Recovery of oryzanol from rice bran oil by silica-based batch adsorption: Radial diffusivity inside particle

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Abstract. In this study, quantitative description on oryzanol batch adsorption from rice bran oil via mathematical model has been developed. The accuracies of the model proposed were tested based on experimental data from literature. The main idea is that the effective radial diffusivity of oryzanol in the adsorbent particle be dependent on the distance to the center of the adsorbent particle. The oryzanol mass transfer rate from the bulk of the liquid to the surface of silica gel particle follows the film theory. Meanwhile the distribution coefficient correlation was used to describe the adsorption equilibrium. The values of the involving parameters were obtained by visual inspection. The model proposed works quantitatively well but in order to get general values of parameters for various particle sizes, further improvement is still required.

1. Introduction

Oryzanol, a valuable compound, is naturally contained in rice bran oil and is an important value-added co-product of rice bran processing. Oryzanol is a mixture of at least five trans ferulic acid esters with phytosterols [1-7]. Literature studies show that oryzanol is proficient to prevent cardiovascular disorder because of the ability of lowering cholesterol levels [8-13].

It had been reported that adsorption-desorption systems are believed as one of promising methods to recover valuable components such as oryzanol from rice bran oil, provided that appropriate mobile phases are available [14, 15]. Quantitative studies of the adsorption equilibrium and kinetics of oryzanol isolation need to be further studied for the purposes of engineering process design and operation. The studies conduct mathematical model simulation to obtain quantitative description of the process as well as to approximate the values of the involving parameters. The experimental data from literature were applied to verify the accuracy of the proposed mathematical model. It is imagined that the adsorption consists of several processes in series which are (1) the mass transfer of oryzanol from the bulk of liquid to the surface of silica gel particle, (2) the intra-particle diffusion through the liquid inside pore from the surface of silica gel particle to the inside part, and (3) the adsorption from the liquid inside pore to the adjacent pore surface. The third process is considered to be fast so the both first two processes affect the rate of oryzanol adsorption. Usually, the adsorption at the pore surface is assumed to be instantaneous, so local adsorption equilibrium always attained.

Experimental studies on batch oryzanol adsorption from rice bran oil have been conducted by [16]. They also proposed mathematical model by assuming oryzanol effective radial diffusivity in the silica.
gel and distribution coefficient for the local equilibrium of adsorption be constant (called as Model 1). Model 1 works quantitatively well, but discrepancies were encountered. The studies show that larger particles better adsorb oryzanol than the smaller one.

The effective radial diffusivities of oryzanol inside silica gel with average diameter of 0.0815 mm and 0.35 mm were 8 x 10^{-3} cm^2/s and 4.2 x 10^{-4} cm^2/s, respectively. It means that the smaller particle has smaller value than the larger one. These phenomena are not conceivable since smaller particle are usually better adsorb solute from solution because the internal diffusion for small particle is faster than the one of larger particle. This study intends to quantitatively explain these discrepancies by assuming that the effective radial diffusivity depends on the distance to the center of the particle. The larger the distance to the center of particle, the higher effective radial diffusivity would be. In this paper the effective radial diffusivity is assumed to be proportional to the distance to the center of particle (Model 2).

2. Mathematical model development
This section explains the proposed mathematical model. The model is elaborated into several subsections as follow.

2.1. Material balance in silica gel particle
Oryzanol material balance in the volume element in the adsorbent particle resulted in partial differential equation as shown in equation (1). In equation (1), the accumulation of oryzanol in the volume element includes the accumulation of oryzanol in the liquid inside the pore and the accumulation of oryzanol adsorbed at the surface of the pore.

$$\frac{\partial}{\partial r} \left[ D_e r^2 \left( \frac{\partial C_{As}}{\partial r} \right) \right] = \varepsilon r^2 \frac{\partial C_{As}}{\partial t} + a_s r^2 \frac{\partial X_{As}}{\partial t}$$  \hspace{1cm} (1)

