluctuation of pH value within the range of 4.0 to slightly above 6.5 was observed during the course of vanillin production by *Pycnoporus cinnabarinus* (Stentelaire *et al*. 2000). Based on the results obtained, pH 6.0 was selected for subsequent experiments because the pH of freshly prepared vanillin solution was approximately 5.9–6.1.

Table 4 shows that the temperature did not have any major effect on vanillin adsorption. This result simplifies the subsequent recovery activities, where the separation of vanillin can be carried out instantly from the fermentation process without having to adjust the temperature to any desired level. As for the thermodynamic parameters, the negative enthalpy value of −17.956

TABLE 3. Effect of Different pH of the Vanillin Solution Towards Vanillin Adsorption onto Adsorbent Resin H103

pH	Vanillin adsorbed (%)
3	97.93
4	98.12
5	98.17
6	98.11
7	98.06

Note: The experiment was done in duplicates at 25 °C and 150 rpm (0.5 g resin, 100 ml of vanillin solution at 50 mg/l). Data were taken after 90 minutes of adsorption process.

TABLE 4. Effect of Temperature on Vanillin Adsorption onto Resin H103 and Thermodynamic Parameters

T (°C)	q_e (mg/g)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol.K)
25	2.45	−9.726	−17.956	−27.617
35	2.43	−9.450		
45	2.44	−9.173		
55	2.40	−8.897		

Note: The experiment was done in duplicates at 25 °C and 150 rpm (0.5 g resin, 100 ml of vanillin solution at 50 mg/l). Data were taken after 90 minutes of adsorption process.

kJ/mol indicated that the adsorption was exothermic, which was in agreement with the fact that the adsorption process is generally exothermic (Ruthven 1984). At the same time, the magnitude of enthalpy obtained shows that the vanillin adsorption onto resin H103 was a physical adsorption, or also called physisorption, as it falls in the range of 2.1–20.9 kJ/mol (Liu 2009). Meanwhile, the negative Gibbs free energy values between –9.726 and –8.897 kJ/mol suggest that the adsorption was spontaneous (Wang *et al.* 2007; Michailof *et al.* 2008). In addition, the increased free energy with increased temperature indicated a decrease in vanillin adsorption at a higher temperature. The negative entropy value of –27.617 J/mol.K suggested a more ordered arrangement of the vanillin molecules on the adsorbent surface (Wang *et al.* 2007; Liu *et al.* 2010).

There was quite a steep increment on the amount of vanillin adsorbed when the resin dosage was increased from 0.5 to 1.0 g (Figure 1), with maximum adsorption at 2.0 g of resin. This trend was in parallel with the principle of adsorption that involved the binding of solutes on the surface of the adsorbent, in which more binding sites will be available as the amount of surface area is increased (Ghosh 2006). However, in the next 1.0-g increment in resin dosage, the adsorption of vanillin onto resin H103 showed small increment and slightly decreased after 3.0 g. By contrast, a reverse trend was observed in the resin equilibrium capacity. The value decreased considerably and plateaued afterwards. This phenomenon can be explained by the fact that there was a reduced amount of vanillin adsorbed per unit mass of resin. This led to more unused adsorption sites, which lowered down the adsorption capacity (Hsu *et al.* 1997; Kumar and Min 2011).
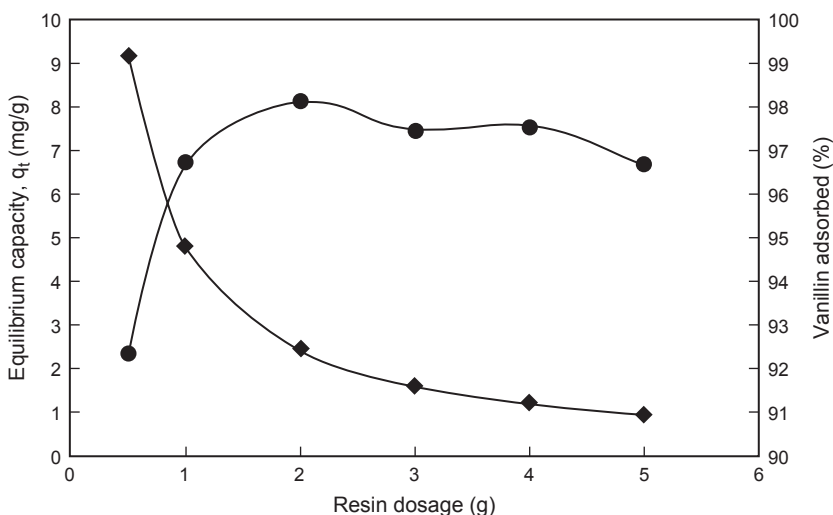

