DYNAMIC SIMULATION ON THE RECOVERY OF 2-ACETYL PYRROLINE (2-AP) IN A PACKED BED COLUMN USING RICE HUSK CHAR AS SOLID ADSORBENT

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ABSTRACT. *Fragrant rice is known to contain the aromatic compound of 2-Acetyl Pyrroline (2-AP). This compound has been known as a major compound that gives fragrant characteristics in rice. However, this compound is volatile and easily escapes from the rice upon the drying process. In order to recover the release of 2-AP from rice upon drying, a packed bed adsorption system is employed using treated agricultural waste as a solid adsorbent. The experimental adsorption study in a batch mode for 2-AP onto treated rice husk char (TRHC) was used as a case study for this present work. Influences of three operational parameters towards the dynamic adsorption of 2-AP onto TRHC in a packed bed column were investigated by measuring the breakthrough and saturation time and mass transfer zone. This study suggests the possibility of treated agricultural waste as an alternative to capture the lost 2-AP during the paddy drying process.*

KEYWORDS. Adsorption; Aromatic rice; Breakthrough curve; Treated rice husk; Simulation

INTRODUCTION

Rice is the most important food in Asia, and is regarded as a staple food for Asian. Aroma is among the important qualities of rice that is responsible for the pleasant smell in rice. The characteristic that gives fragrance to rice is the compound known as 2-acetyl pyrroline (2-AP), with a chemical formula of C_6H_9NO (Hien et al., 2006). 2-AP is a highly volatile aromatic compound in rice; thus, it escapes easily together with moisture contained in the rice during the paddy drying process and during storage, thus making the rapid aroma evaporation highly disadvantageous to the aroma sensory quality of the rice (Baradi & Elepano, 2012). In addition, Yoshihashi et al. (2005) reported that the 2-AP compound in the aromatic rice is present in low concentration, making it easier to lose through diffusion from the rice to the environment. Other than that, storage at high temperature has an effect on the concentration 2-AP in the rice and causes it to decrease (Kongkiattikajorn, 2008). The consequence of the aroma loss in the rice is the loss of profit annually for the global rice production. Therefore, this has prompted numerous advancements in upstream and downstream processes to increase the yield of paddy production while maintaining or improving the sensory quality of the aromatic rice. One of the methods to capture the loss 2-AP during the paddy drying process is the adsorption process. Adsorption method involves the transference of solute from the bulk fluid to the adsorbent's surfaces.

A packed bed column is widely used in practical applications for adsorption in continuous dynamic operation because of its simple operation method for industrial application (Hanafy et al., 2019). Packed bed adsorption column is a device that is filled with a specific adsorbent that adheres to a specific solute adsorbate when passing through the adsorbent bed (Bahrun et al., 2021). Several commercial simulators are available and can solve sets of complex algebraic, partial and ordinary equations of packed bed adsorption columns, and one of them is Aspen Adsorption V11 developed by

AspenTech. Aspen Adsorption is a comprehensive flowsheeting simulator tool for adsorption process with and without reaction (AspenONE, 2009).

This present work seeks to investigate the dynamic behavior of treated rice husk char (TRHC) adsorbent for recovering volatile aromatic compound, 2-Acetyl Pyrroline (2-AP) conducted in a packed bed column. The numerical simulation was conducted using Aspen Adsorption V11 simulation package, by solving the governed mathematical model describing a packed bed adsorption column. The dynamic behaviours of TRHC for 2-AP recovery were investigated from the breakthrough curve performance at different operational conditions including inlet flow rate, inlet concentration and bed column height. The performance was measured in terms of time and mass transfer zone.

