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ISOTHERMAL OR NON ISOTHERMAL MODELLING IN A PELLET ADSORBENT

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Abstract: Understanding the interaction between a fluid and a solid phase is of fundamental importance to design an adsorption process. Because the heat effects associated with adsorption are comparatively large, the assumption of isothermal behaviour is a valid approximation only when uptake rates are relatively slow. In this article, we proposed to determine when you need to choose the isothermal or non isothermal assumptions according to two parameters α and β .

Keywords: Adsorption, non isothermal, modelling, pellet

Since the early sixties, separation processes by adsorption, such as pressure swing adsorption or thermal swing adsorption have become important industrial operations. At present, an application in the field of adsorption heat pumps (AHPs) represents one of the most promising technical applications of the adsorption process. Understanding the interaction between a fluid and a solid phase is of fundamental importance to the design of an adsorption process. These cyclic processes are based on a parallel arrangement of columns packed with adsorbent pellets. Because the heat effects associated with adsorption are comparatively large, the assumption of isothermal behaviour is a valid approximation only when uptake rates are relatively slow.

AHPs are thermally driven and can, therefore, make use of waste heat as well as thermal renewable energy resources. Moreover, AHPs can utilize high energy fuels more effectively than modern condensing boiler heating systems and, consequently, a reasonable amount of the resulted environmental pollution could be avoided. One of the most interesting working pairs for AHPs is zeolite-water. This working pair is non-poisonous, non-flammable and, moreover, has no ozone depletion potential. The adsorption of water vapour into a porous solid adsorbent, such as zeolite, results in the release of the heat of adsorption. Accordingly, the temperature of the adsorbent particle rises, which reduces its water uptake capacity. Therefore, the heat of adsorption has to be removed before a further vapour mass transfer into the adsorbent particle may take place. The evaluation of the heat and mass transfer rates accompanied with such an adsorption process is, therefore, a very important aspect in designing and optimizing the operation of an adsorption heat pump. This study presents the methodology to choose a good adsorbent in particular according to its thermodynamic properties. We focused our attention on the interaction fluid/solid. The simplest case to consider is a single microporous adsorbent particle exposed to a step change in sorbate concentration at external surface of the particle at time zero. Heat transfer is assumed to be sufficiently rapid, relative to the sorption rate, so that temperature gradients both through the particle and between particle and surrounding fluid are negligible. Two cases were developed in this article, firstly the isothermal conditions and secondly adsorption behaviour with temperature effect. According to two developed parameters α (ratio convection/capacity) and β (quantity of energy/capacity), the difference between isothermal and non-isothermal was analysed.

1. ISOTHERMAL ASSUMPTIONS

During adsorption, heat is generated which is partly transferred to the surrounding fluid and partly accumulated in the particle leading to a temperature increase. The calculation of the temperature uptake curves is based on mathematical model of different complexity depending on the simplifying assumptions being made. Firstly, we considered some isothermal conditions in the pellet and the isotherm was linear $q = q_0$.

The system was modelled by the following equations:

$$\left\{ \begin{array}{l} \frac{\partial q}{\partial t} = D_c \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad \forall t > 0, \forall r \ (0 < r < r_c) \\ q(r, t = 0) = 0 \quad \forall r \ (0 < r < r_c) \\ q(r_c, t) = q_0 \quad \forall t > 0 \\ \left. \frac{\partial q}{\partial r} \right|_{r=0} = 0 \quad \forall t > 0 \end{array} \right. \quad (1)$$

The value $q(r_c, t)$ was equal to $q_0 \neq 0$, for solving the system analytically. The analytic solution was, with $\tau = D_c t / r_c^2$;

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 \pi^2 \tau}}{n^2} \quad (2)$$

Where m_t represents the quantity adsorbed in the pellet at time t and m_∞ at final time. We denote $\bar{Q}(\tau) = m_t / m_\infty$.

In practice m_t / m_∞ will be approximated by: $\bar{Q}_N(\tau) = 1 - \frac{6}{\pi^2} \sum_{n=1}^N \frac{e^{-n^2 \pi^2 \tau}}{n^2}$ (3)

