ADSORPTION
IN POORLY SPECIFIED MIXTURE

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INTRODUCTION AND MOTIVATION

Prausnitz (1983) classified complex mixtures into two different kinds. The first one includes those mixtures formed by identifiable components that are physically or chemically dissimilar as, for instance, the mixtures of alcohols or light gases with heavy hydrocarbons. The second kind of complex mixtures are those with too many components with similar properties to be practical, or even possible, to identify all of them as, for instance, polymeric solutions and heavy oil fractions.

In distillation, the mixture is fractionated into groups with the same boiling point called pseudo components. The thermodynamic properties of the pseudo components are predicted based on the correlation built upon numerous studies measuring the properties of pure hydrocarbons.

In pyrolysis oil purification, we have to deal with second type of complex mixture. Unlike distillation, the thermodynamics of adsorption are not intensively researched. Therefore, the complex feed usually is simplified into several key components in order to simulate the adsorption process. We then experimentally measure isotherms for each key component and hope the selected components can accurately describe the complex mixture.

The goal of this study is:
- Introduce the sorption analysis technique as the characterization technique for complex mixture.
- Examines several techniques used to directly characterize complex mixtures in adsorption processes, thereby reducing uncertainty and experimentation effort.
- Compare the different model with experimental sorption analysis on paper to have the rough idea about the advantage and disadvantage of each method.

SOLID-LIQUID EQUILIBRIA (ISOTHERM) PREDICTION MODEL

The knowledge of adsorption equilibrium data provides the basis for assessing the adsorption processes and, in particular, for adsorber design. For a single-solute system, the equilibrium relationship can be described in its general form as:

$$q_{eq}=f(C_{eq}), \quad T=const \qquad\qquad (2.1)$$

Table 2.1: Some models for single solute isotherm

Name	Parameter	Equation	Name	Parameter	Equation
Henry	1	$q_i=H_i C_i$	Toth	3	$q_i=\dfrac{q_{m,i}b_i C_i}{\left[1+\left(b_i C_i\right)^{n_i}\right]^{1/n_i}}$
Langmuir	2	$q_i=\dfrac{q_{m,i}b_i\,C_i}{1+b_i C_i}$	Generalized Langmuir	4	$q_i=q_{m,i}\left[\dfrac{\left(b_i C_i\right)^{n_i}}{1+\left(b_i C_i\right)^{n_i}}\right]^{\frac{m_i}{n_i}}$
Freundlich	2	$q_i=K_i C_i^{n_i}$	Weber van Vliet	4	$C_i=P_1 q_i^{\left(P_2 q_e^{P_3}+P_4\right)}$
Langmuir-Freundlich	3	$q_i=\dfrac{q_{m,i}b_i\,C_i^{n_i}}{1+b_i C_i^{n_i}}$	Fritz-Schlunder4	4	$q_i=\dfrac{K_1\,C_i^{K_3}}{1+K_2 C_i^{K_4}}$
Redlich-Peterson	3	$q_i=\dfrac{K_{RP,1}C_i}{1+K_{RP,2}C_i^{n_i}}$	Fritz-Schlunder5	5	$q_i=\dfrac{K_1\,C_i^{K_3}}{K_5+K_2 C_i^{K_4}}$

For multi-solute adsorption isotherm model, there are two way to describe it:
- Extended model
- Ideal adsorbed solution theory model (IAST)

Thermodynamic calculation of complex mixtures for the adsorption process relies heavily on the following models.
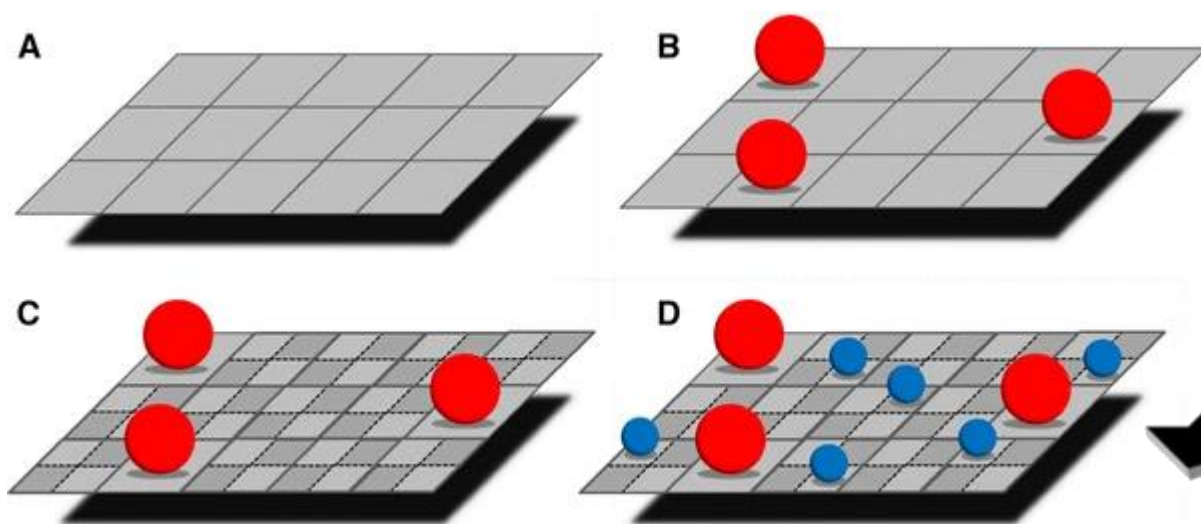

