CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
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DOI: 10.3303/CET0917156

Sorption Kinetics of Riboflavin from Lactose Solutions in Chromatography Columns

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The sorption of riboflavin by Amberlite FPX66 resin was studied using downward flow of riboflavin containing solutions through packed columns at different temperatures and flow rates. In recycled batch mode, the adsorption rate followed the pseudo-first-order kinetic model at a low temperature and the pseudo-second-order model at a higher temperature. During the initial stage of a continuous run the adsorption processes followed the zero-order model. The intra-particle diffusivity D was found to increase linearly with increasing adsorbent/sorbate ratio and flow rates and decreased in lactose solution compared to lactose-free solution. Continuous sorption was superior, removing 1.5 times more riboflavin than the batch mode after two hours.

1. Introduction

Production of high value lactose from whey permeate requires removal of the yellow colour of riboflavin and Maillard browning compounds arising from processing. The fruit juice and sugar industries have been applying activated carbon due to its good performance in removing colorants (Carabasa et al., 1998, Rein et al., 2007). However, the disadvantages of activated carbon, such as its costly operating expenses and complex thermal regeneration requirements have encouraged studies towards using synthetic resin (Gula and Paillat, 2005). The decolourisation of fruit juices and cane sugar solutions using adsorption or ion exchange resin in agitated vessel has been studied with good results (Garcia Agudo et al., 2002; Broadhurst and Rein, 2003; Serpen et al., 2007). Recently Pragono et al. (2008) studied the use of a non-polar adsorbent resin in agitated vessels to remove more than 90% of the riboflavin from whey permeate model solutions containing 8.5 mg/L riboflavin in a 15% lactose solution and in water. This report extends the study of decolourisation of the whey permeate model solution to glass chromatography columns filled with adsorbent resins (AR). Operating the resin beds in a “batch recycled” mode (where the feed was collected at the column exit and recycled) and “continuous” mode (where the feed experienced a single pass through the column) facilitated comparison of the sorption kinetics with the earlier results in agitated vessels (Pragono et al., 2008).

Please cite this article as: Pragono R., Vu L., Hourigan J., Durham R. and Sleigh R., (2009), Sorption kinetics of riboflavin from lactose solution in chromatography columns, Chemical Engineering Transactions, 17, 933-938 DOI: 10.3303/CET0917156

2. Sorption Kinetics Models

The rate of adsorption of colorants onto resins in batch runs will be expressed by two commonly used mathematical models: pseudo-first-order (Eq.1) and pseudo-second-order (Eq.2) equations (Ho and McKay, 1998). In continuous mode this sorption rate can be assumed remaining constant with time (Eq.3). In these three expressions, k with subscripts *1*, *2* and *c* are the rate constants; t stands for time; q_t and q_e are respectively the concentration and equilibrium solid phase concentration calculated by dividing the mass of sorbate by the mass of adsorbent resin (mg/g).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \Rightarrow \frac{q_e - q_t}{q_e} = e^{-k_1 t} \tag{1}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \Rightarrow \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

$$\frac{dq_t}{dt} = k_c \Rightarrow q_t = k_c t \tag{3}$$

The rate of adsorption in porous adsorbent is generally controlled by transport within the pore network, which is considered as a diffusive process. For most adsorbent particle shapes the transient uptake curves can be analysed and interpreted by the diffusion equation shown in Eq.4, assuming constant diffusivity (Ruthven, 1984; Serpen *et a*l, 2007).

$$\frac{\partial q_t}{\partial t} = D\left(\frac{\partial^2 q_t}{\partial a^2} + \frac{2}{a}\frac{\partial q_t}{\partial a}\right) \tag{4}$$

The solution of the second-order partial differential equation (Eq.4) is complex but for the fractional uptake less than 30% or at the earlier time of the adsorption process, a more useful form of the solution as Eq.5 is available to estimate the intra-particle diffusivity D based on an average radius a of macroporous adsorbent particles.

$$\frac{q_t}{q_e} = 6\left(\frac{D}{\pi a^2}\right)^{1/2} t^{1/2} \tag{5}$$

In this paper, experimental data will be fitted to the integrated forms of Eq.1, Eq.2 and Eq.3 to test the consistency of the sorption kinetics. The effect of feed flow rates and different bed dimensions on adsorption kinetics will be explored. A comparison of the performance of batch and continuous modes will also be reported.