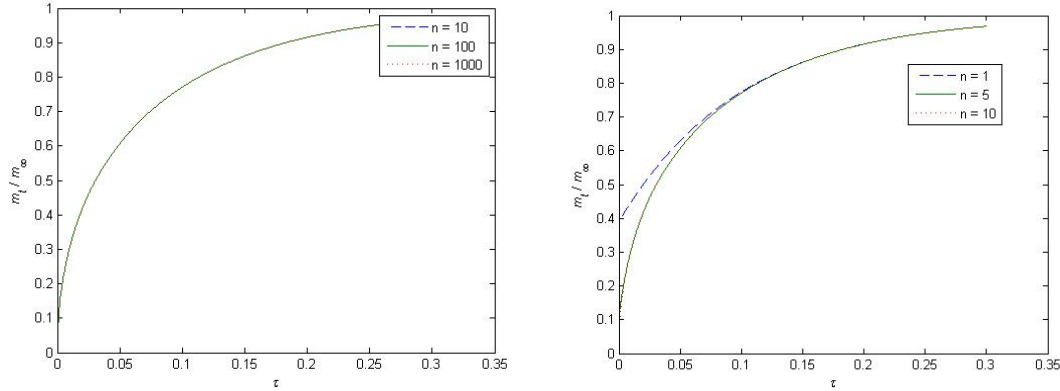


Fig. 1. Numerical approximation on m_t/m_∞ values versus the reduced time τ

Figure 1 shows different approximations and it seems that the convergence is quite fast since, starting from $N=5$, we cannot see any difference of the graphs of the $\bar{Q}_N(\tau)$. Let us check by the following simple error estimation:

$$\begin{aligned}
|\overline{Q}(\tau) - \overline{Q}_N(\tau)| &= \frac{6}{\pi^2} \sum_{n=N+1}^{\infty} e^{-\frac{n^2 \pi^2 \tau}{n^2}} \leq \frac{6}{\pi^2} \sum_{n=N+1}^{\infty} \frac{1}{n^2} \\
&\leq \frac{6}{\pi^2} \int_N^{\infty} \frac{dx}{x^2} = \frac{6}{\pi^2 N}
\end{aligned} \tag{4}$$

This gives for $N=5$ an absolute error of approximately 0.12. But notice that in reality the error is much smaller at least if τ stays away from zero. Indeed, if $\tau \geq \tau_0 \geq 0$, then the upper estimation can be improved to the following exponential error bound:

$$|\overline{Q}(\tau) - \overline{Q}_N(\tau)| = \frac{6}{\pi^2} \int_N^{\infty} \frac{e^{-n^2 \pi^2 \tau_0}}{x^2} dx \leq \frac{3}{\pi^4 \tau_0} \frac{e^{-N^2 \pi^2 \tau_0}}{N^3} \tag{5}$$

For example, if the reduced time is at least $\tau_0 = 0.01$ and if again $N=5$ then we get for the absolute error a much better approximation of 0.000418.

2. NON ISOTHERMAL ASSUMPTIONS

In this case, we assume that intracrystalline diffusion was rapid so that the sorbate concentration throughout each individual adsorbent particle was uniform. Both the thermal conductivity is assumed to maintain an essentially uniform temperature throughout the entire adsorbent particle. The rate of heat transfer between adsorbent and the ambient fluid which is assumed to obey the Newton's law, was finite, so that during the course of the transient adsorption there was a time-dependent temperature difference between the adsorbent and ambient fluid. The system was subjected at time zero, to a small difference step change in ambient sorbate concentration from a previously established equilibrium condition. We assume that concentration equilibrium between fluid phase and adsorbed phase is established quickly at the free surface of the pellet and the equilibrium adsorbed phase concentration is assumed to vary linearly with both temperature and fluid phase concentration. Subject to these approximations, the system may be described by the following equation in reduced value ($Q=q(t)/q_{\infty}$), $\eta=\tau/r_c$ and $\tau=D_c t/r_c^2$). The reduced value permitted to find an analytic solution in the Laplace domain.

$$\frac{\partial Q}{\partial \tau} = \frac{1}{\eta^2} \frac{\partial}{\partial \eta} \left(\eta^2 \frac{\partial Q}{\partial \tau} \right) \tag{6}$$

$$Q(\eta, \tau) = 0, (\tau < 0) \quad Q(\eta, 0^+) = 0, (si 0 \leq \eta < 1) \tag{7}$$

$$Q(1, \tau) = Q_s(T) \tag{8}$$

$$\left. \frac{\partial Q}{\partial \eta} \right|_{\eta=0} = 0 \tag{9}$$

$$\rho(-\Delta H) \frac{d\overline{Q}}{d\tau} = \frac{\rho C_p}{q_{\infty} - q_0} \frac{dT}{d\tau} + \frac{ha}{q_{\infty} - q_0} \frac{(T - T_0)}{D/R_c} \tag{10}$$

The equilibrium relationship at the crystal surface is assumed to be linear:

$$Q_s = 1 + \frac{\partial q^*}{\partial T} \left(\frac{T - T_0}{q_{\infty} - q_0} \right) \tag{11}$$