Figure 1. Vanillin adsorption uptake of resin H103 at different resin H103 dosages. All experiments were performed at 25 °C and 150 rpm (100 ml of vanillin solution at 50 mg/l). Data were taken after 90 minutes of adsorption process. Closed diamonds = equilibrium capacity, closed circles = amount of vanillin adsorbed.

3.3. Adsorption Kinetics

The study of kinetics was performed to determine the effect of time on vanillin adsorption. At the same time, the reaction order and rate were also identified. The most widely used expressions are pseudo-first-order and pseudo-second-order models (Ho 2006b; Liu and Shen 2008). Figure 2
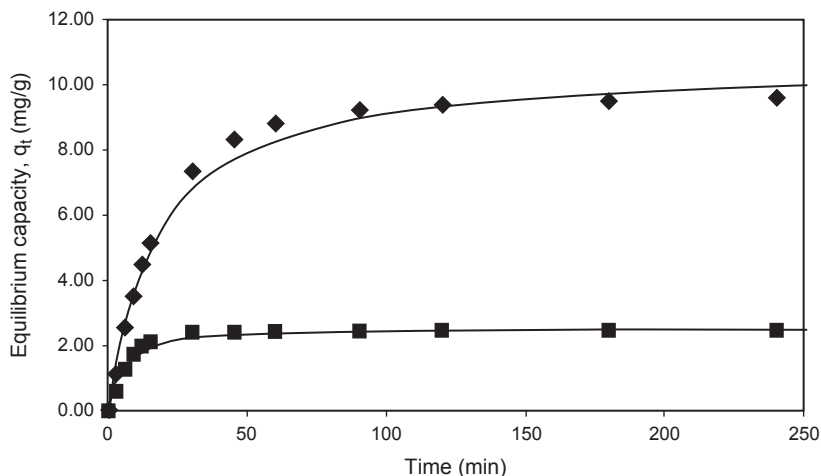
Figure 2. Contact time profile of vanillin adsorption onto resin H103. All experiments were performed at 25 °C and 150 rpm (100 ml of vanillin solution at 50 mg/l). Closed diamonds = kinetics data for 0.5 g of resin, closed squares = kinetics data for 2.0 g of resin.

shows the time course of vanillin adsorption onto resin H103. It was observed that the adsorption was rapid in the first 15 minutes. A similar trend was also observed on the vanillin adsorption onto resin D101, which also has almost identical physical properties as resin H103 (Wang *et al*. 2010). This rapid adsorption might be due to the high surface area of the resin that could adsorb higher amount of solute per unit time during the initial stage of the process. In addition, generally, a reduced mass transfer between the bulk liquid phase and occupied solid surface also could be the reason of slower adsorption rate after a certain period of reaction. A slight difference in equilibrium points for both dosages was also observed. Higher amounts of adsorbent, which provide higher surface area, could accelerate the process towards equilibrium.

The kinetics data were then fitted to pseudo-first-order and pseudo-second-order models, as shown in linearized forms in Figures 3 and 4, respectively. Based on the R^2 values of 0.995 and 0.998 for 0.5 and 2.0 g of resins, respectively, it was obvious that the kinetics of vanillin adsorption onto resin H103 can be described by the pseudo-second-order model. From these figures, the constant parameters for both models were determined and listed in Table 5.