3. Experimental Methods

Model solutions of 8.5 mg/L riboflavin (sorbate) in water and in 15% TS (total solids) lactose were made by dissolving 8.5 ± 0.5 mg of riboflavin (Fluka, HPLC grade) in 1L of deionised water or in lactose solution (157 g pharmaceutical α-lactose monohydrate in 1L solution) (Wyndale Lactose NZ, Hawera, NZ). Whey permeate after reverse osmosis usually contains between 10-15% TS lactose and around 4 mg/L riboflavin but the higher riboflavin concentration in the model solutions helped in generating the colour reduction profile. In the recycled batch mode, a volume of 4.8L of the solution was recirculated through a bed of wet, macroporous food grade Amberlite FPX66 resin (Rohm and Haas) in glass columns at 30, 60˚C or at ambient temperature (AB) while in continuous mode 180-375 bed volumes were passed through the bed once with an additional 30 ml for extra-column volume. Batch run duration was 20 hours, after which there were no longer marked changes in riboflavin uptake. Flow rates tested ranged from 15 to 64 ml/min. Samples were analysed for riboflavin contents by spectrophotometry (1240 UV-Vis) at 270 nm. Glass columns used were from GE LifeSciences (Australia): small Excel Column (1.5D x 30H), medium XK Column (2.5D x 40H) and large XK Column (2.5D x 60H) with D for internal diameter (cm) and H for column length (cm). One batch column cycle had an exact replicate value for k_1 and one stirred beaker run had a standard deviation of 0.0148 for k_2.

4. Results and Discussion

Experimental data of 34 batch runs (in vessels and column) and 9 continuous runs were fitted to the integrated forms of Eq.1, Eq.2 and Eq.3 to test the consistency of the sorption kinetics. Some of the representative results with correlation coefficients approaching 1 ($R^2 > 0.99$) were shown in Table 1. Pragono et al. (2008) found that in all batch cases the sorption in the vessels equipped with the stirrers or placed in the shaker followed the pseudo-second-order kinetic model. This was in agreement with previous studies conducted in shaken or stirred reactors (Serpen *et a*l, 2007; Vadivelan & Kumar, 2005). Meanwhile, those in small, medium and large packed columns followed the pseudo-first-order kinetic model and in the initial stages of continuous runs (up to 120 bed volumes) the sorption followed zero-order model. Obviously during stirring and shaking in the vessels both the sorbate and the adsorbent particles were allowed to move freely, exposing the sorbate to the full surface area of each adsorbent particle. In contrast, in a packed column the sorbate was only in contact with a fraction of the surface area of adsorbent particle in the void volume referred to as the effective surface area. This was confirmed in the kinetic plots of Fig 1. At 30ºC and in a 15% TS lactose solution, adsorption in a batch shaker followed the pseudo-second-order model, which was faster than the pseudo-first-order adsorption in a packed column. Meanwhile, during the beginning of a continuous run up to 120 bed volumes, adsorption could be assumed to follow a linear trend. The continuous adsorption was initially faster than first order-rate and slower than second order rate, but later became faster than both rates in batch modes (Fig. 1). It could be explained that the fresh solution containing the same high sorbate concentration was continuously fed into the system resulting in a higher difference between the concentration of the bulk solution and that at the surfaces of the

resins. In addition to the effect of the system configuration, e.g. packed column or vessel, the adsorbent/sorbate ratio C_{AR} (g/mg) or the mass of resin used over the total mass of sorbate (colorant) in the system and temperature affect the kinetic order. For example, in this work if C_{AR} was 0.05 g/mg or less the adsorption rate at 30°C would follow the first-order model even in a vessel, while at 60°C the second-order model is maintained (Table 1, runs 3 and 5). Similarly at 60ºC the adsorption rate would follow the second order model even in a packed column (Table 1, runs 8 and 10).

