FIXED-BED ADSORPTION OF AQUEOUS VANILLIN ONTO RESIN H103

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ABSTRACT: The main objective of this work was to design and model a fixed-bed adsorption column for the adsorption of vanillin from aqueous solution. Three parameters were evaluated for identifying the performance of vanillin adsorption in fixed-bed mode, which were bed height, vanillin initial concentration, and feed flow rate. The maximum adsorption capacity increased more than threefold to 314.96 mg vanillin/g resin when the bed height was increased from 5 to 15 cm. Bohart-Adams model and Belter equation were used for designing a fixed-bed column and predicting the performance of the adsorption process. A high value of determination coefficient (R^2) of 0.9672 was obtained for the modelling of vanillin adsorption onto resin H103.

ABSTRAK: Tujuan utama kajian ini adalah membentuk dan membina model penyerapan turus-padat bagi penyerapan vanilin daripada larutan akues. Tiga parameter telah dikaji bagi menentukan prestasi penyerapan vanilin dalam mod turus padat, iaitu ketinggian padatan, kepekatan awal vanilin, dan kadar aliran suapan. Peningkatan ketinggian padatan daripada 5 kepada 15 cm telah meningkatkan kapasiti penyerapan maksimum sebanyak lebih daripada tiga kali ganda kepada 314.96 mg vanilin/g resin. Model persamaan Bohart-Adams dan Belter telah digunakan untuk membentuk kolum turus padat dan prestasi proses penyerapan dijangakan menguna pakai persamaan ini. Nilai pekali penentuan (R^2) yang tinggi pada 0.9672 telah diperoleh daripada model penyerapan vanilin menggunakan resin H103.

KEYWORDS: *adsorption; vanillin; fixed-bed; breakthrough curve*

1. INTRODUCTION

A sweet odour characteristic is the main driver for vanillin's use in food and beverage industries, as well as perfumes and cosmetics industries. Vanillin (4-hydroxy-methoxybenzaldehyde, $C_8H_8O_3$, 152.15 g/mol) is produced by a traditional, tedious, and time-consuming process of curing vanilla pods from vanilla plants [1]. It can also be manufactured from several chemicals such as curcumin and eugenol, but the processes deal with high temperatures and pressures [2]. In addition, the waste products from the chemical reactions may impose problems on the environment [3]. Moving forward, biotechnology offers ways of producing vanillin at ambient conditions by the action of microorganisms and/or enzymes on abundant sources of raw material such as biomass.

Several components from biomass are identified as potential sources for the production of vanillin such as ferulic acid, vanillic acid, and lignin [4].

Due to its phenolic and aldehyde functional groups in its molecular structure, vanillin can be toxic to the producing microorganisms. Therefore, a proper separation technique is needed to intermittently remove the vanillin as it is being produced. Membrane separation [5-7], extraction [8], and crystallisation [9] are among the possible separation techniques to recover vanillin directly from the production vessel. In addition, adsorption has gained a lot of interest among researchers to separate vanillin using several types of polymeric adsorbents such as Sephabeads SP206, NKA-2, S-8, and DM11 [10-17]. An anisole-modified hyper-cross-linked polystyrene HJ-108 [15] and Sepabeads SP700 [17] are among the recent reported polymeric resins to be used for vanillin adsorption in batch and fixed-bed modes.

Compared to the batch adsorption process, fixed-bed mode offers a greater insight into the adsorption behaviour. The adsorbent is packed in a column and solution is passed through the adsorbent bed. The packed column can be attached to an automatic delivery system or let gravity perform all the work. From the process, the most studied part is the breakthrough analysis. The solution is pumped through the packed column for continuous adsorption, until a point where the adsorbent is saturated with the target molecule. During the continuous feed, the concentration of target molecule is monitored in the effluent. A plot of the ratio of effluent to feed concentration (C_t/C_0) versus time (t) explains the behaviour of the adsorption process in fixed-bed mode, which is known as a breakthrough curve. A breakthrough point is where an acceptable amount of target molecule appears in the effluent that could be discarded (t_b – breakthrough time, C_b – breakthrough concentration). The breakthrough point value depends on any particular application. Normally, the range is 1% to 10% of the feed concentration [18], but there are often cases where the acceptable limit is taken as 5% [19].

