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Breakthrough Curves Modelling**

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A Critical Short Review of Equilibrium and Kinetic Adsorption Models for VOCs Breakthrough Curves Modelling

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ABSTRACT: Volatile organic compounds emission has important effects over the environment and human beings health. When these substances cannot be substituted, adsorption systems are still a very common solution to VOCs emission, but for their design, previous laboratory work is necessary: adsorption isotherms and breakthrough curves must be obtained. The first ones establish the maximal amount of adsorbate retained over the solid adsorbent for a certain pressure of the adsorbate, and the second ones define the adsorption process kinetics. Once this information is studied, a theoretical breakthrough time model can be built up, and then the scale up of the adsorption system can be developed. This process is rather complex for multicomponent gas mixtures, where a competition between adsorbates happens. Thus, the aim of this paper is to establish a guide for authors willing to develop breakthrough time prediction models for multicomponent systems through a critical review of different adsorption and kinetic models.

Keywords: Adsorption modelling, kinetic model, VOC, multicomponent mixture.

1. INTRODUCTION

VOCs (Volatile Organic Compounds) are all those hydrocarbons which are at gas phase, or highly volatile at room temperature. These compounds consist of a chain of less than twelve carbon atoms, which can contain some elements like oxygen, fluorine, chlorine, sulphur or nitrogen. The number of VOCs is over one thousand, but the most numerous ones are methane, toluene, n-butane, i-pentane, ethane, benzene, n-pentane, propane and ethylene. There are both, natural (biogenic VOCs) and antropogenic (mainly due to organic solvents evaporation and fossil fuels combustion) sources of VOCs.

VOCs participate in many different reactions in the troposphere and in the stratosphere, taking part in the photochemical smog production process and in the greenhouse effect. In addition some of them are precursors of the tropospheric ozone, which might produce breathing illnesses. On the other hand, most of VOCs are toxic, mutagenic, carcinogenic, so their emission is usually associated to very important health damage over the human beings.

For this reason, worldwide and more specifically in the European Union, the current legislation for environmental and people's health protection is focused on the antropogenic VOCs emissions reduction. In this direction the European Directive 2001/81/CE of the European Parliament and the Council, of 23 October 2001 on national emission ceilings for certain atmospheric pollutants was transposed to each country in the EU, and annual VOCs emission limits were settled.

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In addition, Directive 2008/50/CE of the European Parliament and of the Council, of 21 May 2008 on ambient air quality and cleaner air for Europe, establishes quality sampling targets and measurement and sample analysis methods for air quality improvement, while Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) pretends to cut down industrial pollution by enhancing industries control. In order to reduce VOCs emission, Directive 2010/75 establishes annual solvent consumption threshold values and emission limit values in waste gases for different industrial installations and activities using organic solvents.

Accordingly, the abatement of VOCs emissions should occur in first place by substituting VOCs by less contaminating substances and, when this may not be possible, end of pipe solutions should be applied. Among the available techniques for gas treatment, the control of VOCs emissions to the atmosphere by a non-destructive technology has the advantage of solvent recovery to be used again.

Adsorption is defined as the enrichment of material or increase in the density of the fluid in the vicinity of an interface (Rouquerol et al. 1999). Most available data on adsorption systems are determined by the adsorption isotherm, which can be called static or batch adsorption in which equilibrium can be reached. However, in dynamic adsorption, in which equilibrium is difficult to reach, how to determine the breakthrough curve is an important issue because it provides the basis to design a column adsorption system (Xu et al. 2013).

Despite some reviews can be found concerning fixed-bed adsorption modelling in aqueous systems (Xu et al. 2013) or concerning only adsorption kinetic models (Qiu et al. 2009) a critical review for gas adsorption is missed. In this context, this critical review is focused on analyzing different adsorption models for VOCs over carbon and zeolites, for both single and multicomponent gas mixtures, to establish a firm guide for researchers who want to develop adsorption models for breakthrough curves simulation.

2. METHODOLOGY

In order to design an adsorption model valid for VOCs emission coming from industrial applications, it is first necessary to accurately know the inlet gas stream rate and its composition. Then, laboratory adsorption experiments must be performed in order to study the adsorption equilibrium and the adsorption kinetics. Analyzing the isotherms obtained in previous static adsorption experiments in the laboratory, a suitable adsorbent is selected. Later, experimental breakthrough times are obtained from kinetic experiments. From the results of these static and dynamic experiments a mathematical model can be developed in order to predict breakthrough time with the final goal to scale-up the adsorption system. Figure 1 depicts a complete flow of the necessary steps to achieve the full scale model for VOCs adsorption.

Breakthrough curves are obtained by measuring the outlet adsorbate concentration at different times of the dynamic adsorption processes. Figure 2 shows the typical shape of the breakthrough curve for the adsorption of a single VOC component in the gas stream.

Initially the adsorbate is completely adsorbed, and thus its outlet concentration is zero. But as the experiment progresses and the total treated gas volume increases, part of the adsorbent gets saturated and the bed can no longer retain all the adsorbate and, in consequence, the adsorbate outlet concentration increases.

Finally, the adsorbent slowly reaches its maximal adsorption capacity and the adsorbate can no longer be retained, so the adsorbate outlet concentration is equal to the adsorbate inlet concentration.