The analytic solution, similar to Ruthven et al., 1980, is given by:

$$\bar{Q}(\tau) = 1 + \sum_{n=1}^{\infty} \frac{-9 \left(\frac{q_n \cot(q_n) - 1}{q_n^2} \right)^2 e^{-q_n^2 \tau}}{\frac{1}{\beta} + \frac{3}{2} \left[(q_n \cot(q_n)) \left(\frac{(q_n \cot(q_n)) - 1}{q_n^2} \right) + 1 \right]} \quad (12)$$

$$\text{where } q_n \text{ are the roots of this equation } (\alpha - q_n^2 - 3\beta) \sin(q_n) + 3\beta q_n \cos(q_n) = 0 \quad (13)$$

$$\text{and with } \beta = \frac{\Delta H}{Cp} \left(\frac{\partial q^*}{\partial T} \right) \text{ and } \alpha = \frac{ha}{\rho Cp} \frac{Rc}{D}$$

The parameters α and β were in a first approach variables used to solve the PDE system. But these two parameters represent respectively the ratio between the conductivity and the heat capacity and the ratio between the quantity of energy and heat capacity.

3. LOCATION OF THE ROOTS q_n AND DISCUSSION OF THE SOLUTION \bar{Q}

In order to understand the solution \bar{Q} we first have to discuss the roots of the transcendental equation (13). Then we give an error estimation of the N^{th} approximation of \bar{Q} similar to the one obtained in the isothermal case.

3.1 Location of the roots.

Let us start with having a look on the particular situation $\beta = 0$ which is again the isothermal case; it signifies infinitely large heat capacity. Then (13) becomes simply $(\alpha - q_n^2) \sin(q_n) = 0$ and the roots are $q_n = n\pi$, $n \in N$ plus a special root say $q' = \sqrt{\alpha}$.

The general case is not so much different. Indeed, suppose $\beta > 0$, then it is easy to conclude from the periodicity of the sine and cosine functions that every interval of the form $(n\pi, (n+1)\pi)$ contains exactly one root q_n of (13). In addition, there is one more, say special root q' coming from the factor $\alpha - q_n^2 - 3\beta$ in (13). The location of q' depends on the sign of $\alpha - 3\beta$:

- If $\alpha - 3\beta > 0$, then $q' \approx \sqrt{\alpha - 3\beta}$. More precisely, we have that $|q' - \sqrt{\alpha - 3\beta}| \leq \pi$.
- If $\alpha - 3\beta \leq 0$, then $q' \in (0, \pi/2)$.

In particular, one must take care of this root in the numerical approximations of \bar{Q} if $\alpha - 3\beta$ is small or negative.

3.2 Error bound.

Based on (13), we can reformulate the expression of Q in order to get $\bar{Q}(\tau) = 1 - 6 \sum_{n=1}^{\infty} C_n \frac{e^{-q_n^2 \tau}}{q_n^2}$ with C_n

depending on α , β and q_n . One can show that $|C_n| \leq 2$ which, together with the location of the roots q_n , allows us to proceed like in the isothermal case. Let us simply indicate how to get the estimation corresponding to (1). In order to do so, we make the convention that the summation of the approximation \bar{Q}_N is taken over the first N roots plus the special one q' if $q' \leq N\pi$. If $q' > N\pi$ then we have the following estimation (otherwise the error is a little smaller):

$$|\overline{Q}(\tau) - \overline{Q}_N(\tau)| \leq 12 \left(\frac{e^{-q^2}}{q^2} + \sum_{n=N+1}^{\infty} \frac{e^{-q_n^2}}{q_n^2} \right) \leq 12 \left(\frac{e^{-(N\pi)^2}}{(N\pi)^2} + \sum_{n=N+1}^{\infty} \frac{e^{-(n\pi)^2}}{(n\pi)^2} \right) \leq \frac{12}{\pi^2} \left(\frac{1}{N^2} + \frac{1}{N} \right)$$

for every $N \geq 2$

which is about two times the error estimation obtained in the isothermal case. If the reduced time $\tau \geq \tau_0 > 0$ then one has again the exponential decay of the error like in (2) due to the factor $e^{-N^2\pi^2\tau_0}$.

4. NON ISOTHERMAL AND ISOTHERMAL DIFFERENCE

The adsorption characteristics of water vapor on zeolite are essential data in determining the energetic performance of adsorption chillers. From the viewpoint of the fundamental design of adsorption chillers, the investigation of the adsorption isotherm is pertinent for the purpose of system modeling.