One of the advantages of utilising the fixed-bed mode is a large volume of the solution can be introduced to the adsorbent, but feeding the solution beyond the breakthrough point would result in loss of the target molecule. On the other hand, feeding a small volume of the solution would result in incomplete utilisation of the adsorbent's capacity in the column [18]. This breakthrough analysis can determine the performance of a fixed-bed, and at the same time, a minimum number of experiments can be done so that the prediction of a larger scale fixed-bed adsorption could be done as well [20-23]. For all the advantages of the fixed-bed mode, this work was executed to evaluate the vanillin adsorption onto resin H103 in a fixed-bed mode. The use of resin H103 has been reported earlier for the adsorption of vanillin in batch mode [24].

2. METHODOLOGY

2.1 Materials Preparation

Resin H103 was purchased from Shanghai Sunny Scientific Collaboration Co. (Ltd). Vanillin used in this work was purchased from Acros Organics (Belgium). Fixed-bed column adsorption studies were performed in Tricon columns supplied by GE Healthcare (i.d. 10 mm). The column was packed with resin H103 at certain heights. Prior to packing, the resin was soaked in absolute methanol and subsequently filtered and washed with distilled water [25]. All experiments were performed at room temperature with an ÄKTAexplorer 100 system (Amersham Pharmacia Biotech).

2.2 Scale-Up Analysis for Vanillin Adsorption

The general methods were based on a previous work with slight modifications [26]. Three bed heights were used in this work: 5, 10, and 15 cm. The initial flow rate used was 5 mL/min and the vanillin solution was prepared at 1,000 mg/L [12, 27]. The effluents from the column were collected at fixed time intervals of 6 min and analysed offline using a UV-visible spectrophotometer at 280 nm [28].

The breakthrough curve analysis was done by varying any one of the parameters. In this work, by fixing the bed height at 10 cm, two other parameters were varied, which were the flow rate (10 mL/min) and vanillin initial concentration (900 mg/L). Subsequently, a breakthrough curve was plotted as the ratio of effluent vanillin concentration to vanillin initial concentration (C_t/C_0) versus time (t).

2.3 Fixed-Bed Column Design

A Bohart-Adams model was used in the design of a fixed-bed vanillin adsorption column, as shown in Eq. (1).

$$ln\left(\frac{C_0}{C_b}-1\right)=ln\left(exp\frac{kNZ}{V}-1\right)-kC_0t \tag{1}$$

where, C_0 is the initial vanillin concentration (mg/L), C_b is the breakthrough vanillin concentration (mg/L), k is the rate constant (g/mg·h), N is the adsorption capacity (mg/g), Z is the bed height (cm), V is the linear velocity (cm/min), and t is the breakthrough time (min) [26, 29].

For the determination of adsorption capacity (N) and rate constant (k), the model was then linearised, as shown in Eq. (2).

$$t=\frac{NZ}{C_0V}-\frac{1}{kC_0}ln\left(\frac{C_0}{C_b}-1\right) \tag{2}$$

where, the slope (m) is $\frac{N}{C_0V}$, and the intercept (c) is $-\frac{1}{kC_0}ln\left(\frac{C_0}{C_b}-1\right)$. A plot of time versus bed height was used to determine the adsorption capacity and rate constant.

At $t = 0$, Eq. (2) was used to determine the minimum bed height of resin H103 to give an effluent concentration of C_b, or critical bed height (Z_0), as shown in Eq. (3).

$$Z_0=\frac{V}{kN_0}ln\left(\frac{C_0}{C_b}-1\right) \tag{3}$$

For designing a new fixed-bed adsorption column based on a different vanillin initial concentration, the slope and intercept parameters in the linearised plot were determined by the following relationships in Equations (4) and (5) [26].

$$m_2=m_1\frac{C_1}{C_2} \tag{4}$$

$$c_2=c_1\left(\frac{C_1}{C_2}\right)\left[\frac{\ln(C_2-1)}{\ln(C_1-1)}\right] \tag{5}$$

where m_1 and m_2 are the slope parameters for the original and new vanillin initial concentrations, respectively, and C_1 and C_2 are the original and new vanillin initial concentrations, respectively.

