UNIVERSITI PUTRA MALAYSIA

OPTIMIZATION OF BATCH ADSORPTION AND FIXED-BED ADSORPTION OF VANILLIN ONTO RESIN H103

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By

ROZAIMI BIN ABU SAMAH

Thesis submitted to the School of Graduate Studies,
Universiti Putra Malaysia, in Fulfilment of the
Requirements for the Degree of Doctor of Philosophy

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Dedicated to

Mai Saharah binti Uda, my beloved mother, you are everything to me

Tuan Suhaini binti Tuan Samad, my lovely wife, thank you for everything

Najlaa & Najah, my beautiful minions, you are the colours of my life

Say, "If the sea were ink for [writing] the words of my Lord,
the sea would be exhausted before the words of my Lord were exhausted,
even if We brought the like of it as a supplement."
Al-Kahfi 18:109

And if whatever trees upon the earth were pens and the sea [was ink],
replenished thereafter by seven [more] seas, the words of Allah would not be exhausted.
Indeed, Allah is Exalted in Might and Wise.
Luqman 31:27

Abstract of thesis presented to Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Doctor of Philosophy

OPTIMIZATION OF BATCH ADSORPTION AND FIXED-BED ADSORPTION OF VANILLIN ONTO RESIN H103

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January 2016

Chairman: Professor Suraini binti Abd Aziz, PhD
Faculty: Biotechnology and Biomolecular Sciences

Vanillin is a widely used chemical especially in food and beverages industries. Its sweet odour also results in its application in perfumes and cosmetics industries. Traditionally, vanillin is produced by curing vanilla pods from vanilla plants. However, it is a very tedious and time-consuming process. It can also be produced chemically from several chemicals or intermediates, but the processes are either imposing an environmental issue (waste product), or dealing with high pressures and temperatures. Researchers are finding ways to produce vanillin via bioprocesses so it can be produced at slightly elevated temperature, by the act of certain microorganisms on several substrates from plant-based materials or biomass. However, due to its phenolic and aldehyde components in its molecular structure, vanillin can be toxic to the microorganisms when it is produced at certain concentration.

Adsorption is one of the possible techniques to use for vanillin recovery from fermentation broth. However, the fermentation broth contains a variety of biomolecules that might interfere with the preliminary characterisation of the adsorbent. Therefore, researchers normally start the related works by using either an aqueous solution of the target biomolecule, continue with a simulated solution of fermentation broth, and finally test the characterised adsorbent with the actual fermentation broth containing the target product to be recovered.

In this work, six adsorbent resins, namely Amberlite XAD-16, Amberlite XAD-2, Sepabeads SP207, Diaion HP-20, DM11 and H103, were tested for vanillin adsorption in aqueous solution. Other than Amberlite XAD-2 and DM11, the other resins gave more than 95% adsorption. For subsequent work, resin H103 was selected due to its high adsorption capacity of more than 98%, and its low purchasing price at approximately US$115 per kilogram.

Vanillin adsorption using resin H103 was investigated based on five parameters, which were contact time (minute), resin dosage (g), pH, temperature (°C), and vanillin initial concentration (mg/L). No large effect of vanillin adsorption within pH and temperature range tested. Thermodynamics data revealed that the adsorption process involved was an exothermic reaction, due to a negative sign of its enthalpy value. The magnitude of -17.956 kJ/mol also revealed that the adsorption of vanillin onto resin H103 was a physical adsorption.

It was also revealed that the vanillin adsorption onto resin H103 followed a pseudo-second order kinetics, with values of constant parameters of q_e of 10.684 mg/g and k_2 of 0.006 g/mg.min. The linearized form gave a high determination coefficient (R^2 = 0.995 for 0.5 g resin). Based on two most widely used isotherms (Langmuir and Freundlich), it was found that the former was slightly better fitted than the latter with an R^2 value of 0.994. Subsequently, it was determined that the maximum capacity of resin H103 was 73.015 mg vanillin/g resin, and the Langmuir constant, K_L, was determined to be 0.039 L/mg.