MATERIALS AND METHODS

2.1. THE ORETICAL ASSUMPTIONS OF SIMULATIONS

The following general assumptions were considered for simulation in a packed bed column:

a) The behavior of the fluid is assumed as a plug flow
b) A linear driving force (LDF) model is used to represent the transmigration between solid-fluid phases
c) A lumped mass transfer equation is used with solid-film resistance. The lumped mass transfer equation consists of external film resistance and intraparticle surface resistance
d) The equilibrium adsorption is sufficiently described using Langmuir equation
e) The isotherm constants of 2-AP on TRHC in aqueous-phase is assumed to be similar as in gas-phase

2.2. GOVERNING MATHEMATICAL MODEL OF A PACKED BED COLUMN

The ideal plug-flow mathematical model describing the adsorption process in a packed bed column is expressed as in Equation 1 (AspenONE, 2009).

$$\upsilon_i \frac{\partial C_i}{\partial z} + \varepsilon \frac{\partial C_i}{\partial t} + \rho_s \frac{\partial Q_i}{\partial t} = 0 \quad (1)$$

where ρ_s is the bulk solid density (kg/m^3), ε is the bed voidage (m^3 void/m^3 bed), v_i is the superficial velocity (m/s) of component *i*, C_i is the gas-phase concentration (mg/L) of component *i*, and Q_i is the solid-phase loading (mg/g) of component *i*.

The terms $\partial Q/\partial t$ can be well-represented by a simplified kinetic model, known as linear driving force (LDF) approximation. The LDF model assumed the mass transfer driving force is a linear function of the solid phase loading. Equation 2 shows the LDF model equation (Glueckauf, 1955).

$$\frac{\partial Q_i}{\partial t} = k_{LDF}({Q_i}^* - Q_i) \quad (2)$$

where k_{LDF} is the lumped mass transfer coefficient (1/s). In this work, two independent mass transfer diffusions were lumped by linear addition into the LDF mass transfer coefficient (Bono, 1989).

$$\frac{1}{k_{LDF}} = \frac{R_p}{3(1 - \varepsilon)k_f} + \frac{{R_p}^2}{15D_s} \quad (3)$$

For the range of $0.0055 < Re_p < 55$ found in this work, the film mass transfer coefficient, k_f (m/s) can be calculated using Sherwood, Sh correlation

$$Sh = \frac{2R_p k_f}{D_m} = \frac{1.09}{\varepsilon} Sc^{0.33} Re^{0.33} \quad (4)$$

where R_p is TRHC adsorbent particle radius (m), D_m is the molecular diffusivity (m^2/s), and Sh, Re and Sc are Sherwood, Reynolds and Schmidt dimensionless numbers, respectively. The molecular diffusivity of 2-AP in air, D_m can be calculated using Fuller equation as expressed in Equation 5 (Coker, 2007; Fuller et al., 1966).

$$D_m = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{\frac{1}{2}}}{P\left[(\sum V_A)^{\frac{1}{3}} + (\sum V_B)^{\frac{1}{3}}\right]^2} \quad (5)$$

where T is temperature (K), P is pressure (atm), M_A and M_B are molecular weights of 2-AP and air, and V_A and V_B are molar volumes of 2-AP and air, respectively. For the determination of intraparticle surface diffusion, D_s (cm^2/s), the correlation developed by Suzuki & Kawazoe (1975) for volatile organic compounds is used as a preliminary value for model input, as expressed in Equation 6.

$$D_s = 1.1 \times 10^{-4} e^{\left(\frac{-5.32 T_b}{T}\right)} \quad (6)$$

where T_b is the boiling point of 2-AP adsorbate (K), and T is the adsorption temperature (K). The intraparticle surface diffusion, D_s values obtained for this study were in the range of 10^{-7} cm^2/s, which is in agreement with the range reported for gaseous-phase surface diffusivity (Green & Perry, 2008).

2.3. DATA EXTRACTION FOR CASE STUDY

This current work was based on the experimental data by Sarmento (2021), and it was used as a case study for this simulation. The dynamic adsorption simulation was conducted by using Aspen Adsorption V11. The required data for the simulation on the adsorbent properties and adsorption isotherm are presented in Table 1 and Table 2, respectively.

Table 1: Some physical properties of treated rice husk char (TRHC) adsorbent

Parameter	Value
TRHC adsorbent particle diameter, mm	1.00
Bulk density, kg/m^3	455
Bulk porosity (m^3 void/m^3 bed)	0.35

Table 2: The Langmuir adsorption isotherm constant for 2-AP onto treated rice husk char (TRHC) (Sarmento, 2021)

Langmuir isotherm	Q_{max} (mg/g)	625
	b (L/mg)	0.00146
	R^2	0.9925

2.4. PARAMETRIC STUDIES ON PACKED BED COLUMN PROCESS PARAMETERS

Various operating process parameters were conducted to investigate the performance of the packed bed adsorption column at various operating conditions by evaluating the breakthrough curve profile. The varying parameters included inlet 2-AP flow rate, inlet 2-AP concentration, and bed column height while keeping the bed column diameter at 1.5 m. The base case concentration used in this work (0.0610 ppm) was assumed to follow the concentration of a commercialized Basmathi rice as taken from Nadaf et al. (2006). The parametric studies were conducted by changing around the original base value, as described in Table 3.