Similarly, for designing a new fixed-bed adsorption column based on a different feed flow rates, the slope and intercept parameters in the linearised plot were determined by Eq. (6) [26].

$$m_2 = m_1 \frac{Q_1}{Q_2} \tag{6}$$

where Q_1 and Q_2 are the original and new feed flow rates, respectively. The intercept value change is assumed insignificant with respect to different feed flow rates [29].

2.4 Modelling of Breakthrough Curve

The breakthrough curve for fixed-bed vanillin adsorption onto resin H103 was modelled based on a two-parameter model [30], as shown in Eq. (7).

$$\frac{C_E}{C_F} = \frac{1}{2}\left[1 + erf\left(\frac{t - t_0}{\sqrt{2}\sigma t_0}\right)\right] \tag{7}$$

where C_E and C_F are the vanillin concentrations in the effluent and feed, respectively, t_0 is the time at which the vanillin concentration in the effluent is half in the feed (determined experimentally), erf(x) is the error function of x, and σ represents the standard deviation, a measure of the slope of the curve (determined experimentally). The experimental data were calculated using the above equation, and plotted on the same plot of C_t/C_0 versus time of the experimental data. The experiments were done with the bed height of 10 cm, volumetric flow rate of 5 mL/min, and initial vanillin concentration of 900 mg/L. Coefficient of determination (R^2) was determined to verify whether the model obtained was acceptable or not.

3. RESULTS AND DISCUSSION

3.1 Breakthrough Curve Analysis for Fixed-bed Adsorption

Three parameters are usually varied in fixed-bed adsorption, namely bed height, solute initial concentration, and feed flow rate. By varying these three factors, the behaviour of the adsorption in the fixed-bed column can be determined. In this work, only bed height was varied to determine the dynamic behaviour of vanillin adsorption onto resin H103 that was packed in a column.

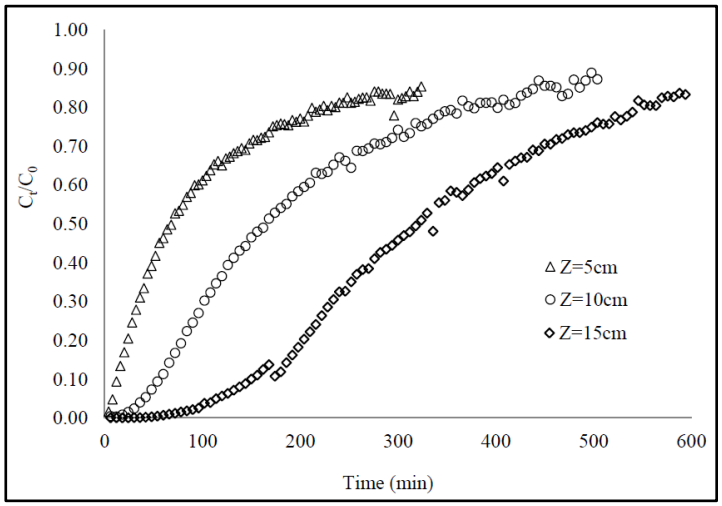

Fig. 1: The effect of bed height on breakthrough curves for vanillin adsorption onto resin H103.

Fig. 1 shows the effect of bed height on the breakthrough curves for vanillin adsorption onto resin H103. The breakthrough time decreased considerably with the increasing bed height. For 15-cm bed height, the exit concentration of vanillin increased very slowly at the beginning of the process, as compared to the other two bed heights. For 5-cm bed height, the vanillin was detected in the quite early stage of the feeding process. For a breakthrough point of 10%, the time taken in a 15-cm bed height was 150 min. It was reduced to 60 min for 10-cm bed height and roughly 12 min for 5-cm bed height. In the actual separation process using this mode, it would be beneficial to stop the feeding of the sample when the effluent reaches this breakthrough point, and the adsorbed solutes are eluted out from the column. After that, the adsorbent is normally regenerated for the next cycle of adsorption process, or the spent adsorbent is discarded [31].