In terms of the adsorption chiller performance, the adsorbent must have good thermal conductivity as well as a large specific surface area. To estimate dynamic adsorption capacity using the parameter, we compared two assumptions isothermal or non isothermal. In the table 1., we resumed the used data (Kim et al., 2003) (Kim et al., 2005, 2004) and (Ryu et al. 2001). In this case, we found $\alpha=16.3$ and $\beta=2.07$.

Table 1 the used values found in the literature

ΔH	$\frac{\partial q^*}{\partial T}$	Cp	h	a	Rc	ρ	D
-36.10^3 J.mol ⁻¹	-0.053 mol.kg ⁻¹ .K ⁻¹	920 J.kg ⁻¹ .K ⁻¹	10 m ² .K.W ⁻¹	2.48 m ⁻¹	1.1 mm	1100 kg.m ⁻³	2.10 ⁻⁹ m ² .s ⁻¹

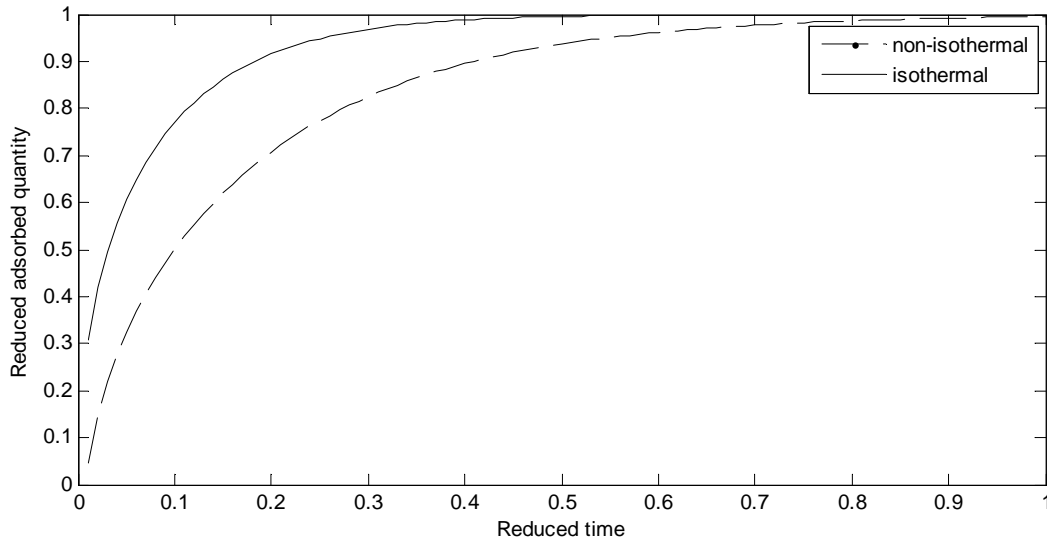


Fig 2 Comparison between isothermal or non isothermal water zeolite adsorption

Figure 2 shows the difference between the two models. In the non-isothermal modelling, the uptake curve commonly shows a rapid initial uptake followed by a slow approach to equilibrium because the external heat transfer controlled the adsorption. Let us recall that the isothermal model represents the ideal condition in the heat adsorption process.

In fact, in the isothermal case, the equilibrium was reach very quickly. The maximum difference between the two models is obtained in the beginning of the batch adsorption. This phenomenon is due to the fast temperature rising when the adsorption starts. The heat adsorption produced in the pellet is not transferred into the fluid due to the external heat transfer.

To increase the process efficiency, it is necessary to raise the external heat transfer. It can be modified by the hydrodynamics around the pellet. The values of α and β can determine the “efficiency” of the heat adsorption process. In fact, if β value is small and /or near to zero, the adsorption curve can be analysed as in isothermal case. But the heat adsorption process cannot be operated because it will not produce enough heat. The α value was more significant, because it represent the ratio between the convection and the thermal capacity. To reach the ideal case, α should tends toward infinity. The external heat transfer will not be a limited phenomenon then the adsorption is closed to the isothermal case.

CONCLUSIONS

In this article, we show the importance of the pellet adsorption study before to design a heat adsorption process. The difference between the two models isothermal or non isothermal could be measured by the value of α and β . In fact, when $\alpha \rightarrow \infty$ (infinitely high heat transfer coefficient) or $\beta \rightarrow 0$ (infinitely large heat capacity), the limiting case was isothermal. When diffusion was rapid (α small) the kinetics of sorption was controlled entirely by heat transfer. If the adsorption process might be used as a heat pump, it shall be represented by an isotherm model with α and β as higher as possible. Then, these two parameters could determine if the couple adsorbant/ adsorbate can be used in the case of an adsorption heat pump process.

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