

# Purification of 1,3-pd from complex fermentation broth



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MTZ is calculated as Eq. 6[24], where  $H$  is adsorption bed height (cm).  $t_b$  is the time (min) of breakthrough point, which defined as the time when  $C_t/C_0 = 0.05$ .  $t_e$  is the time (min) of saturated point, which defined as the time when  $C_t/C_0 = 0.95$ .

As showed in Table 2, increasing the 1, 3-PD concentration,  $t_b$  and  $t_e$  decreased. The dynamic adsorption of 1, 3-PD to resin usually fails to achieve adsorption equilibrium. When the concentration of 1, 3-PD achieved a certain high value, the breakthrough point and saturated point came early.

The adsorption process in a fixed bed for a single adsorbate can be classified into three zones: the saturated zone, mass transfer zone and fresh zone[24]. The smaller the mass transfer zone and fresh zone were, the higher efficiency of the adsorption process. When the concentration of 1, 3-PD was  $35.2 \text{ g L}^{-1}$ , the maximum value of mass transfer zone (MTZ) is 23.2 cm, which indicated that the saturated zone was small and the efficiency was low. On the contrary, when the concentration of 1, 3-PD was  $25.0 \text{ g L}^{-1}$ , the MTZ was minimum while the efficiency of adsorption was 63.5% as the highest point. However, the production efficiency was lower for saturated time delayed.

The breakthrough curves of glycerol were showed in Fig. 3B with three concentrations of 1, 3-PD. When 1, 3-PD attained saturated point, glycerol did not saturate and the adsorption is 428, 388 and 266 mg/g, respectively, which indicated the decreasing of the fermentation broth concentration increased the adsorption of glycerol. Considering both adsorption rate and

efficiency, fermentation broth with  $30.0 \text{ g L}^{-1}$  concentrations were used in the following experiments.

Data was fitted based on Yoon-Nelson model, which was showed in Fig. 4. Simulated parameters were listed in Table 2.

The results indicated that  $k$  increased with the 1, 3-PD concentration, while  $x_{exp}$  decreased, which indicated that increasing concentration shortened the saturated time in the adsorption bed. Furthermore,  $x_{exp}$  was similar with  $x$ , which indicated that Yoon-Nelson model can be applied to simulate the adsorption process with different concentrations.

### 3.3 The effect of flow rate

The effect of flow rate to the adsorption of 1, 3-PD was showed in Fig. 5A. From Fig. 5A, increasing the flow rate lead to the increasing of curves slope, the breakthrough time was shortened and the changing of the concentration difference was quicker. The main reason was that with the increasing of flow rate, exchanging time of adsorbate and resin was shortened. Further analysis showed in Table 3.

From Table 3, with the setting up of flow rate, the saturated point of 1, 3-PD decreased quickly and MTZ increased. High flow rate would make it difficult for 1, 3-PD to transfer into resin porosity, which went against for the mass transfer of 1, 3-PD and the undisturbed 1, 3-PD increased. When the flow rate was  $0.800 \text{ mL min}^{-1}$ , the adsorption rate was 62.2%. However, low flow rate lead to the delay of 1, 3-PD saturated point and low adsorption rate, which is not benefit for industrial production.

Data fitting based on Yoon-Nelson kinetic model, the result of 1, 3-PD breakthrough curves showed in Table 3 and Fig. 6.

As showed in Fig. 6,  $k$  increased with the increasing flow rate and  $x_{exp}$  shared a similarity with  $x$ , indicating that Yoon-Nelson kinetic model can imitate adsorption process at different flow rates.

### 3. 4 The effect of temperature

The effect of temperature in the adsorption of 1, 3-PD showed in Fig. 7A. As showed in Fig. 7A,  $t_b$  and  $t_e$  increased with temperature. The breakthrough point delayed, which was similar to the result of a steady state adsorption. Increasing temperature promotes the adsorption of 1, 3-PD to resin.

However, the effect of temperature on breakthrough curves is not obvious on the slope of three curves was almost equal. The breakthrough curves of glycerol were shown in Fig. 7B. When the adsorption of 1, 3-PD achieved saturate point, glycerol did not saturate and the adsorption is 310, 388 and 433 mg/g, respectively. Additional analysis was showed in Table 4.

Although increasing temperature is beneficial to adsorption, the value of  $A$  in 313 K did not remarkably increase (Table 4). It was due to that the migration velocity and the contact between glycerol molecules and resin also increased and influence the adsorption of 1, 3-PD by occupying adsorption sites. The adsorption of 1, 3-PD to the resin was spontaneous and endothermic. The adsorption kinetics was accurately represented by the shell progressive model and indicated that the particle diffusion was the rate-limiting step[19].