Table 3: Parametric studies with their respective varying parameters value

Simulation no.	Inlet flow rate, Q (kmol/s)	Inlet concentration, C_0 (ppm)	Bed column height, H (m)
1	3.8879×10^{-7}	0.0610	2.0
2	4.8599×10^{-7}		
3	5.8319×10^{-7}		
4	4.8599×10^{-7}	0.0488	2.0
5		0.0610	
6		0.0732	
7	4.8599×10^{-7}	0.0610	1.6
8			2.0
9			2.4

2.5. DYNAMIC ADSORPTION PERFORMANCE ANALYSIS

The results from the converged numerical iteration are presented in both data tables and graphical presentation. Three key indexes are used to describe the performance of the dynamic adsorption in a packed bed column. There are breakthrough time (t_b), saturation time (t_s), and length of mass transfer zone (L_{MTZ}). The breakthrough time, t_b is taken when the C/C0 reached 0.05, while the saturation time, ts is taken when the C/C_0 reached 0.95. The length of the mass transfer zone, L_{MTZ} is calculated following Equation 7.

$$L_{MTZ} = H\left(1 - \frac{t_b}{t_s}\right) \quad (7)$$

RESULTS AND DISCUSSION

Once all the required input parameters and physical properties have been determined, the mathematical model framework could be solved by numerical solution built in the software. Three parameters' effects on the bed column performance were investigated to evaluate the dynamic behavior of the system when certain operational parameters change. The three parameters include inlet flow rate, inlet concentration, and bed column height. The bed column performance was measured by assessing the breakthrough time (t_b), saturation time (t_s), as well as the length of the mass transfer zone (L_{MTZ}).

3.1. INFLUENCE OF INLET 2-ACETYL PYRROLINE FLOWRATE ON BREAKTHROUGH CURVE

A strong influence of the inlet 2-AP flowrate on the breakthrough and saturation time was observed in Figure 1(a). The inlet flow rates were varied at 3.8879×10^{-7}, 4.8599×10^{-7}, and 5.8319×10^{-7} kmol/s, while keeping constant the 2-AP concentration at 0.061 ppm and TRHC column height at 2.0 m. At the increasing inlet 2-AP flow rate, the breakthrough time and saturation time decrease. This is due to the insufficient contact time between 2-AP molecules with the TRHC adsorbent bed, thus making the 2-AP molecules to have limited reach towards the active sites of the adsorbent (Ahmed et al., 2020). In terms of the breakthrough shape and gradient, the higher the flow rate, the broader the gradient of the breakthrough curve, as reported in Table 4. Broaden breakthrough curve indicated by the higher L_{MTZ}. Changes in the gradient of the curves indicated that changing inlet 2AP flow rate affects the mass transfer resistance (da Rosa et al., 2015). The details on the breakthrough time, saturation time and length of mass transfer zone at different inlet flow rate are summarized in Table 4.

Table 4: Parametric studies - dependence on inlet 2-AP flow rate

Flowrate (kmol/s)	t_b (hour)	t_s (hour)	L_{MTZ} (m)
3.8879×10^{-7}	74.55	112.34	0.6729
4.8599×10^{-7}	59.54	89.79	0.6738
5.8319×10^{-7}	49.54	74.76	0.6747

3.2. INFLUENCE OF INLET 2-ACETYL PYRROLINE CONCENTRATION ON BREAKTHROUGH CURVE

The effect of inlet 2-AP concentration on the breakthrough curve was investigated by varying the inlet 2-AP concentration while keeping the same inlet flow rate of 4.8599×10^{-7} kmol/s and bed height of 2.0 m. The concentrations under study were 0.0488, 0.0610 and 0.0732 ppm. The breakthrough curves at different inlet 2-AP concentrations were illustrated in Figure 1(b). It was observed that increasing inlet 2-AP concentration caused earlier breakthrough and saturation time.