Factorial screening was utilized to determine significant factors affecting the adsorption process. Each parameter was randomly subjected to 2^5 fractional factorial design for the identification of significant parameters, and subsequently optimized using response surface methodology (RSM). Sixteen experiments were carried out for the screening process, and 13 experiments for optimization. With the aid of Design Expert version 7.1.6 for statistical analysis, it was determined that vanillin initial concentration and resin dosage were significant factors affecting the vanillin adsorption onto resin H103 (determination coefficient value, or R^2, of 0.9996). While the other insignificant factors were kept constant, the two significant factors were then subjected to an optimization process using response surface methodology. The tested range for optimization did not reveal any optimum level, despite its high R^2 value of 0.9515. It was observed that the optimum point might fall outside the tested range.

Further adsorption process via fixed bed mode was also investigated, with the aim of elucidating the dynamic adsorption behaviour of vanillin onto resin H103 packed in a column attached to ÄKTAexplorer 100 system. It was also used to describe the scaling analysis of a fixed bed adsorption column. Three parameters were investigated, which were bed height, vanillin initial concentration, and flow rate of the feed. Plots of effluent concentration versus time, or breakthrough curves, revealed that the fixed bed vanillin adsorption onto resin H103 can be described by both Bohart-Adams and Belter's equation, with a high R^2 of 0.9672. From the breakthrough curves, the dynamic adsorption capacities of the fixed bed were determined to be 96.813, 194.125, and 314.960 mg vanillin/g adsorbent, for bed heights of 5 cm, 10 cm, and 15 cm, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENGOPTIMUMAN PENJERAPAN VANILIN SECARA KELOMPOK DAN PENJERAPAN VANILIN SECARA TURUS PADAT OLEH BAHAN PENJERAP H103

Oleh

ROZAIMI BIN ABU SAMAH

Januari 2016

Pengerusi: Profesor Suraini binti Abd Aziz, PhD
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Vanilin adalah sejenis bahan kimia yang mempunyai pelbagai kegunaan terutamanya dalam industri makanan dan minuman. Baunya yang harum menyebabkan vanilin juga digunakan dalam bidang wangian dan kosmetik. Secara lazimnya vanilin dihasilkan dengan cara mengeringkan lenggai (kekacang) vanila daripada pokok vanila. Namun, proses tersebut adalah rumit dan memakan masa yang lama. Ia juga boleh dihasilkan melalui tindak balas kimia, tetapi proses tersebut sama ada memberi kesan kepada persekitaran melalui bahan-bahan sisa tindak balas kimia tersebut, atau melibatkan tekanan dan suhu yang tinggi. Penyelidik berusaha untuk menghasilkan vanilin melalui proses biologi yang berlaku pada suhu persekitaran melalui tindak balas beberapa jenis mikroorganisma terhadap substrat daripada bahan tumbuhan atau biomas. Namun begitu, kewujudan sebatian fenolik dan aldehid pada struktur keseluruhan vanilin, ia boleh menjadi toksik kepada mikroorganisma pada jumlah kepekatan yang tertentu.

Proses penjerapan adalah salah satu teknik yang boleh digunakan untuk memisahkan vanilin daripada kaldu fermentasi. Namun, kaldu fermentasi mempunyai pelbagai biomolekul yang mungkin mengganggu proses perincian bahan penjerap. Untuk itu, kebiasaannya para penyelidik akan memulakan kerja-kerja berkaitan dengan menggunakan larutan akueus bahan yang ingin dipisahkan, disambung dengan menggunakan larutan simulasi, dan akhirnya diuji dengan menggunakan larutan kaldu fermentasi yang sebenar.

Untuk kajian ini, enam bahan penjerap dikaji untuk proses penjerapan vanilin iaitu Amberlite XAD-16, Amberlite XAD-2, Sepabeads SP207, Diaion HP-20, DM11 dan H103. Kesemua bahan penjerap menunjukkan kadar penjerapan melebihi 95%, kecuali Amberlite XAD-2 dan DM11. Bahan penjerap H103 digunakan untuk eksperimen seterusnya kerana bahan penjerap tersebut mempunyai kapasiti penjerapan yang tinggi

melebihi 98% daripada keseluruhan vanilin, dan juga disebabkan oleh harga belian yang rendah pada US$115 per kilogram.