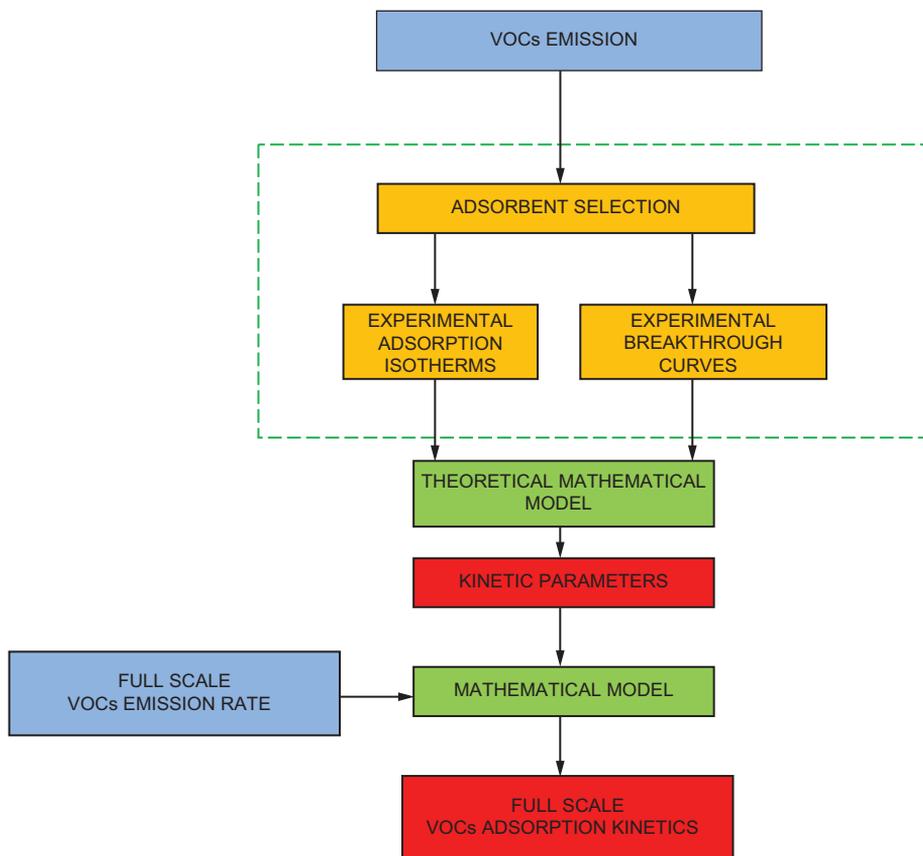


Figure 1. Adsorption system design process.

Before starting a more detailed review of the adsorption models, it is necessary to point out that every adsorption model for breakthrough curves prediction is based on an adsorbate mass balance.

This mass balance is conditioned by the system fluid dynamics, the adsorbate mass transfer mechanism from the gas phase to the solid surface, the adsorption energy, the adsorption equilibrium and the initial and the boundary conditions (Figure 3).

The fluid dynamics strongly depends on the solid bed dimensions and inlet gas flow. In most of the dynamic experiments fixed beds are widely used, and as their length is well over their diameter, and the gas flow remains constant, axial dispersion is ignored and plug flow approximation is assumed.

Under these considerations, the adsorbate mass balance in a bed layer remains like this (Eq.1):

$$\epsilon \frac{dC}{dt} + \rho_a \frac{dW}{dt} + u \frac{dC}{dz} = 0 \quad (1)$$

The second term of the mass balance is referred to the variation of adsorbate mols retained on the solid adsorbent, namely the adsorption rate, which is also called by several authors the “kinetic model”. This adsorption rate can be controlled by one of these three stages:

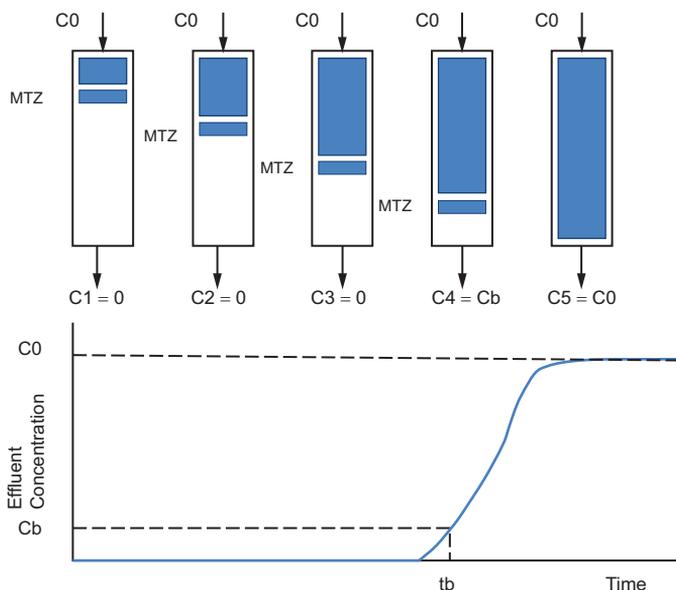


Figure 2. Breakthrough curve for a single component in the gas stream. C_0 : inlet concentration of the adsorbate; C_b : outlet concentration of the adsorbate at breakthrough time t_b ; MTZ: Mass Transfer Zone.

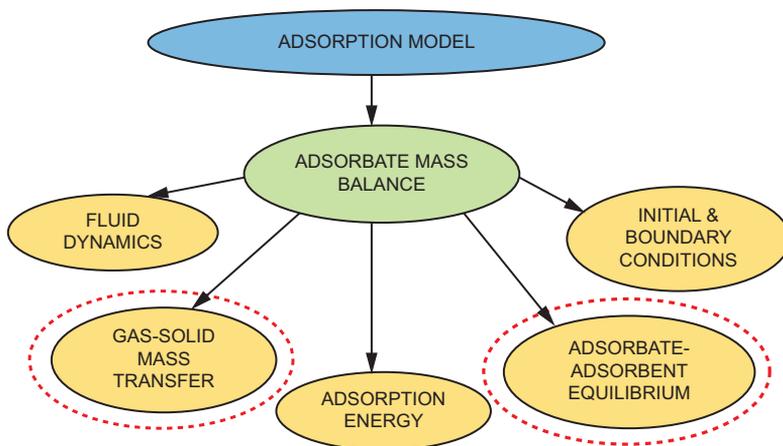


Figure 3. Conditioning factors in adsorption models for breakthrough curves simulation.

- In the first step, the adsorbate is transferred from the bulk gas stream to the external surface of the adsorbent material (mass transfer step).

- In the second step, the adsorbate diffuses from the relatively small area of the external surface into the macropores, transitional pores, and micropores within each adsorbent (diffusion step). Most adsorption occurs in the micropores, where the majority of available surface area is.

- In the third step, the VOC molecule adsorbs to the surface in the pore (adsorption step), which is governed by the adsorption kinetics.