By assuming that local oryzanol adsorption equilibrium at the surface of pore is always attained, and the equilibrium follows distribution coefficient model, equation (1) becomes equation (2).

$$\frac{\partial}{\partial r} \left[ D_e r^2 \left( \frac{\partial C_{As}}{\partial r} \right) \right] = (\varepsilon + a_s K_f) r^2 \frac{\partial C_{As}}{\partial t}$$  \hspace{1cm} (2)

Equation (2) can be manipulated into equation (3). In equation (3), $D_e$ is radial effective diffusivity of oryzanol through the pore of the particle (cm/s) and responsible to the oryzanol concentration gradient in silica gel particle.

$$\frac{\partial C_{As}}{\partial t} = \frac{1}{(\varepsilon + a_s K_f) r^2} \frac{\partial}{\partial r} \left[ D_e r^2 \left( \frac{\partial C_{As}}{\partial r} \right) \right]$$  \hspace{1cm} (3)

In the previous work, the developed model assumed constant $D_e$ and constant $K_f$ [16]. The model well describes the dynamics of oryzanol concentration inside silica gel at various time, but cannot logically explain the phenomenon that the larger particles better adsorb oryzanol than the smaller ones.

The model proposed in this study is intended to logically describe the discrepancies found in the previous study. The basic idea is that the effective radial diffusivity is proportional to the distance to the center of particle (r). The argument of this idea is based on the fact that silica gel particles was made by granulation. The initial solid formed (the inner part of silica gel particle) is more compact than the later one (the outer part of silica gel particle) so the porosity in the inner part is smaller than the one of the outer part. As a result, the effective radial diffusivity of the outer part is larger than the one of the inner part. Mathematically the effective radial diffusivity is modeled by equation (4).

$$D_e = \mathcal{D} r$$  \hspace{1cm} (4)
with $\mathcal{D}$ is a constant. Combination of equation (3) and (4) gives equation (5).

$$\frac{\partial C_{AS}}{\partial t} = \frac{\mathcal{D}}{(\varepsilon + a_s K_f)} \left[ r \frac{\partial^2 C_{AS}}{\partial r^2} + 2 \frac{\partial C_{AS}}{\partial r} \right]$$

(5)

2.2. Material balance in the bulk of the liquid

Oryzanol concentration inside the adsorbent particle was not uniform and was assumed to be depending on the distance to the center of the silica gel particle. The mass of oryzanol in the particle ($m_{AS}$) was calculated by integrand and mathematically formulated as shown in equation (6).

$$m_{AS} = N_b \int_0^R 4\pi r^2 (\varepsilon C_{AS} + a_s X_{AS}) dr$$

(6)

Since the local oryzanol adsorption equilibrium at the surface of pore is always attained, and the equilibrium follows distribution coefficient model, equation (6) can be written as equation (7).

$$m_{AS} = 4\pi N_b (\varepsilon + a_s K_f) \int_0^R C_{AS} r^2 dr$$

(7)

The concentration of oryzanol in the liquid can be computed using equation (8).

$$C_{AI} = C_{AI0} - \frac{4\pi N_b}{V} (\varepsilon + a_s K_f) \int_0^R C_{AS} r^2 dr$$

(8)

where $C_{AI}$ is oryzanol concentration in the bulk of the liquid (mg/ml), $C_{AI0}$ is initial oryzanol concentration in the bulk of the liquid (mg/ml), $N_b$ is number of adsorbent particles, $V$ is volume of liquid (ml), $\varepsilon$ is porosity of the adsorbent particles, $a_s$ is pore specific surface area of the adsorbent particles (cm$^2$/cm$^3$), $K_f$ is distribution coefficient, $C_{AS}$ is oryzanol concentration inside the pore of particle (mg/ml), and $r$ is distance to the center of the particle (cm).