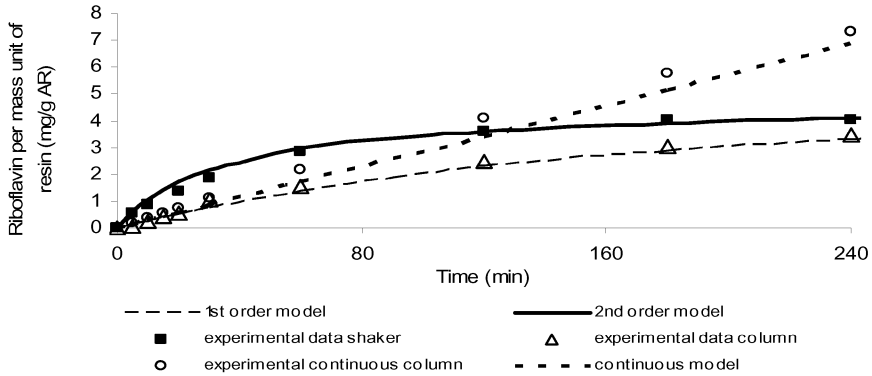

Figure 1 Profiles of riboflavin adsorption from 15% TS lactose model solution

The rate constants k with subscripts *1, 2* and *c* were not comparable but the intra-particle diffusivity D could be used instead for comparison. D calculated from Eq.5 was dependent on the surface area of the adsorbent (πa^2) and the solid phase concentration at equilibrium (assuming after 20 hours) q_e. As explained above, batch vessels allowed a larger total surface area of resins exposed to the colorant resulting in higher values of D compared to those of packed columns at the same operating conditions and similar C_{AR}. A power function (R^2 = 0.991) in Eq.6 was derived from 18 runs and describes the relationship of q_e (mg/g) and C_{AR} (g/mg).

$$q_e = 1.0287\, C_{AR}^{(-0.884)} \tag{6}$$

Diffusivity was found to be functionally increased with C_{AR}, and linearly increased with flow rates as shown in Fig. 2 for both batch and continuous run. Other variables such as temperature and total solid lactose in the feed slightly affected D. For example D was slightly increased with an increase in temperatures from 30ºC to 60ºC (runs 7 and 8; 9 and 10). On the other hand, D of 15% TS lactose solution was smaller than that of lactose-free solution at the same temperature (runs 7 and 9; runs 8 and 10). Reducing the resin bed height from 21 cm to 8 cm (Table 1, runs 15-17) while maintaining flow rate and C_{AR} increased D and k_1 relatively linearly as expected, due to an increase in column back pressure. Fig. 2 and Table 1 (runs 9 compared to 19) also suggest that D found in a continuous run was higher than that of a batch run at the same operating conditions. After two hours, 84% of riboflavin was removed in continuous sorption and 54% in the batch.

Table 1 Rate and film diffusion constants of batch adsorptions in various configurations