Essentially, there is no reason to fix the kinetics to be either order unless detailed adsorption mechanisms are well explained (Liu and Shen 2008). The authors also mentioned that reaction order cannot be predicted theoretically as there might be mixed-order reactions with its own fractional reaction rate. However, another report explained that the adsorption of lower molecular weight solutes on smaller adsorbent particles can be better explained by pseudo-second-order kinetic model (Wu *et al*. 2009).

3.4. Adsorption Isotherm

Figure 5 shows the experimental data that were fitted to both Langmuir and Freundlich equations by utilizing linear regression and non-linear regression methods. The values for each constant are presented in Table 6. The experimental data obtained fitted well to both isotherms; however, the Langmuir model slightly better fitted than the Freundlich model (based on
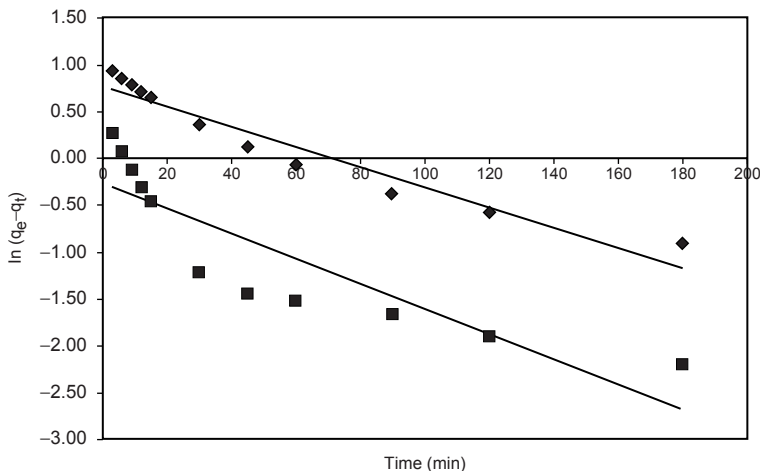
Figure 3. Pseudo-first-order kinetics of vanillin adsorption onto resin H103. Closed diamonds = linearized data for 0.5 g of resin, closed squares = linearized data for 2.0 g of resin.
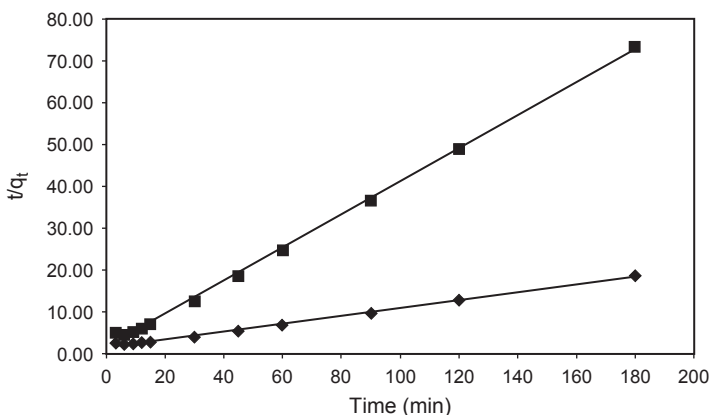

Figure 4. Pseudo-second-order kinetics of vanillin adsorption onto resin H103. Closed diamonds = linearized data for 0.5 g of resin, closed squares = linearized data for 2.0 g of resin.

TABLE 5. Kinetics Parameters for Vanillin Adsorption onto Resin H103

Resin dosage (g)	Pseudo-first-order model			Pseudo-second-order model		
	q_e (mg/g)	k_1 (minute^{-1})	R^2	q_e (mg/g)	k_2 (g/mg.minute)	R^2
0.5	6.095	0.025	0.935	10.684	0.006	0.995
2.0	0.553	0.031	0.775	2.540	0.090	0.998