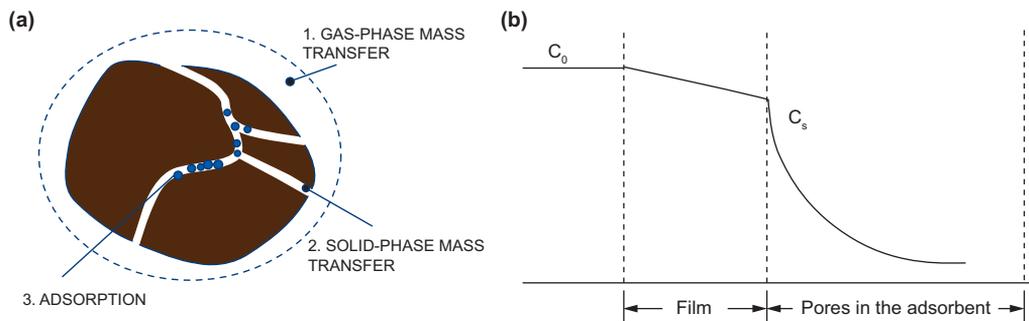


Figure 4. Gas adsorption steps (particle and profile).

First and second steps occur because of the concentration difference between the bulk gas stream passing through the adsorbent and the gas near the surface of the adsorbent. This means that at low VOC concentration the concentration difference is low and consequently these steps are slow and the equilibrium under these conditions will be difficult to reach.

Although a number of variables affect adsorption capacity under dynamic mode, the characteristics of the adsorbent gas, the type of adsorbate, the adsorption temperature and the gas velocity are very important to determine the breakthrough capacity (Martínez de Yuso et al. 2013).

Figure 4 (a and b) shows a simplified image of an adsorbent particle with the above described adsorption stages (adapted from Gupta, 2012).

The adsorption kinetics is typically considered the fastest stage, so the adsorbate transfer in the gas and/or in the solid phase can be considered the controlling stage of the adsorption process. The comparison with adsorption at the liquid-solid interface is further complicated by the fact that some adsorbents cannot be outgassed without an irreversible change in their texture. Also, changes in texture may occur when the adsorbent is immersed in a pure liquid or a solution (Rouquerol et al. 1999). For these reasons, here methodology is concerning gas-solid interactions.

Depending on the controlling adsorption stage (the slowest one) and the mathematic equation used to describe it, different “adsorption rate models” are proposed.

In most of the adsorption experiments, temperature can be assumed constant. Thus, the development of the adsorption model energy balances to the system is usually not required. Nonetheless, in more puristical models energy exchange is considered.

Adsorbate-adsorbent equilibrium is described through the different adsorption isotherm models. Within the classical isotherm models are Langmuir (Langmuir 1916), Freundlich (Zeldowitsch 1934), BET (Brunauer et al. 1938), Dubinin-Radushkevich and Dubinin-Astakhov models (Dubinin 1987). In most of the cases, these models can reproduce rather well experimental adsorption data, not only for one component adsorption, but also for multicomponent mixtures adsorption.

Nevertheless, in some cases the former models cannot precisely predict multicomponent adsorption experimental isotherms, and in other ones although these models can perfectly predict the experimental adsorption results, they are not able to explain the adsorption mechanism. Thus, several authors have developed physically, chemically and thermodynamically consistent equilibrium adsorption models that will also be studied in this review.

In that way, the development of a theoretical model to predict the breakthrough curves obtained in dynamic adsorption processes of multicomponent gas systems mainly requires the definition of the adsorption equilibrium and the adsorption kinetics. This information combined with the fluid

dynamics, the thermodynamics, and initial and boundary conditions of the system, leads us to a global prediction model.

3. THEORY AND DISCUSSION

According to the number of adsorbates, the adsorption models can be classified in single component and multicomponent models.

3.1. Single Component Models

Although the emission of just one VOC in industrial gas streams is not very realistic, the adsorption model of an adsorbate from a gas stream is the simplest one, as the competition between different adsorbates is not considered. Due to its simplicity, this kind of models establishes the basis for multicomponent adsorption models.

3.1.1. Adsorption Equilibrium

The previously mentioned adsorption equilibrium models (Langmuir, Freundlich, BET, DA, DR. . .) can accurately simulate single component adsorption equilibria.

The former models can be divided in two different categories: Flat Surface Isotherms and Pore-Filling Isotherms.

Most of the classical adsorption equilibrium models belong to the first group, and each one was developed to describe adsorption equilibrium under certain conditions. For example, the Langmuir isotherm (Langmuir 1916) is widely used to describe the adsorption equilibrium in flat homogeneous adsorbents, while the BET classical isotherm (Brunauer et al. 1938) describes multilayer adsorption in flat and homogeneous adsorbents. The classic Freundlich isotherm (Zeldowitsch 1934) and the Toth isotherm (Toth 1971) can be used to describe adsorption process in heterogeneous adsorbents in a wide range of adsorbate concentrations.

Other important flat surface isotherms are Radke-Prausnitz (Radke and Prausnitz 1972), Sips (Sips 1948), and UNILAN isotherms (Honig and Reyerson 1952; Le Van et al. 1998).

Pore-Filling Isotherms are grounded on Polanyi's Potential Theory, which considers the existence of an attracting potential energy field adjacent to the adsorbent surface that concentrates vapors there. Thus, it is considered that the adsorption occurs when the strength of the field is high enough to compress the vapor up to a partial pressure over its saturated vapour pressure. The best known model of this category is Dubinin-Radushkevich (Dubinin 1987) isotherm.

3.1.2. Adsorption Kinetics

The steady-state condition never exists in the fixed bed during adsorption. Hence, a finite adsorption rate always prevails in the bed. The steady-state is achieved only when the bed reaches the saturation.

A summary of the general rate models based on the Fick's law can be found in the review of Xu et al. (2013), with special devotion to pore diffusion model (PDM) (Du et al. 2008), homogeneous surface diffusion model (HSDM) (Tien 1994) and pore and surface diffusion model (PSDM) (Liu et al. 2010). However, the main limitation to solve the general rate models is a time-consuming and computationally troubled work.

Within the common kinetic models, it is to mention the Linear Driving Force model (LDF) (Glueckauf and Coates 1947; Glueckauf 1955) to describe the adsorption phenomenon in chromatography. This model is widely used because it is rather simple and physically consistent (Chirara and Suzuki 1983; Gemmingen 1993; Hartzog and Sicar 1995; Raghavan et al. 1986).