The steepness of the curve determines the utilisation of the packed adsorbent. For a good and efficient fixed-bed, a very steep breakthrough curve would be observed, which means that most of the adsorbent capacity is utilised for the adsorption process [19]. In this work, the steepness of the curves obtained was considered as gradual, and this shows that the fixed-bed columns were of medium performance, as shown in Table 1 that the fraction of total bed was only used up to 0.417. In a published work, polymeric adsorbent Sephabeads SP206 gave a good utilisation of the adsorbent in a fixed-bed mode for the recovery of vanillin by obtaining steep breakthrough curves [12]. A similar trend was also reported on the effect of bed height in the adsorption of gallic acid onto activated carbon cloth and activated carbon I-60 [26].

Table 1: The effect of bed height towards breakthrough capacity

Bed height (cm)	Amount of adsorbent (g)	Breakthrough time (min)	Breakthrough capacity (mg vanillin/g adsorbent)	Fraction used up to breakpoint	Maximum adsorption capacity (mg/g)
5	2.5	12	10.43	0.107	96.813
10	5.0	60	51.99	0.268	194.125
15	7.5	150	131.44	0.417	314.960

In a fixed-bed column of resin H103, an increase of its bed height caused the vanillin to have more time to be in equilibrium with the resin. This resulted into an increased time observed to detect vanillin in the effluent, hence the longer breakthrough time, as shown in Table 1 [32, 33]. It may be because the increase in bed height gives more time for the solutes to have contact with the adsorbent, which results into higher removal capacity and lower solute concentration in the effluent. Besides, at larger bed height, more effective surface area of adsorbent is available that offers more active sites for adsorption. For this work, when the bed height was increased threefold, the breakthrough capacity of the fixed-bed adsorption increased more than tenfold from 10.43 to 131.44 mg vanillin/g adsorbent. The maximum adsorption capacity also increased approximately threefold.

3.2 Designing Fixed-bed Column for Vanillin Adsorption

A Bohart-Adams model was used on the assumption that the adsorption process is continuous where equilibrium is not attained instantaneously [34]. This model was used for designing a fixed-bed column, by varying any one of the parameters. The model explains the performance of a continuous column via Eq. (1). The equation was rearranged to obtain a linearised plot of service time versus bed height, as shown in Fig. 2.

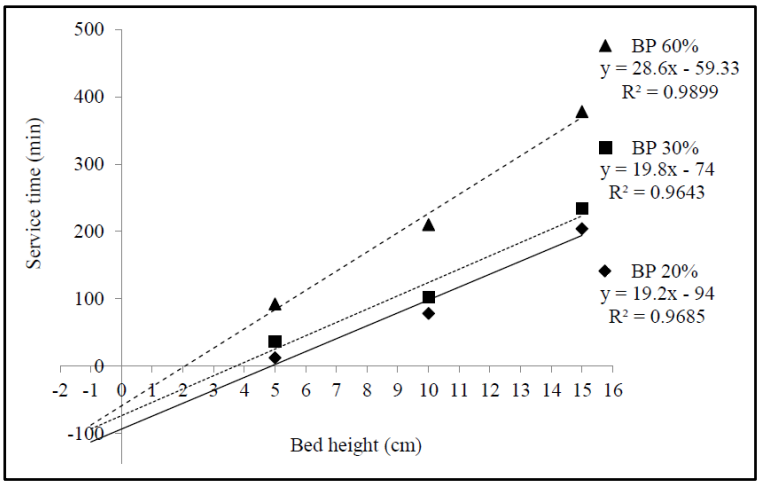

Fig. 2: Bohart-Adams model for different breakthrough points (BP) at different bed heights, constant flow rate (5 mL/min), and constant vanillin initial concentration (1,000 mg/L).

Under a constant condition of flow rate (5 mL/min) and vanillin initial concentration (1,000 mg/L), three different breakthrough points (20%, 30%, and 60%) were utilised for this model analysis. The slopes and intercepts of each linear line were used to obtain the dynamic adsorptive capacity and adsorption rate constant, as shown in Table 2.

Table 2: Bohart-Adams model constants for the vanillin adsorption onto fixed-bed resin H103.