Penjerapan vanilin di atas bahan penjerap H103 dikaji berdasarkan lima parameter, iaitu jangka masa proses (minit), jumlah bahan penjerap (g), pH, suhu proses, dan kepekatan awal vanilin (mg/L). Didapati pH dan suhu tidak memberikan kesan yang ketara terhadap proses penjerapan tersebut. Data termodinamik menunjukkan proses penjerapan vanilin di atas bahan penjerap H103 adalah secara eksotermik, berpandukan tanda negatif pada nilai entalpi. Nilai entalpi -17.956 kJ/mol juga menunjukkan bahawa proses penjerapan vanilin adalah dalam kategori penjerapan fizikal.

Data kinetik pula menunjukkan proses tersebut mengikut tindak balas tertib kedua dengan nilai parameter pemalar q_e 10.684 mg/g dan k_2 0.006 g/mg.min. Data kinetik yang dilinearkan memberikan nilai pekali penentuan yang tinggi (R^2 = 0.995 bagi 0.5 g bahan penjerap). Berdasarkan dua isoterma penjerapan yang sering digunakan iaitu *Langmuir* dan *Freundlich*, isoterma penjerapan *Langmuir* lebih tepat menggambarkan proses tersebut dengan nilai pekali penentuan 0.994. Seterusnya, kapasiti maksimum bahan penjerap H103, q_e, adalah 73.015 mg vanilin/g bahan penjerap dan pemalar *Langmuir*, K_L, bersamaan 0.039 L/mg.

Penyaringan faktoran digunakan bagi menentukan faktor-faktor yang bererti dalam proses penjerapan. Setiap parameter dikaji secara rawak melalui rekabentuk faktoran pecahan 2^5 dan seterusnya melalui proses pengoptimuman menggunakan metodologi permukaan sambutan. Sebanyak 16 ujikaji dijalankan bagi proses penyaringan dan 13 ujikaji untuk proses pengoptimuman. Dengan menggunakan perisian Design Expert 7.1.6 untuk analisa statistik, kepekatan awal vanilin dan jumlah bahan penjerap didapati adalah faktor-faktor yang bererti dalam proses penjerapan vanilin di atas bahan penjerap H103 dengan nilai pekali penentuan R^2 bersamaan 0.9996. Kedua-dua faktor tersebut seterusnya melalui proses pengoptimuman, dengan faktor-faktor lain yang tidak bererti ditetapkan pada satu nilai masing-masing. Julat ujikaji bagi faktor-faktor bererti tersebut tidak menunjukkan sebarang nilai optimum walaupun nilai pekali penentuan proses pengoptimuman tersebut sangat tinggi pada 0.9515. Dijangka nilai optimum tersebut berada di luar julat faktor-faktor yang dikaji.

Seterusnya, proses penjerapan vanilin dilakukan dalam mod turus padat dengan tujuan untuk mendapatkan gambaran proses penjerapan vanilin di atas bahan penjerap H103. Ia juga berfungsi untuk analisa penambahbesaran turus padat. Ujikaji dilakukan dengan menggunakan sistem ÄKTAexplorer 100 terhadap tiga parameter iaitu tinggi padatan, kepekatan awal vanilin, dan kadar aliran suapan. Plot kepekatan efluen melawan masa, atau lengkung bulus, menunjukkan proses penjerapan vanilin di atas bahan penjerap H103 dalam mod turus padat boleh digambarkan menggunakan persamaan Bohart-Adams dan persamaan Belter, dengan nilai pekali penentuan yang tinggi pada 0.9672. Nilai kapasiti penjerapan dinamik yang diperolehi adalah 96.813, 194.125, dan 314.960 mg vanilin/g bahan penjerap, untuk ketinggian turus masing-masing 5 cm, 10 cm, and 15 cm.