The Chemical Potential Driving Force-Model (CPDF) (Barrer 1971) is more rigorous than the LDF model because it describes the adsorbate transport inside the adsorbent particle.

Other kinetic models are the Quadratic Driving Force (QDF) (Vermeulen 1953) and the Wheeler modified equation (Wheeler and Robell 1969), which is obtained from the Reaction Kinetics Model (Hiester and Vermeulen 1952).

In the following paragraphs a brief summary of these kinetic models is presented.

The LDF Model considers that the adsorbate concentration per mass unit of solid adsorbent changes with time as a function of the adsorbate concentration in the adsorbent, the adsorbate concentration in the gas phase and the kinetic coefficient of the controlling diffusion process:

$$\frac{dW}{dt} = k \cdot f(W, C) \quad (2)$$

When the diffusion process in the solid is the controlling stage (Brosillan et al. 2001; Sicar and Hufton 2000), the adsorption kinetic is described by the following equation:

$$\frac{dW}{dt} = k_L [W^* - W] \quad (3)$$

When the diffusion process in the gas phase around the solid particle (external mass transfer) is the controlling stage, LDF equation is:

$$\frac{dW}{dt} = \frac{kf \cdot Sp \cdot (C - Cs)}{\tilde{n}_L} \quad (4)$$

The CPDF Model (Barrer 1971), according to Fick's law, considers radial diffusion through the adsorbent particles:

$$J(r, t) = -B \cdot C(\lambda, t) \left[\frac{\partial \{ \lambda(r, t) / R_g T \}}{\partial r} \right]_t \quad (5)$$

For the special case of isothermal adsorption process, Equation 5 leads to the isothermal Fickian diffusion (FD) model for isothermal pure gas adsorption:

$$J(r, t) = -D \cdot \left(\frac{\partial C}{\partial r} \right)_t \quad (6)$$

Although CPDF model (even when constant temperature is considered) permits a much more rigorous description of the adsorbate transport inside the adsorbent particle than the LDF model, it also has an important disadvantage: impractically large computational times for process simulation under realistic conditions (Sicar and Hufton 2000). For this reason, LDF model is usually preferred to CPDF model.

The QDF Model, as its own name suggests, assumes that the adsorbate mass change per adsorbent mass unit, when diffusion inside the solid adsorbent particle is the controlling stage, is a quadratic function of $W(t)$ and $W^*(t)$, as defined in the LDF Model:

$$\frac{dW}{dt} = k_Q \left[\frac{W^{*2} - W^2}{2W} \right] \quad (7)$$

The main advantage of this model, also known as Alternate Driving Force Model, is that a better fit of the experimental breakthrough curves than LDF for low adsorbate concentration in the gas phase can be obtained.

Nevertheless QDF model, unlike LDF, can only be used when diffusion inside the solid adsorbent is the controlling stage of the adsorption process.

The Reaction Kinetics approximation considers first order reaction kinetic as the controlling stage. This is typical in chemisorption processes and also when the adsorption occurs very slowly. Nevertheless, this model offers also very good results, even when the adsorbate diffusion is the controlling stage (Wood and Stampfer 1993).

Due to its apparent second order kinetics, as well as the QDF Model, it leads to a better adjustment of the experimental breakthrough curves than the linear models:

$$\frac{dW}{dt} = k_a \left[\frac{C_0 (W^* - W) - RW (C_0 - C)}{1 - R} \right] \quad (8)$$

The modified Wheeler equation (Busmundru 1993; Jonas and Rehrmann 1972; Jonas and Sivirbely 1972; Wood and Stampfer, 1993), which is based on the Reaction Kinetic model, allows the calculation of breakthrough times in fixed beds as a function of a series of variables:

$$t_b = \frac{W^* W_L}{C_0 Q} - \frac{W^* \rho_a}{C_0 k_v} \ln \left[\frac{(C_0 - C_x)}{C_x} \right] \quad (9)$$

When the adsorbent mass, the bed density, the gas flow, and the adsorbate concentration at the inlet stream are known, the former equation (Eq. 9) can fit experimental breakthrough curves, obtaining two adjustment parameters: k_v and W^* (Busmundru 1993; Wood and Stampfer, 1993; Wood 1994; Yoon et al. 1992). Other authors introduce in the Wheeler equation the adsorption isotherm equation. Thus, when adjusting the experimental breakthrough curves, instead of obtaining k_v and W^* , the characteristic parameters of the adsorption isotherm are obtained (Jonas and Rehrmann 1972; Wood and Moyer 1991; Wood 1994).

3.2. Multicomponent Models

Multicomponent breakthrough curves are rather more complex to simulate than the single-component ones, as competition between the different adsorbates to adsorb on the solid active sites occurs. This competition is especially strong between water steam and VOCs non-polar molecules (Harding et al. 1998).

Therefore, several authors have proposed different equilibrium adsorption models that consider the above mentioned competition.

3.2.1. Adsorption Equilibrium Models for Multicomponent Systems

Although plenty of models can be found in the literature (a summary can be found in Xu et al. 2013), the most commonly used ones are:

- Markham and Benton model (Markham and Benton 1931).
- Fritz and Schlünder model (Fritz and Schlünder 1974).
- MBET Model (Hill 1946).
- MPD Model (Myers and Praunitz 1965).
- VMC Model (Appel 1998).

The Langmuir extended isotherm (Markham and Benton 1931) is the simplest multicomponent isotherm because it assumes no interaction between the adsorbed molecules. This model calculates the amount of adsorbed molecules by means of the following equation:

$$W_i^* = \frac{W_{0i}k_iP_i}{1 + \sum k_iP_i} \quad (10)$$

When using Eq. 10 for a bicomponent mixture, two different equations are obtained (Eq. 11 and Eq. 12):

$$W_1^* = \frac{W_{01}k_1P_1}{1 + \sum k_iP_i} \quad (11)$$

$$W_2^* = \frac{W_{02}k_2P_2}{1 + \sum k_iP_i} \quad (12)$$

Equation 11 and 12 are thermodynamically consistent when $W_{01} = W_{02}$, but even when these two values are different this model also offers good results if adsorbates 1 and 2 have a similar nature and individually meet the Langmuir isotherm (Markham and Benton 1931). When the monolayer capacities of both adsorbates are very different, the equation to use obeys a power series (Frey and Rodrigues 1994; Le Van and Vermeulen 1981).