Breakpoint (%)	Bed height (cm)	Service time (min)	Slope, *m* (min/cm)	Adsorption capacity, *N* (mg/g)	Intercept, *c* (min)	Adsorption rate constant, *k* (g/mg·h)	Critical depth, Z_0 (cm)
20	5	12	19.2	116.41	−94	0.929	4.896
	10	78					
	15	204					
30	5	36	19.8	120.05	−74	0.721	3.737
	10	102					
	15	234					
60	5	92	28.6	173.40	−59.33	~0	2.075
	10	210					
	15	378					

The adsorptive capacity increased according to the increment of the breakthrough point. This reflects the amount of vanillin adsorbed onto the resin. In the Bohart-Adams model, this value is used to predict the performance of the fixed-bed adsorption processes with different parameters. Meanwhile, critical depth denotes a minimum height sufficient for the breakthrough concentration. Critical depths (Z_0) of 4.9, 3.7, and 2.1 cm were obtained from the calculation and they were in agreement with the graphical determination shown in Fig. 2 (by extrapolating the linear lines).

Values in Table 2 were used in predicting the performance of the fixed-bed adsorption of vanillin onto resin H103 at different vanillin initial concentrations and feed flow rates. The method applied was based on Eq. (1). For a new vanillin concentration, it was possible to predict the performance of the fixed-bed column using the slope and

intercept parameters in the linearised plot (Fig. 2). The prediction of new slope (m_2) and intercept (c_2) were made using Eqs. (4) and (5), respectively.

Table 3 lists the new slopes and intercepts and the predicted and observed times that occurred for fixed-bed adsorption with a new vanillin concentration of 900 mg/L. The predicted times for three different breakthrough points of 20%, 30%, and 60% were 110, 139, and 253 min, respectively. Meanwhile, the observed times obtained through experiments were 108, 132, and 198 min, respectively. The times taken for each experimental breakthrough using 900 mg/L of vanillin feed concentration were also compared to the values of 1,000 mg/L of vanillin. It was proven that a lower feed concentration produced a longer breakthrough time because given the same amount of adsorbent resin, it took a longer time for the total adsorbent resin to be saturated with vanillin.

Table 3: Predicted breakthrough times using a Bohart-Adams constant for new vanillin initial concentration (900 mg/L). Flow rate and bed height were kept constant at 5 mL/min and 10 cm, respectively.

Breakthrough point (%)	Slope, m_2 (min/cm)	Intercept, c_2 (min)	Predicted time (min)	Observed time (min)	Observed time for 1,000 mg/L
20	21.33	-102.85	110	108	78
30	22	-80.97	139	132	102
60	31.78	-64.92	253	198	210

A small variation in the calculated and experimental values was observed in the fixed-bed adsorption of gallic acid [26]. A duration of 1.25 h experimental breakthrough time at 10% breakthrough was obtained for the change of feed concentration from 50 to 100 mg/L of gallic acid, compared to 1.66 h of the predicted or calculated breakthrough time. In another work, 20 min was the observed breakthrough time at 20% breakthrough, compared to 22.3 min, when the inlet concentration of Cr(VI) was reduced from 10 to 5 mg/L [35]. Similar results were obtained for the adsorption of textile dye Blue 86 using a carbon-alumina composite [33]. Therefore, it can be concluded that the design parameters can be utilised to predict or design the column adsorption for other feed concentrations.

Table 4: Predicted breakthrough times using Bohart-Adams constant for new flow rate (10 mL/min). Vanillin initial concentration and bed height were kept constant at 1,000 mg/mL and 10 cm, respectively.

Breakthrough point (%)	Slope, m_2 (min/cm)	Predicted time (min)	Observed time (min)	Observed time for 5 mL/min
20	9.6	50	66	204
30	9.9	75	84	234
60	14.3	155	144	378

Table 4 lists the predicted and observed times that occurred for the new feed flow rate of 10 mL/min. The breakthrough points greatly reduced when the flow rate was doubled. When the flow rate was increased from 5 to 10 mL/min, it only took 66 min to reach the 20% breakthrough point, as compared to 204 min. It was also obvious that the differences between the predicted and observed times were small. It was observed that 66, 84, and 144

min were the points of breakthrough for 20%, 30%, and 60%, respectively, while the calculated points were calculated to be 50, 75, and 155 min. The possible reason for the shorter breakthrough caused by increased feed flow rate might be due to the lesser contact time between vanillin and resin H103, or shorter residence time [33, 36].