In order to solve the mathematical models proposed, initial and boundary conditions are required. Initially, the oryzanol concentration in the bulk of the liquid is $C_{AI0}$ while the oryzanol concentration in the silica gel particle is zero. Mathematically it can be written as: $C_{AI}(0) = C_{AI0}$ and $C_{AS}(r, 0) = 0$. The first boundary condition is that at every time the value of $C_{AS}$ at the center of silica gel particle is minimum or mathematically: $\frac{\partial}{\partial r} C_{AS}(0, t) = 0$. The second boundary condition is that at any time, the flux of oryzanol at the surface of silica gel particle is continuous or mathematically: $-D_e \frac{\partial}{\partial r} C_{AS}(R, t) = k_c(C_{AS}(R, t) - C_{AI}(t))$.

2.3. Numerical calculations

The equations were numerically solved using Finite Difference Approximation (FDA). The implicit method was applied [17]. Meanwhile, the integral for calculating the amount of oryzanol in the particle was conducted by Simpson’s rule.

3. Results and discussions

The previous experiment was performed for two different sizes of silica gel particles (diameter of 0.0815 mm and 0.35 mm) at the same initial oryzanol concentration in the liquid which was 0.011288 mg/mL and at the same of ratio of mass of adsorbent to the volume of solution (140 mg adsorbent per 7 mL liquid).

The results studies from [16] are presented in figure 1 and table 1. In figure 1, fractions of remaining oryzanol in the liquid ($C_t/C_0$) for both of particle sizes were plotted versus time.
Figure 1. Fraction of remaining oryzanol mass in the bulk of the liquid in batch adsorption.

Model 2 was then applied to the data from [16]. In these calculations the values of the involving parameters are obtained by visual inspection. The computational results using Model 2 are shown also in figure 1. The values of the parameters obtained for Model 2 are also listed in table 1.

| Parameters                        | Values          |
|-----------------------------------|-----------------|
| Model 1                           | Model 2         |
| Average particle diameter, mm     | 0.0815          | 0.35           |
| Effective radial diffusivity, $D_e$, cm$^2$/s | $8 \times 10^{-5}$ | $4.2 \times 10^{-4}$ |
| Constant of effective radial diffusivity, $\mathcal{D}$, cm$^2$/s | -               | $4 \times 10^{-4}$ |
| Distribution coefficient, $K_f$, g silica/ml solution | $1.2 \times 10^6$ | $1.7 \times 10^6$ | $2.1 \times 10^6$ |
| Mass transfer coefficient, $k_c$, 1/s | 0.825           | 0.825          |
| Sum of Squares of Errors, SSE,%   | $2.8 \times 10^{-5}$ | $2.5 \times 10^{-7}$ | $2.5 \times 10^{-5}$ | $2.6 \times 10^{-7}$ |

Even though the values of Sum of Squares of Errors for Model 2 are slightly smaller but the two values are almost comparable. Furthermore, figure 1 shows that the accuracies of Model 1 and Model 2 are visually comparable. Hence, it can be concluded that the computational results as of Model 1 and Model 2 are comparable.

The gain of Model 2 is that the model can logically explain the phenomena that larger particle can adsorb oryzanol from solution faster than the one of smaller particle. However, the values of constant of effective radial diffusivity (Ω) as well as the distribution coefficient ($K_f$) for smaller particle differ to the ones of larger particle. Further improvement of the model is still needed and we are still working on that study.

The comparison of time consumed for the calculation using Model 1 and Model 2 at the same computer showed that the time of calculation for Model 2 was approximately six time to the one of Model 1. It implies that Model 2 is significantly more complicated than Model 1.

4. Conclusion
This study concluded that Model 2 which assumes that the effective radial diffusivity is proportional to the distance to the center of the particle works well for adsorption of oryzanol from solution system
using silica gel adsorbent. However further improvement is still required to obtain the general values of parameters that can be applied for particles at different sizes.

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