Apart from that, it was noted in Figure 1(b) that the influence of inlet 2AP concentration does not much affect the breakthrough and saturation time. A change in ±20% inlet 2-AP concentration only caused the breakthrough and saturation time to change by approximately 2%. This, by means of changing the concentration by ±20%, is relatively small compared to the amount of adsorbentpresent in the bed column that is readily available for adsorption sites. Though small changes were observed when initial

2-AP concentration changed, it is worth noting that increasing inlet 2-AP concentration leads to a steeper breakthrough curve, as indicated by a lower L_{MTZ} at a higher inlet 2-AP concentration in Table 5. This is because a larger concentration gradient is provided at higher inlet concentration, which enhances the mass transfer rates in both fluid and solid phases (da Rosa et al., 2015). The details on the breakthrough time, saturation time and length of mass transfer zone on different inlet concentrations are tabulated in Table 5.

Table 5: Parametric studies - dependence on inlet 2-AP concentration

Concentration (ppm)	t_b (hour)	t_s (hour)	L_{MTZ} (m)
0.0488	60.42	91.33	0.6770
0.0610	59.54	89.79	0.6739
0.0732	58.84	88.57	0.6713

3.3. INFLUENCE OF BED COLUMN HEIGHT ON BREAKTHROUGH CURVE

The analysis of the influence of TRHC column height on the breakthrough curve performance is presented in Figure 1(c). The bed column heights investigated were 1.6 m, 2.0 m, and 2.4 m, while keeping inlet flow rate and concentration constant at 4.8599×10^{-7} kmol/s and 0.0610 ppm, respectively.

The breakthrough curve in Figure 1(c) indicates that the breakthrough time of the TRHC column increases from 47.54 hours to 71.55 hours as the TRHC bed column height increases from 1.6 m to 2.4 m. A longer bed column height means a large amount of TRHC in the column bed. Consequently, it provides a large surface area available for adsorption binding sites leading to an increase in the breakthrough time. Moreover, longer bed column height enhances the gas-solid contact time in the column, eventually causing a deep transport of 2-AP onto TRHC adsorbent (Hymavathi & Prabhakar, 2019; Tan et al., 2020). In terms of the gradient of the curve, longer bed column height causes the length of the mass transfer zone to increase, as stated in Table 6. A reasonable explanation for this is most probably due to abundant mass transfer zones at higher bed column height, and thus less rapid transference of adsorbate to the adsorption sites (Jangde et al., 2019). The details on the breakthrough time, saturation time, and length of mass transfer zone at different bed column height were presented in Table 6.

Table 6: Parametric studies - dependence on bed column height

Bed column height (m)	t_b (hour)	t_s (hour)	L_{MTZ} (m)
1.6	47.54	71.75	0.5400
2.0	59.54	89.79	0.6738
2.4	71.55	107.83	0.8076