Similarly, in the adsorption of Cr(VI), small differences were also observed, which were 7 min for 20% breakthrough, compared to the calculated time of 6 min [35]. This shows that Bohart-Adams model applied to the current data indicated good agreement between both calculated and experimental values. This analysis also enables the researchers to predict the performance of a given fixed-bed adsorption column without having to perform any further and extensive experiments for different process parameters [37]. The possible reason for the shorter breakthrough caused by increased feed flow rate might be due to the lesser contact time between vanillin and resin H103, or shorter residence time [33, 36].

Another approach in predicting the breakthrough curve was made using a simple two-parameter model. Figure 3 shows the comparison between the experimental data for a fixed-bed adsorption and the model using Eq. (7). The experiment was performed using a bed height of 10 cm, flow rate of 5 mL/min, and new vanillin initial concentration of 900 mg/L. It was obvious that the simple two-parameter model could also predict the behaviour of vanillin adsorption onto resin H103 at different parameters, with a determination coefficient (R^2) value of 0.9672. Compared to the Bohart-Adams model, this approach is considered to be a simpler method because a minimum of one experiment is needed for the prediction of the fixed-bed adsorption behaviour. The standard deviation value (σ) obtained from the modelling can be used for the determination of the changes in the breakthrough curve for a new fixed-bed adsorption column at different lengths and feed flow rates [30]. This approach was also tested and improved for the modelling of the adsorption of cadmium ions by marine algae [38], *Ascopyllum nodosum* [39], and the adsorption of copper ions by polyvinyl formal-immobilised *Rhizopus arrhizus* and native *Mucor miehei* [40]. Based on the model obtained, the saturation bed capacity, or maximum adsorption capacity, was determined to be 165.9 mg of vanillin/g of adsorbent for the bed height of 10 cm.

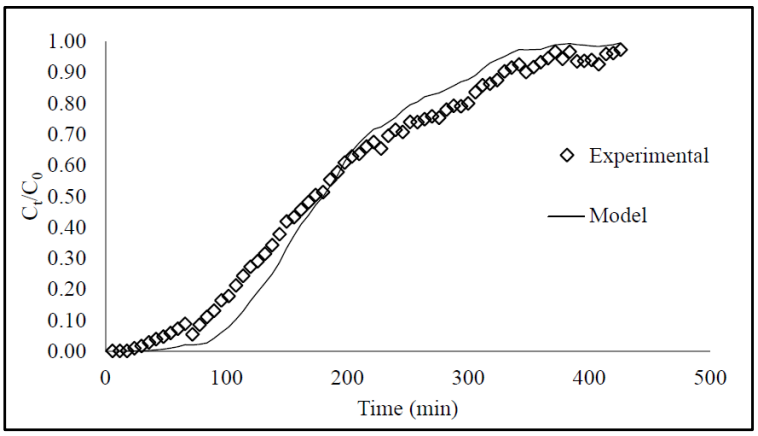

Fig. 3: Mathematical modelling using Belter equation.
The experiments were done with a bed height (Z) of 10 cm,
volumetric flow rate (Q) of 5 mL/min, and
initial vanillin concentration (C_0) of 900 mg/L.

4. CONCLUSION

The vanillin adsorption from aqueous solution in fixed-bed mode was successfully performed and modelled. Fixed-bed mode can be utilised to predict the behaviour of the adsorption of vanillin onto resin H103. A Bohart-Adams model and a Belter equation were used to perform scaling analysis of a fixed-bed adsorption. The dynamic adsorption capacities at 10% breakthrough point were experimentally determined to be 96.813, 194.125, and 314.960 mg of vanillin/g of adsorbent for different bed heights of 5, 10, and 15 cm, respectively. For comparison, the modelled maximum adsorption capacity for a 10-cm bed height obtained was slightly different at the value of 165.9 mg of vanillin/g of adsorbent.

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