Lewis et al. (1950) showed how for a bicomponent mixture at constant pressure ($P = P_1 + P_2$) the following relation between the amounts adsorbed of each component (W_1 and W_2) is fulfilled (Lewis equation):

$$W_1^*/W_{01} + W_2^*/W_{02} = 1 \quad (13)$$

As mentioned before, the Langmuir extended isotherm holds for any gas mixture of hydrocarbons meeting the single component Langmuir equation, but has limited applicability to liquid phase adsorption isotherms because few pure component at this stage can be explained by the Langmuir isotherm.

Several authors have made attempts to extend the Freundlich isotherm to gas mixtures. In this direction (Fritz and Schlünder 1974) it was proposed the following equation for predicting the amount of each compound of gas mixture adsorbed per unit of solid adsorbent:

$$W_i^* = \frac{a_i C_i^{b_i + b_{ij}}}{C_i^{b_{ii}} + a_{ij} \cdot j^{b_{ij}}} \quad (14)$$

The problem with such equations is that they are inconsistent with single component isotherm data. Moreover they do not have a thermodynamic background. However, as this type of model uses a large number of empirical parameters, adjustment of experimental data is satisfactory (Suzuki 1990).

MBET adsorption model (Hill 1946) is a variant of BET model but for multicomponent systems.

To adjust the adsorption isotherm of each substance “*i*” in a mixture formed by “*s*” adsorbates, the MBTE model proposes Eq. 15:

$$W_i^* = \frac{W_{im} E_0 x_i}{(1-E) + E_0 (1-E^n)} \left[\frac{B_i (1-E^n)}{E_0} + \sum_{k=2}^n E^{k-2} (1-E^{n-k+1}) \right] \quad (15)$$

Where:

$$E_0 = \sum_{i=1}^s x_i B_i \quad (16)$$

$$E = \sum_{i=1}^s x_i \quad (17)$$

According to this method (MBET), the adjustment of experimental adsorption isotherms is achieved by means of three parameters: W_{im} , B_i , and n .

This model was tested in adsorption experiments of toluene and trichloroethylene binary mixtures in the presence of water in low concentrations, on sand and Yolo silt loam (Amali et al 1994). For low relative humidity in the gas stream (lower than a molecular layer) and low VOC relative vapor pressures, the model predicted adsorbed amounts of both adsorbates below the experimental values. By contrast, increasing the relative humidity, the model predicted values of trichloromethane and toluene adsorption above the experimental values. Thus, it was concluded that the MBET equation can successfully be used to model VOC adsorption on geological material and soil over the range of water content corresponding to between one and two molecular layers.

Adsorption simulations in ternary systems of trichloromethane, toluene and water provided analogous results that corresponding in binary mixtures.

A limitation of the MBET model is the lack of meaning of the parameter “ n ”. While for pure species “ n ” makes reference to the maximal number of adsorbate layers, for multicomponent systems the meaning of “ n ” is not so clear. This parameter could be referred to the maximal number of adsorbates in the mixture, but it can also make reference to an equivalent maximal number of layers of the species “ i ”.

The MPD model is based on the combination of Myers-Prausnitz equilibrium theory (IAST-Ideal Adsorbed Solution Theory, Myers and Prausnitz 1965), and the adsorption isotherm model proposed by Dubinin (Dubinin-Astakhov and Dubinin-Radushkevich equation, Dubinin 1987).

The Ideal Adsorbed Solution Theory proposed by Myers and Prausnitz considers that for gas mixtures at high temperatures and low pressures the Ideal Gas Equation is met, the solid adsorbents are thermodynamically inert and their specific surfaces do not change with the temperature.

This theory establishes the condition that the integrals of pure adsorption isotherms of each adsorbate divided by the pressure ($W_i^*(P)/P$), calculated between zero and their respective equilibrium pressure in the gas phase (p_i^0), are equal (Eq. 18):

$$\phi_i(p_i^0) = \int_0^{p_i^0} \frac{W_i^*(P)}{P} dP = \text{constant} \tag{18}$$

Besides, this theory considers that the potentials of each component “*i*” in the gas and in the adsorbent are the same. Thus, the component “*i*” pressure in the gas phase (p_i), is related to pressure p_i^0 (which depends on the total adsorbed amount, and when the microporous solid is saturated with the gas mixture this value coincides with its saturated vapor pressure of substance *i* at pressure *P* and temperature *T*), by means of an equation (Eq. 19) similar to Raoult’s law:

$$p_i = P \cdot y_i = x_i^a \cdot y_i^a \cdot p_i^0 \tag{19}$$

And equations 20 and 21 are met:

$$\sum x_i = 1 \tag{20}$$

$$\sum y_i = 1 \tag{21}$$

When using the IAST theory, the molar fractions of each component in the solid phase (x_i^a) can be calculated by means of an iterative process using the partial pressure of each component (p_i). Finally, using the former molar fractions in the solid phase, the adsorbed amounts of each component by mass unit of solid adsorbent can be calculated.

When applying the Ideal Adsorbed Theory, if the adsorption isotherms of the pure adsorbates can be described by the Dubinin-Ashtakov model (Eq. 22), the MPD model is obtained:

$$W^* = W_0 \exp \left[- \left(c \frac{RT}{\hat{a}} \ln(p^0 / p) \right)^n \right] \tag{22}$$

Where β and *c* are specific parameters that depend on the adsorbate and the solid adsorbent, and *n* is the parameter setting of the model (equals 2 for activated carbons, in which case the adsorption equilibrium model is called the Dubinin-Radushkevich model).

Several authors (Ladugie et al. 1992; Lavanchy and Stoeckli 1997; Stoeckli et al. 1997) have obtained good predictions of each component adsorption over microporous solids using the Ideal Adsorbed Solution Theory and the Dubinin-Astakhov and Dubinin-Radushkevich pure component equations.