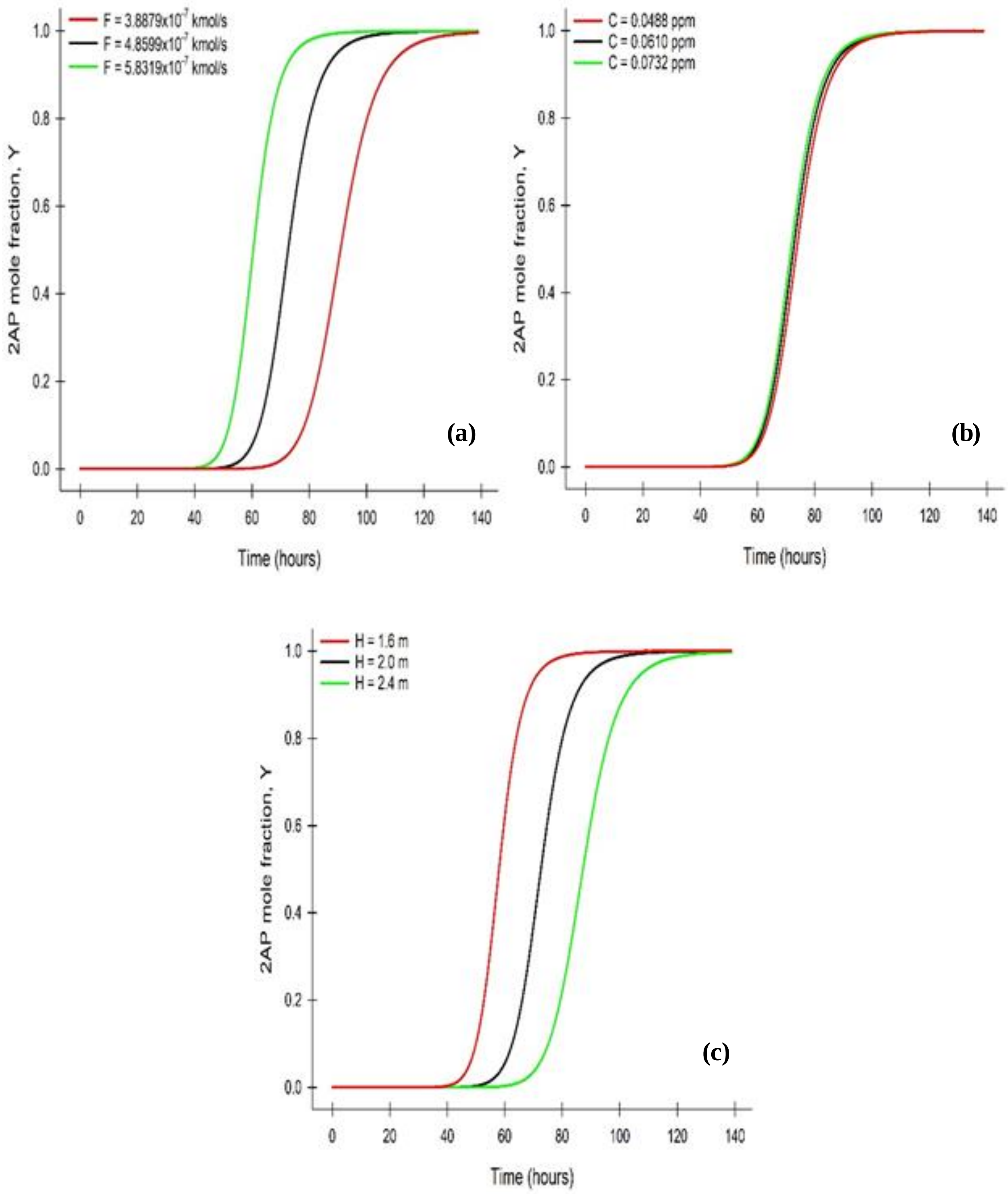

Figure SEQ Figure * ARABIC 1: Effect of (a) inlet flowrate [C_0=0.0610 ppm, H=2.0 m]; (b) inlet concentration [F=4.8599×10^{-7} kmol/s, H=2.0 m]; (c) bed column height [F=4.8599×10^{-7} kmol/s, C_0=0.0610 ppm] on the breakthrough curve

CONCLUSION

This present work seeks to investigate the dynamic adsorption of a volatile aromatic compound, 2-Acetyl Pyrroline (2-AP), onto treated rice husk char (TRHC) in a packed bed column. The investigations were conducted through numerical computation using Aspen Adsorption V11, using data from the batch experimental study and some reliable predictions using available correlations. Based on this present study, some conclusions could be drawn:

1. An alternative in using treated agricultural waste (TRHC) to recover volatile compound (2-AP) gives promising results through dynamic simulation;
2. The packed bed column filled with treated rice husk char with column height and diameter of 2.0 m and 1.5 m, with inlet 2-AP flow rate and concentration of 4.8599×10^{-7} kmol/s and 0.0610 ppm, respectively able to capture volatile 2-AP with 89.79 hours operation time, so that the user just needs to replace the whole packed bed column in every 89.79 hours or 3.74 days;
3. The influence of inlet 2-AP flow rate and concentration are inversely proportional to the saturation (operation) time of the system;
4. On the other hand, the influence of TRHC bed column height is directly proportional to the system's operation time.

However, further investigation needs to be executed to establish and verify the assumption of similar adsorption constants for 2-AP onto TRHC in aqueous and gas phases.

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