R^2 values). The adsorbent resin H103 used in this study showed a comparable vanillin adsorption capacity of 89.60 mg/g using number 1 macroporous resin (Wang *et al*. 2005), but it was very much higher than resin D101, with only 3.13 mg/g (Wang *et al*. 2010). It was also
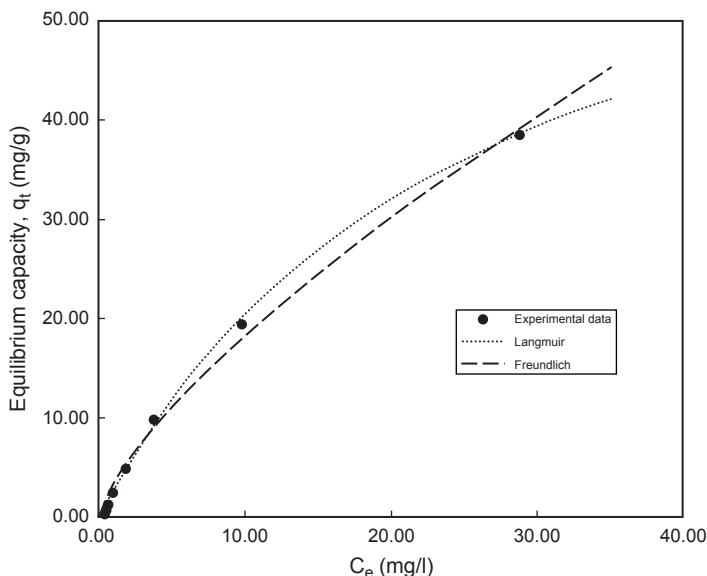
Figure 5. Equilibrium adsorption isotherms at 25 °C for vanillin adsorption onto adsorbent resin H103. Langmuir isotherm was the best to explain the adsorption of vanillin onto resin H103 (represented by dotted line, obtained by non-linear regression). Closed circles = experimental data, dotted lines = Langmuir fitting, dashed line = Freundlich fitting.

TABLE 6. Vanillin Adsorption Isotherm Parameters Obtained by Linear and Non-Linear Regression

Isotherm	Langmuir			Freundlich		
Parameter	q_m (mg/g)	K_L (l/mg)	R^2	K_F (mg/g)	$1/n$	R^2
Linear regression	73.529	0.038	0.9891	2.912	0.80	0.9875
Non-linear regression	73.015	0.039	0.9984	3.477	0.72	0.9891

obvious that a modified resin gave a better capacity with a value of 211.20 mg/g (Jin and Huang 2012). In addition, a biosorbent, adsorbent prepared from biomass, also gave a good adsorption capacity as high as 191.41 mg/g (Michailof *et al*. 2008). In a different approach using column adsorption, a very high maximum capacity of resin H103 with the value of 416 mg/g was observed (Zhang *et al*. 2008).

The separation factor for vanillin adsorption onto resin H103 was favourable as the value of R_L for initial concentration (C_0) of vanillin of 50 mg/l was 0.00027. The $1/n$ value in the Freundlich isotherm could tell the extent and favourability of the adsorption process, in which the $1/n$ value between 0.1 and 1.0 was found to favour adsorption (Treybal 1980), whereas a value between 0.1 and 0.5 represents a good adsorption. All the other $1/n$ values represent a moderately difficult adsorption. Based on the result obtained ($1/n = 0.72$), the adsorption of vanillin using resin H103 can be considered favourable, which complemented the R_L value obtained by Langmuir model.

4. CONCLUSIONS

In this work, the adsorbent resin H103 has shown good ability for vanillin adsorption. It was estimated that 95% of vanillin was adsorbed after 90 minutes of reaction time with marginal effects from pH and temperature. Both linear and non-linear regression methods were used for Langmuir and Freundlich isotherm fitting. Based on the coefficient determination, the process was better fitted to Langmuir model ($R^2 = 0.9984$), which gave a value of 0.039 l/mg and 73.015 mg/g for Langmuir constant (K_L) and maximum adsorption capacity (q_m), respectively. The kinetics study also revealed that the adsorption was spontaneous and followed a pseudo-second-order kinetic model. From these results, further work proceeds with the adsorption of vanillin onto resin H103 in a fixed-bed column and its adsorption behaviour will be evaluated.

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