The main advantage of using the Dubinin equations is the reduced number of required parameters to describe and predict the adsorption in a wide range of pressures and temperatures. When the IAST is combined with the Dubinin equation for pure substances, it can successfully predict binary mixtures adsorption, like for example dichlorobenzene and carbon tetrachloride, or

1-3-dichlorethane and benzene over industrial activated carbon at room temperature (Ladugie et al. 1992; Lavanchy and Stoeckli 1997; Stoeckli et al. 1997).

In an attempt to improve the prediction capacity of the Dubinin equations, at the beginning of the fifties Bering and Serpinski (Bering et al. 1971) proposed an empirical model to extend the Dubinin-Radushkevich to multicomponent gas mixtures. Although it was able to predict the adsorption in several systems, its success was shrunk due to the need of using a subsidiary equation to reduce the number of adjustment parameters, and finally it was abandoned.

In order to simulate the adsorption of several aqueous binary solutions (phenol/p-nitrophenol, p-nitrophenol/p-chlorophenol, p-nitrophenol/benzoic acid, etc) over active carbon, other authors (Lossens et al. 1978) obtained good results by combining the Toth equation and the Myers and Prausnitz model (IAST). However, they later developed a new adsorption isotherm for highly heterogeneous surfaces, where different heats of adsorption were considered. This final model led to a more accurate simulation of two of the aqueous binary systems: the p-nitrophenol/phenol and p-nitrophenol/p-chlorophenol pairs, while for the other binary systems the error between the experimental and theoretical data was important.

Vahdat decided to implement the Langmuir extended isotherm over the Ideal Adsorbed Solution Theory obtaining also satisfactory results for ethylene-propane and acetone-m-xylene binary mixtures on activated carbon, and for a binary mixture of carbon dioxide-water vapor on a molecular sieve (Vahdat et al. 1994).

In conclusion, the Ideal Adsorbed Solution Theory is useful to predict the adsorption equilibrium in binary systems by using different adsorption isotherms models. The most frequently used isotherm is the Langmuir isotherm for multicomponent gas mixtures.

The VMC model (Virial Mixture Coefficient), based on the Two-dimensional Virial Equation of State, describes the adsorption equilibrium of the different adsorbates in a multicomponent mixture by combining the two-dimensional Virial Equation of State (EOS) and the adsorption isotherms of each adsorbate of the gas mixture.

This adsorption equilibrium model for multicomponent systems combines the effectiveness of the isotherm models for pure substances with the capacity of the two-dimensional Virial EOS to describe the adsorbate-adsorbent interactions.

The innovation of this model is the substitution of the EOS for pure substances by the Virial two-dimensional EOS, which is used to develop multicomponent mixture adsorption isotherms.

Among the advantages of the VMC model can be highlighted its robustness, its thermodynamic consistency and its relative simplicity.

The following paragraphs describe the methodology that is necessary to apply the VMC model, which uses the two-dimensional Virial EOS (Eq. 23):

$$\frac{PA}{RT} = W^* + \frac{1}{A} \sum_i \sum_j W_i^* W_j^* B_{ij} + \frac{1}{A^2} \sum_i \sum_j \sum_k W_i^* W_j^* W_k^* C_{ijk} + \dots \quad (23)$$

Adsorbate-adsorbent interactions are described by means of the Henry's Coefficient (H). Interactions between molecules of the same substance are represented by Virial Coefficients with equal sub-indexes (e.g. B_{11} , or C_{333}). Interactions between different molecules are represented with different sub-indexes (e.g. B_{12} , C_{123}), where it is met that the order of the sub-indexes does not change the value of the coefficients (e.g. $B_{12} = B_{21}$).

Reorganizing the different terms of the two-dimensional EOS by means of separating individual and mixture terms, Equation 24 is obtained:

$$\begin{aligned}
 \frac{PA}{RT} &= W_1^* + \frac{1}{A} B_{11} W_1^{*2} + \frac{1}{A^2} C_{111} W_1^{*3} + \dots \\
 W_2^* &+ \frac{1}{A} B_{22} W_2^{*2} + \frac{1}{A^2} C_{111} W_2^{*3} + \dots \\
 \frac{2}{A} B_{12} W_1^* W_2^* &+ \frac{3}{A^2} C_{122} W_1^{*2} W_2^* + \frac{3}{A^2} C_{122} W_1^* W_2^{*2} + \dots \\
 &= \frac{PA}{RT_{pure1}} + \frac{PA}{RT_{pure2}} + \frac{PA}{RT_{mixture}} \tag{24}
 \end{aligned}$$

Appel proposed (Appel 1998) the following methodology to obtain the former Virial coefficients of a binary mixture: In the first step the adsorption isotherm data of each pure components (B_{11} , B_{22} , C_{111} , C_{222} , . . .) are introduced in the Virial EOS obtaining the individual coefficients; in the second step the Virial coefficients of the bicomponent mixture (B_{12} , C_{112} , etc) are obtained by introducing the pure component coefficient previously obtained and then substituting the mixture adsorption equilibrium data in the two-dimensional Virial EOS.

By analogy, for a three component system, one additional step in which the adsorption equilibrium data of the ternary mixture will be necessary to determine the Virial coefficients of the tricomponent mixture.

Definitely, the VMC method permits the description of the multicomponent adsorption equilibrium with fewer terms that would require an equivalent series of power series, being its application much easier.

The description of multicomponent mixtures adsorption equilibria through the VMC method leads to thermodynamically consistent adsorption isotherms. The main advantage of this model against other correlation methods is its accuracy when describing systems that deviate from the ideality using a relative small number of parameters.

The VMC method was successfully used for modeling multicomponent adsorption equilibria when their pure components equilibrium data correspond to Langmuir type isotherms (Appel 1998), like for example carbon dioxide, sulphidric acid and propane adsorption over H-mordenite. For binary systems of these components, when utilizing the Toth isotherm to model the pure component equilibria, only nine coefficients were necessary: three for each pure isotherm and three for the virial mixture B and C terms. The ternary system was described by three parameters for each pure isotherm, three virial coefficients for each binary mixture, and one virial coefficient for the ternary mixture.

For other adsorption systems containing non-Langmuirian adsorbates, such as hexane/water over BPL activated carbon, the VMC method allowed a rather good approach at all hexane loadings when the E terms of the Virial EOS were included. However, this equilibrium was more difficult to describe due to the shape of the pure water isotherm.