Considering decreasing operating cost and simplifying experiments, the temperature was fixed at 298 K.

Data was fitted based on Yoon-Nelson kinetic model, the results of simulating parameters shows in Table 4 and Fig. 8.

As showed in the Fig. 8, the value of  $k$  decreased with the increasing of temperature. The value of  $x_{exp}$  by using model and  $x$  shared a similar result, indicated that Yoon-Nelson kinetic model can simulate the adsorption process under different temperatures.

### 3. 4 The effect of stack height on adsorption

The effect of stack height on adsorption was studied with 10. 0, 15. 0 and 30. 0 cm respectively (Fig. 9A).

Experiment condition: flow rate, 1. 00 mL min<sup>-1</sup>, fermentation broth with 1, 3-PD, 30. 0g L<sup>-1</sup>; stacking height, 10. 0, 15. 0, 30. 0 cm; temperature, 298 K.

As showed in Fig. 9A, the slope of the breakthrough curve gradually decreased with the increasing of stack height, indicated that high stack height promoted adsorption. Supplementary analysis shows in Table 5.

As showed in Table 5,  $q_{total}$  and  $A$  was low when  $H$  was 10. 0 cm for the resin quantity and the active sites of fixed bed decreased. The MTZ (8. 44 cm) was nearly as the whole bed height, showing that the relative low efficiency of the adsorption. The parameter was small owing to reasons above, placing competing adsorption between 1, 3-PD and glycerol, also the shorter contact time between resin and solution for decreasing height. Comparably, the <https://assignbuster.com/purification-of-13-pd-from-complex-fermentation-broth/>

values of breakthrough parameters when H equaled to 30.0 cm were fine: the maximum of  $q$  total attained 2.13 g, which was significantly higher than other values and the value of  $A$  was also maximum. The main reason was the increasing stack height resulted in the increasing of contacting time between resin and adsorption sites for better adsorption. On the other hand, with the adding of resin in adsorption bed, improved the capability of adsorption to 1,3-PD ( $t_e$  increased, the slope of breakthrough curves, the adsorption of resin increased). The breakthrough curves in three stack heights showed in Fig. 9B. The adsorption of glycerol is 117, 269 and 388 mg/mg, respectively. Moreover, the increasing of bed height increased the number of theoretical plates in separation degree. Considering the value of  $t_b$ ,  $t_e$  and  $A$ , 30.0 cm was chosen for the following experiments.

Data fitting based on Yoon-Nelson kinetic model, the results of simulating parameters of the adsorption process in Table 5 and Fig. 10. The value of  $k$  decreased with the increasing of stack height and  $x_{exp}$  was similar to  $x$ , indicating that Yoon-Nelson kinetic model can fit the adsorption in different stack height.

$M_0$  (g) is the elution quantity of 1,3-PD,  $M_1$  (g) is the quantity of glycerol

The effect of ethanol concentration on elution curves was studied with three different ethanol volumes (30%, 50%, 75%), which were showed in Fig 11.

As shown in Fig 11, 1,3-PD was the eluted out firstly. The retention time of 1,3-PD and glycerol enlarged in the column were due to the stack height of this fixed bed (30.0 cm). The overlapping of curves between components

decreased obviously. It also prolonged the adsorption time between 1, 3-PD and glycerol with resin. 1, 3-PD and glycerol separated through continuous adsorption and desorption. Resin prefers the adsorption of glycerol to 1, 3-PD. Glycerol replaced the 1, 3-PD which adsorbed on the resin, caused the glycerol layer enlarged while 1, 3-PD layer moved down. Furthermore, ethanol selectively eluted 1, 3-PD. Therefore, the 1, 3-PD was the firstly been eluted. With the elution of 1, 3-PD, the percentage of 1, 3-PD in eluent decreased. The ability of the eluent increased so glycerol been eluted down. Besides, when the volume percentage of ethanol increasing from 30% to 75%, both peaks of 1, 3-PD and glycerol improved and concentrated, indicating that high concentration of ethanol was advantageous for the collection of components.

The elution quantity of 1, 3-PD ( $M_0$ ) and elution quantity of glycerol ( $M_1$ ), were calculated according to elution curves and showed in Table 6.