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In the name of Allah, the Entirely Merciful, the Especially Merciful. [All] praise is [due] to Allah, Lord of the worlds. The Entirely Merciful, the Especially Merciful. Sovereign of the Day of Recompense. It is You we worship and You we ask for help. Guide us to the straight path. The path of those upon whom You have bestowed favour, not of those who have evoked [Your] anger or of those who are astray.

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I certify that a Thesis Examination Committee has met on 14 January 2016 to conduct the final examination of Rozaimi bin Abu Samah on his thesis entitled "Optimization of Batch Adsorption and Fixed-Bed Adsorption of Vanillin onto Resin H103" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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%	Percent
σ	standard deviation
ΔG°	Gibbs free energy
ΔH°	enthalpy
ΔS°	entropy
ΔX_t	step change
1/n	affinity constant
Å	Angstrom
ANOVA	analysis of variance
C_0	initial concentration
$C_{1/2}$	original/new concentration in breakthrough analysis
$c_{1/2}$	intercept parameters in breakthrough analysis
C_b	breakthrough concentration
CCD	central composite design
C_e	equilibrium concentration of solute in liquid @ unbound solute
C_t	residual concentration
erf(x)	error function
g	gram
g/L	gram per litre
h	hour
HCl	hydrochloric acid
k	rate constant in breakthrough analysis
K	Kelvin
k_1	pseudo-first order rate constant
k_2	pseudo-second order rate constant
k_{id}	intraparticle diffusion rate constant
K_C	thermodynamic equilibrium constant
K_F	Freundlich constant
K_L	Langmuir constant
L	litre
m	meter
$m_{1/2}$	slope parameters in breakthrough analysis

mg	milligram
min	minute
mL	millilitre
N	adsorption capacity in breakthrough analysis
NaOH	sodium hydroxide
^{o}C	degree Celcius
OD	optical density
OPEFB	oil palm empty fruit bunch
q	adsorption capacity
$Q_{1/2}$	original/new feed flow rate in breakthrough analysis
q_e	amount of solute adsorbed at equilibrium
q_m	Maximum adsorption capacity
q_t	amount of solute adsorbed at time t
R	gas constant
R^2	coefficient determination
R_L	separation factor
rpm	revolution per minute
RSD	relative standard deviation
RSM	response surface methodology
s	second
t	time
T	temperature
V	volume
V	linear velocity in breakthrough analysis
X_0	actual value of the *i*th independent variable at the centre point
x_i	coded value of the *i*th independent variable
X_i	actual value of the *i*th independent variable
Z	bed height
Z_0	critical bed height
µL	microlitre
µm	micrometer

CHAPTER 1

INTRODUCTION

1.1 Background and problem statement

Vanillin is the most widely used flavour. In the form of vanilla extract, it is extensively used in two major industries, which are food and beverages, and perfumes and cosmetics (Buccellato, 2010). It also finds a good interest in pharmaceuticals and agricultures. Vanilla extract is traditionally obtained from the beans of vanilla orchid, which takes years after the planting of the orchids. This contributes to the high price of the natural vanilla extract. For that reason, the demands for vanilla flavour cannot be met by vanilla extract, mainly due to the minute amount of vanillin component (2 %) in the whole vanilla extract (Havkin-Frenkel and Belanger, 2009).

Due to its dark brown colour, the incorporation of vanilla extract in food or beverages affects the final appearance of the product. Therefore, certain applications require a pure vanillin, as it is in crystal form. This has led to a chemical synthesis of vanillin, which normally involves high temperature and pressure. One of the earliest chemical processes of producing vanillin was from curcumin. The reaction was set to a very high temperature of 316 °C and also very high pressure at 114 atm (Dolfini *et al.*, 1990). Vanillin can also be produced from ortho-chloronitrobenzene, from which guaiacol is produced as an intermediate product for further chemical reactions to produce vanillin, along with nitroanisole and anisidine as byproducts (Vidal, 2008). Guaiacol is then subjected to condensation process with dimethyl aniline and nitroso derivative. This process, with urotropine as catalyst, produces vanillin and para-amino dimethyl aniline as side products. However, this process needs several steps of purification which involve wastewater treatment of toxic raw materials and side products.