Mode	Configuration	Flow rate or resin bed height	T (°C)	Lactose (%TS)	C_{AR} (g/mg)	k	Order (zero, pseudo-first or -second)	R^2	q_e (exp) (mg/g)	D (m^2/s)	Run number:
BATCH	Stirred beaker #		30	0	0.58	0.3325	2nd	0.9997	1.665*	9.55E-12	1
				15	0.54	0.1009		0.9975	1.774*	5.03E-12	2
	Shaker#		30	15	0.05	0.0041	1st	0.9929	13.937	3.06E-13	3
					0.10	0.0014	2nd	0.9931	8.479	4.51E-13	4
			60	15	0.05	0.0010	2nd	0.9935	11.119	3.94E-13	5
					0.10	0.0027		0.9944	7.469	6.53E-13	6
	Small column	44 ml/min	30	0	0.22	0.0104	1st	0.9995	4.369	7.27E-13	7
			60		0.22	0.0041	2nd	0.9914	3.871	8.11E-13	8
			30	15	0.21	0.0069	1st	0.9937	4.468	6.14E-13	9
			60		0.23	0.0097	2nd	0.9882	3.991	6.95E-13	10
	Large column	24 ml/min	30	0	1.83	0.0085	1st	0.9500	0.603*	5.92E-13	11
		34 ml/min			1.83	0.0117		0.9300	0.604*	6.78E-13	12
		44 ml/min			1.85	0.0150		0.9393	0.596*	8.73E-13	13
		54 ml/min			1.85	0.0159		0.9696	0.597*	1.00E-12	14
	Medium column	8 cm	AB	0	1.17	0.0385	1st	0.9993	0.895*	2.47E-12	15
		14 cm			1.14	0.0200		0.9989	0.916*	1.41E-12	16
		21 cm			1.13	0.0166		0.9851	0.923*	8.58E-13	17
CONTINUOUS	Small column	44 ml/min	30	15	0.21	0.0368	zero	0.9965	4.168*	1.46E-12	18
		15 ml/min			0.19	0.0127		0.9998	4.461*	4.41E-13	19
		27 ml/min			0.24	0.0214		0.9992	3.674*	9.49E-13	20
		35 ml/min			0.22	0.0297		0.9998	3.863*	1.24E-12	21
		52 ml/min			0.23	0.0431		0.9986	3.705*	1.96E-12	22

*indicates predicted values using Eq. 6 #Pragono et al. (2008)

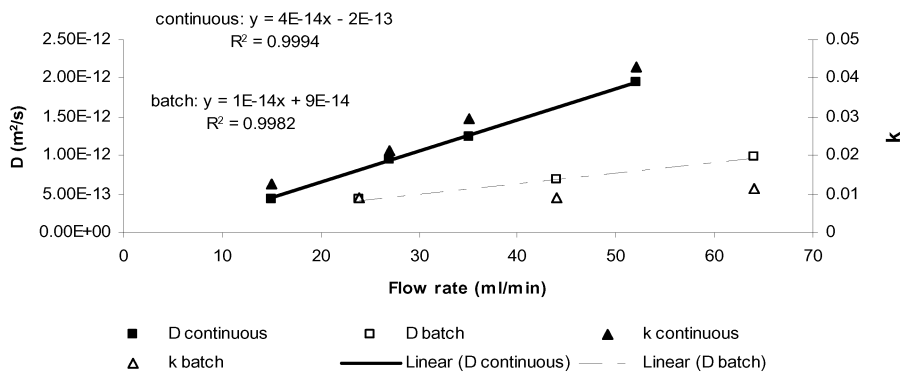

Figure 2 Relationship between flow rates, intra-particle diffusion (D) and rate constant in continuous and batch adsorption of riboflavin in lactose solution

5. Conclusion

This work studied the sorption kinetics in chromatography columns having different resin bed dimensions and operated in batch and continuous modes at different temperatures, flow rates and adsorbent resin concentrations. The adsorption processes in small, medium and large packed columns operated in cyclic batch mode followed the pseudo-first-order kinetic model at 30°C and second-order kinetic model at 60°C. Initially in continuous runs the adsorption process followed a zero-order model. For comparison of kinetics of different models, the intra-particle diffusivity was used instead of rate constants. This diffusivity was strongly dependent on the equilibrium solid phase concentration and on total surface areas. Therefore the diffusivity linearly increased with increasing adsorbent/sorbate ratio and feed flow rates. Other variables such as temperature, feed compositions and column configurations may have slight and indirect influences on diffusivity. The continuous process has a two-fold larger diffusivity than the batch process at the same operating condition.

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