As showed in Table 6, the elution rate of 1, 3-PD improved from 64. 3% to 95. 3%, indicating that high concentration ethanol was helpful to the elution of relevant components. Meanwhile, both elution ratio of 1, 3-PD and glycerol increased and attained a maximum when ethanol was 75%. The mass ratio of 1, 3-PD and glycerol in eluent improved from 6: 1 to 14. 6: 1 in broth, and the concentration of 1, 3-PD increased from 85. 7% to 93. 6%, indicating that both of 1, 3-PD and glycerol been divided efficiently. Moreover, with the increasing of ethanol volume percentage, the elution amount of both 1, 3-PD and glycerol increased. However, the increasing of elution amount of glycerol was little, which mean the combination force between glycerol and resin was stronger that 75% ethanol could not eluted glycerol down. 100% ethanol was <https://assignbuster.com/purification-of-13-pd-from-complex-fermentation-broth/>

also used for elution and caused severe dehydration of resin. Therefore, 75% ethanol was used as eluent.

### 3. 6 The effect of the elution flow rate

The flow rate increasing from 1. 00 to 2. 00 mL min<sup>-1</sup> to investigate the effect of elution flow rate on 1, 3-PD and glycerol. The results showed in Fig. 12 and relevant parameters in Table 7.

As showed in Fig. 12, increasing flow rate, the elution peak of both 1, 3-PD and glycerol decreased. In Table 7, with the increasing of flow rate, the elution of 1, 3-PD decreased while that of glycerol improved. Meanwhile, the mass ratio of 1. 3-PD to glycerol decreased from 14. 6 to 9. 88, indicating that increasing elution rate was not favorable to the separation of 1, 3-PD and glycerol. Therefore, the elution efficiency and 1, 3-PD separation could be improved significantly if slow down elution rate and increasing contact time between eluent and 1, 3-PD in the resin.

As shown in Fig. 11 and Fig. 12, when the flow rate was 1. 00 mL min<sup>-1</sup> and the concentration of ethanol is 75%, 1, 3-PD and glycerol showed a seemingly separation on the curve: the curve of glycerol appeared from 54 mL which means before that the system only contained 1, 3-PD; after 98 mL 1, 3-PD and glycerol coexist in the mixture. It is known by calculation that before 54 mL the quantity of 1, 3-PD was 1. 64 g as a percentage of 80. 8%. Mixture collected could return to the fermentation broth for the next adsorption process. 1, 3-PD could be acquired by first 54 mL eluent after vacuum distillation.



Further resolution of the two substances with the flow rate as 0.500 mL min<sup>-1</sup> were studied. The overlapping degree of 1, 3-PD and glycerol curves reduced, but could not be completely separated. Meanwhile, the time increased remarkably as 304 min, indicating that although decreasing flow rate was helpful to improve separation efficiency, the production efficiency decreased. Therefore, 1.00 mL min<sup>-1</sup> was selected as the best flow rate.

### 3.7 Purification of the 1, 3-propanediol

Vacuum distillation, which is energy saving due to the decline of boiling point, is preferred to traditional distillation. 324 ml eluent was collected after six times adsorption and elution separation. No glycerol has been tested by HPLC. The eluent was added into rotary evaporator (vacuum 0.093-0.097 MPa and temperature 60-65 °C) for ethanol recycling. After recycling, the remaining solution transferred to vacuum distillation under Vacuum degree at 0.093-0.097 MPa. Collecting impurity below 129 °C and 1, 3-PD fraction between 129-149 °C. The purity of 1, 3-PD has been tested by HPLC is 99.2% (sample has been sent to the independent third test institution for detection).

## 4 Conclusion

Recovery and purification of 1, 3-PD from complex fermentation broth represents a technological challenge and true bottleneck in the development of a commercially viable bioprocess of this promising bulk chemicals. The present work provides a novel technique for purification of 1, 3-propanediol from crude glycerol-based fermentation broth. Separation and purification of  
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1, 3-propanediol was achieved by four simple steps: removal of cells and proteins by chitosan flocculation, decoloration by activated carbon, adsorption by fixed bed cation exchange resin, and vacuum distillation. Furthermore, in order to predict the breakthrough curves and to determine the characteristic parameters of the column, Yoon-Nelson models were applied to the experimental data. Parameters as adsorption capacity at breakthrough time ( $t_b$ ) and saturation time ( $t_s$ ), length of the mass transfer zone (MTZ) were obtained for the different operation conditions used in the adsorption experiments. The characteristic column parameters were calculated for process design. The overall yield of 1, 3-propanediol recovery is calculated to be 80.8% with 99.2% of purity. This process, which is simple, fast, and efficient, will promote the commercialization of 1, 3-propanediol production.