In contrast, biotechnology deals with a milder condition for the productions of specialty chemicals and molecules. Most of the fermentations occur at ambient environment, as opposed to chemical processes that take place at harsh conditions. At the same time, there is increasing concern on the natural products among the consumers which requires researchers and manufacturers to look into ways of obtaining vanillin via biotechnology routes. The use of microorganisms takes place in the overall production line. The utilization of living cells and natural substrates fulfil the definition of natural products. Many components are able to be used as the precursors or substrates for the production of vanillin such as ferulic acid, vanillic acid, eugenol and lignin (Walton *et al.*, 2000).

Such precursors are easily obtained from the biomass waste all over the country. For example, ferulic acid is one of the components contain in the lignocellulosic biomass and one of the sources for lignocellulosic biomass is oil palm empty fruit bunches (OPEFB), which is the most abundance biomass in Malaysia. The utilization of oil palm biomass is in line with the country's aspiration to generate its gross national income with the

launching of National Biomass Strategy that identified oil palm biomass as the next potential resource (Agensi Inovasi Malaysia, 2011). Launched in November 2011, it aims in the utilization of the biomass for variety additional end uses, apart from the production of wood products, pellets, bioenergy, biofuels and biobased chemicals. Many of the bioproducts from this biomass need to be carefully and systematically purified before they can be used for their specific use. Therefore, there is increasing challenges in the downstream section. The separation engineers need to find specific and cost effective techniques in recovering the target products.

As for vanillin, its recovery can be done by a few techniques, namely extraction (de Brito Cardoso *et al.*, 2013), distillation (Bryan, 1950), crystallization (Taber *et al.*, 2007), membrane separation (Zabkova *et al.*, 2007b; Wu *et al.*, 2008; Zhang *et al.*, 2008a; Sciubba *et al.*, 2009; Brazinha *et al.*, 2011; Camera-Roda *et al.*, 2013; Mohamad Yusof and Kobayashi, 2013) and adsorption by adsorbent resin such as β-cyclodextrin polymer resin (Li *et al.*, 1998), resin HD-8 (Zhao *et al.*, 2006), resin Sephabeads SP206 (Zabkova *et al.*, 2006), resin DM11 (Hua *et al.*, 2007), and resin D101 (Wang *et al.*, 2010), anisole-modified hyper-cross-linked polystyrene resin (Jin and Huang, 2012), and p-acetaminophen resin (Xiao *et al.*, 2012). In addition, there are also a vast amount of reports on adsorption recovery method for other aromatic compounds or bioproducts from fermentation broth, for example resin XAD-2, XAD-4 and Lewatit 1064 for n-butylbutanoate, benzaldehyde and 4-decanolide (Krings *et al.*, 1993; Krings and Berger, 1995), anion exchange resin for citric acid (Jianlong *et al.*, 2000), and resin S-8 for taurine (Zhigang *et al.*, 2001).

Adsorption also offers a high-throughput yet simple procedures. In the general sequence of bioseparations which consists of four stages (recovery, isolation purification and polishing), adsorption is categorized in the purification stage. Normally, separation techniques classified in this stage is considered specific techniques, which means that it captures the target product selectively. However, there are many types of adsorbent available, and each adsorbent performs differently for a single solute. Thus, this study was conducted to initially determine the capability of polymeric resins to adsorb vanillin in aqueous solution, and further characterize the related parameters in the adsorption process.

1.2 Objectives

The objectives of this study are:

1. to characterize adsorption parameters of resin in the recovery of vanillin from aqueous solution,
2. to identify significant factors affecting vanillin adsorption in batch mode by utilizing experimental design approach, and
3. to elucidate vanillin adsorption behaviour in fixed bed column via dynamic adsorption capacity and rate constant.

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