3.2.2. Dynamic Adsorption Models for Multicomponent Mixtures

The breakthrough curves for multicomponent mixtures are much more complex than those for pure compounds, and their complexity lies in the different adsorption capacities of each component on the bed. Taking as reference a gas mixture with two components, always one of the

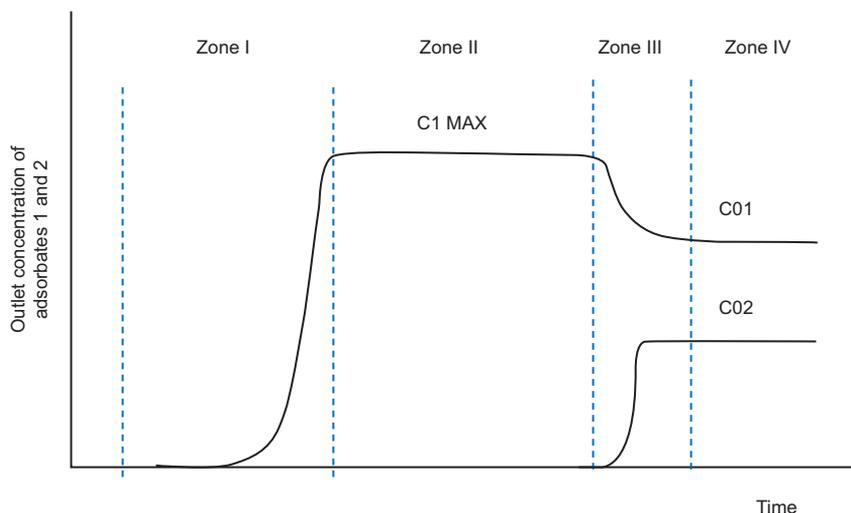


Figure 5. Breakthrough curves shape for binary mixtures (C_{01} and C_{02} ; Inlet concentrations of adsorbates 1 and 2 respectively; C_{1MAX} : Maximal outlet concentration of adsorbate 1 due to the “rolled-up” effect).

components (1) is adsorbed on the solid more weakly than the other component (2), travelling quickly over the bed. A typical representation of the breakthrough curves of a binary gas mixture comprises four zones, as it is represented in Figure 5.

Depending on how the concentration of each adsorbate changes at the outlet gas stream, four different zones are observed:

Zone I: The concentration of the compound with lower adsorption capacity increases until it reaches a maximal value.

Zone II: The concentration of the compound with lower adsorption capacity remains constant.

Zone III: The concentration of the compound with higher adsorption capacity increases up to a maximal value while the concentration of the weakest-adsorbed compound decreases. This is the so called “rolled-up” effect.

Zone IV: The concentrations of both compounds remain constant and equal to their inlet concentrations (C_{01} and C_{02}).

Some breakthrough prediction models combine the adsorption kinetic models proposed for pure substances (3.1.2) with certain equilibrium models for multicomponent mixtures previously described (3.2.1).

Thus, some authors base their kinetic models on the LDF model (Linear Driving Force). Appel (Appel 1998) combined the VMC (Virial Mixture Coefficient) multicomponent equilibrium theory with the LDF model (considering that both diffusion in the gas phase and diffusion in the solid adsorbent are the controlling stages). The resulting model was used to describe the adsorption process of several water-organic systems (water, water-methanol, water-ethanol, water-dichloromethane, water-ethanol-dichloromethane) over a fixed bed of activated carbon. For all these systems the dynamic simulations showed good agreement with experimental data, being the adsorption dynamics strongly dependent on relative humidity.

Similarly, other authors (Lavanchy and Stoeckli 1997) proposed a model that combines the MPD equilibrium model with the LDF model when the step that controls the adsorption kinetics

is diffusion in the gas film. This model was applied to the adsorption of binary mixtures of 2-chloropropane, carbon tetrachloride and chlorobenzene in a dry air stream, on charcoal (Lavanchy and Stoeckli 1997), and good agreement between the theoretical and experimental results was met. Later, some authors (Lavanchy and Stoeckli 1999) performed adsorption experiments of ternary mixtures of the former compounds in dry air over charcoal were performed, and for low concentrations of the three vapours present in the stream this model led to very good prediction. In addition, adsorption experiments of water and 2-chloropropane mixtures, two immiscible adsorbates, showed also good agreement between the predictions and the theoretical model. In these last experiments, the largest differences between experimental and theoretical data were observed for low inlet relative concentrations of 2-chloropropane (0,003%) and for high relative humidity (65%).

In conclusion, the advantage of the MPD combined with the LDF model is its relative simplicity of calculation, obtaining satisfactory results when predicting breakthrough curves of the studied systems, even when considering three component mixtures, or water presence. However, it is limited to physisorption phenomena. Note that this mathematical model has been tested also introducing adsorption models different to Dubinin, such as adsorption models of Langmuir and Toth, but the predictive power of the mathematical model in these cases has been much worse.

Other authors, instead of considering the LDF kinetic model, base their models on the Wheeler equation. As indicated before (3.1.2) although the Wheeler equation is obtained from the Reaction Kinetic Model, which considers that the reaction rate is the limiting step in many cases, its application is also extended to those processes where the controlling stage is the internal and/or external diffusion (Wood and Stampfer 1993). So, Vahdat (Vahdat and Swearengen 1994; Vahdat 1997; Lavanchy and Stoeckli 1999) developed his model based on the Wheeler equation and the Ideal Adsorbed Solution Theory combined with the Langmuir adsorption isotherm extended to multicomponent mixtures (Markham and Benton model). This model was successfully applied to bicomponent mixtures of acetone-m-xylene, acetone-styrene, and carbon dioxide-water (Vahdat and Swearengen 1994).

Yoon developed an empirical dynamic model based on the Wheeler equation to predict rupture curves of binary mixtures, obtaining satisfactory results in adsorption experiments with acetone-m-xylene (Yoon et al., 1991) and acetone-styrene mixtures (Yoon et al. 1992) on activated carbon.

As it has been stated before (Xu et al. 2013) when the breakthrough curves deviate from the ideal S-shape, the models are not as powerful as demanded. In this way, the modification of some parameters during experimental work can change the steepness of the breakthrough curves. When external mass transfer is controlling the process the flow rate is the most sensitive parameter and low flow rates could lead to very low step curves. On the other hand, the effect of pore diffusivity on adsorption rate could be significant at high flow rates if adsorption process is limited by pore diffusion whereas the effect of pore diffusivity on adsorption rate could be insignificant at lower flow rates implying adsorption process to be external mass transfer controlled (Gupta 2012; Martínez de Yuso et al. 2013; Pan et al. 2005).

The decrease of particle size could lead to steeper breakthrough curves and to an increase of breakthrough times suggesting the use of adsorbent with smaller diameter which also increase the length of bed utilized up to breakthrough and efficiency of the adsorbent.

Other parameters such as pore diffusivity (related with pore size distribution in the adsorbent), bed height and adsorbate concentration could also change the steepness of the breakthrough curves leading to a failing in the breakthrough curves prediction.

4. CONCLUSIONS

The development of a model to predict the breakthrough curves in multicomponent systems requires the selection of equilibrium and kinetic models. This selection is easy for single component adsorption process, but multicomponent adsorption is more complex and the selection of the equilibrium and kinetic models should be based on the knowledge of the adsorbate-adsorbent interactions.

Equilibrium models to describe multicomponent adsorption based on Ideal Adsorbed Solution Theory combined with single component adsorption isotherm give accurate prediction without the need to use multicomponent equilibrium systems (Fritz and Schündler, MBET or VMC), which are calculation time consuming.

Adsorption kinetics for multicomponent systems can be described by mass transfer models (Driving Force Models) and reaction kinetics models (Wheeler Equation based Models).

By considering the equilibrium and the kinetics models of the adsorption process, and other aspects like the system fluid-dynamics and initial and boundary conditions, successful breakthrough curves simulation models have been developed.

Therefore, to develop a successful mathematical model for breakthrough time curves prediction a deep study of the literature is necessary. In this respect, this short review pretends to be a starting point for revision and discussion of both adsorption and kinetic models.

LIST OF SYMBOLS

A	Specific surface area of the adsorbent.
a_i	Activity coefficient of component “ i ”.
B	Mobility of the adsorbate at concentration C and temperature T .
B_i	Molar heat of adsorption of the adsorbate “ i ” on bare adsorbent surface.
B_{ij}	Virial coefficients that consider interactions between two molecules of equal or different adsorbates located on the adsorbed phase.
c	Structural parameter in Dubinin-Ashtakov equation related to adsorption energy in the micropores.
C	Adsorbate concentration in the gas external film around the particle.
$C(r,t)$	Instantaneous local adsorbate concentration.
C_0	Inlet concentration of the adsorbate
C_{0i}	Inlet concentration of adsorbate “ i ”.
C_b	Adsorbate Outlet concentration of the adsorbate at breakthrough time.
C_i	Outlet concentration of the adsorbate at time “ T ”.
C_{ijk}	Virial coefficients that consider interactions between three molecules of equal or different adsorbates located on the adsorbed phase.
C_s	Concentration of the adsorbate in the particle surface.
C_x	Concentration of the adsorbate at the outlet stream.
C_0	Concentration of the adsorbate at the inlet stream.
D	Fickian diffusivity.
E_0	Molar pondered mean heat of adsorption of a gas mixture on bare adsorbent surface.
E	Sumatory of the molar fractions of each compound on the solid phase.

E^n	Molar pondered mean heat of adsorption of a gas mixture on the “ n ” layer of the adsorbent surface.
H_i	Henry’s coefficient of substance “ i ”.
$J(r,t)$	Flux of a pure adsorbate (moles per unit area per time) at radius $r(0 \leq r < R)$ of the adsorbent particle at time t .
k	Kinetic coefficient of the controlling diffusion process.
K_a	Reaction kinetics Model mass transfer coefficient.
k_f	External mass transfer coefficient.
k_i	Langmuir equilibrium constants of adsorbate “ i ” defined as the ratio of the molar fraction of each substance in the liquid and in the gas phase ($k_i = x_i/y_i$).
k_L	LDF mass transfer coefficient.
k_Q	QDF mass transfer coefficient.
k_v	Adsorption rate coefficient.
n	Number of layers of the gas mixture adsorbed on the solid for the MBET model; Parameter of the Dubinin-Ashtakov model.
n_i	Amount adsorbed of component “ i ”.
P	Pressure.
P_i	Partial pressure of substance “ i ”.
P^0	Saturation pressure.
P_i^0	Saturation pressure of substance “ i ”.
Q	Gas flow.
r	Radial distance in spherical particles of the adsorbent.
R	Adsorption separation factor
R_g	Gas constant.
S_p	Particle surface.
t	Time.
T	Temperature.
t_b	Breakthrough time (time necessary to reach a certain adsorbate concentration at the outlet stream).
$T(r,t)$	Instantaneous local temperature.
u	Gas speed.
W	Mean adsorbate loading at time t .
W^*	Equilibrium adsorbate loading.
W_i	Adsorbate “ i ” loading at time t .
W_i^*	Equilibrium loading of adsorbate “ i ” when this substance is in a gas mixture in equilibrium with the solid phase at a certain global pressure P .
W_{im}	Mass of species “ i ” necessary to form a monolayer on the unit mass of solid adsorbent.
W_L	Mass of adsorbent in the bed.
W_{0i}	Langmuir equilibrium constant of adsorbate “ i ” defined as the maximal quantity of this substance that can be absorbed by mass unit of solid adsorbent when the pure substance is in contact with the solid adsorbent at its own saturated vapor pressure (P_i^0).
x_i	Molar fraction of component “ i ” in the adsorbed phase.
y_i	Molar fraction of component “ i ” in the gas phase.
z	Bed height.

GREEK SYMBOLS

β	Adsorbate affinity coefficient, expressing the ratio of the characteristic adsorption energies of the test and the reference vapors.
ϵ	Bed porosity
ρ_{β}	Bed density.
$\dot{i}(r,t)$	Instantaneous local chemical potential of the pure adsorbate inside the adsorbent at r and t.

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