Figure 2.1. Representation of a lattice of adsorption sites **(a),** partially filling the lattice sites with adsorbate 1 with smallest saturation capacity **(b)**, subdividing the remaining free sites **(c)**, partially filling the small lattice sites with adsorbate 2 with the largest saturation capacity **(d)**
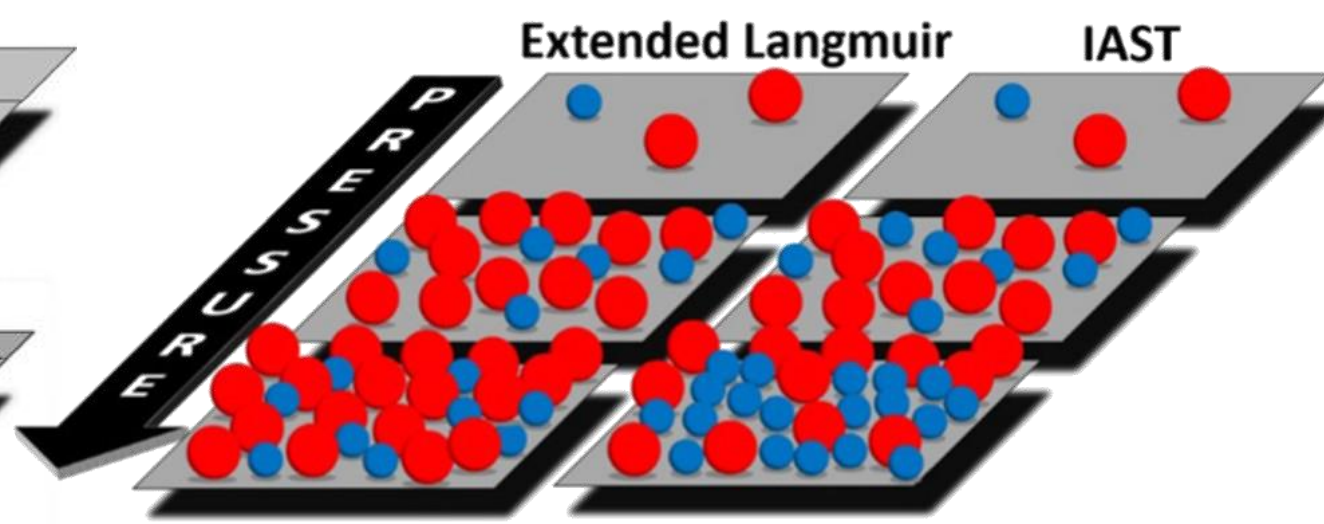
Figure 2.2. Representation of an adsorption size effect: equimolar fluid mixture at increasing pressure. The red adsorbates have twice the Henry constant and half the saturation capacity (larger size) of the blue ones. At higher pressures, the two models deviate as the smaller molecule is preferred for models that include a size effect.

Table 2.2 : Some multicomponent isotherm model (Extended Model)

Name	Parameter	Equation
Extended Langmuir	$2 \times N_{compound}$	$q_i = \dfrac{q_{m_i} b_i C_i}{1 + \sum_{k=1}^{n} b_k C_k}$
Stoichiometric	$2 \times N_{compound}$	$q_i = \dfrac{a_{m_i} b_i C_i}{\sum_{k=1}^{n} b_k C_k}$
Extended Langmuir Freundlich	$3 \times N_{compound}$	$q_i = \dfrac{q_{m_i} b_i C_i^{n_i}}{1 + \sum_{k=1}^{n} b_k C_k^{n_k}}$
Extended Redlich–Peterson	$3 \times N_{compound}$	$q_i = \dfrac{q_{m_i} b_i C_i}{1 + \sum_{k=1}^{n} b_k C_k^{n_k}}$
Competitive Langmuir	$3 \times N_{compound}$	$q_i = \dfrac{q_{m_i} b_i \gamma_i C_i}{1 + \sum_{k=1}^{n} b_k \gamma_k C_k}$
Dual site-Langmuir	$4 \times N_{compound}$	$q_i = \dfrac{q_{m_i} b_i C_i}{1 + \sum_{k=1}^{n} b_k C_k} + \dfrac{q'_{m_i} b'_i C_i}{1 + \sum_{k=1}^{n} b'_k C_k}$
Competitive Redlich–Peterson	$4 \times N_{compound}$	$q_i = \dfrac{q_{m_i} b_i \gamma_i C_i}{1 + \sum_{k=1}^{n} b_k (\gamma_k C_k)^{n_k}}$
Competitive Freundlich	$N_{compound}^2 + 1$	$q_i = K_i C_i^{1-n_i} \left(\sum \alpha_{ij} C_j \right)$

Ideal adsorbed solution theory **(IAST)** is a widely-used thermodynamic framework to readily predict multi-solute adsorption isotherms from a set of pure-component adsorption isotherms.

The IAST was originally developed by **Myers and Prausnitz (1965)**. Later, this theoretical approach was extended by **Radke and Prausnitz (1972)** to the competitive adsorption from dilute solutions. Solving IAST model consists of solving the following 4 equations (* mean single-solute parameter):

Gibbs adsorption isotherm, calculate of spreading pressure (π_i)

$$\frac{\pi_i A_m}{RT} = \int_0^{C_i^*} \frac{q_i^*}{C_i^*} dC_i^* \qquad (2.2)$$

Raoult's law for dilute solution

$$C_i = C_i^*(\pi) z_i \qquad (2.3)$$

Total adsorbed amount

$$q_T = \left[\sum_{i=1}^N \frac{z_i}{q_i^*(\pi)} \right]^{-1} \qquad (2.4)$$

Partial adsorbed loading

$$q_i = z_i q_T \qquad (2.5)$$

Following these steps will allow you to calculate the concentration in solid phase if you already know the concentration of each component in the liquid phase.
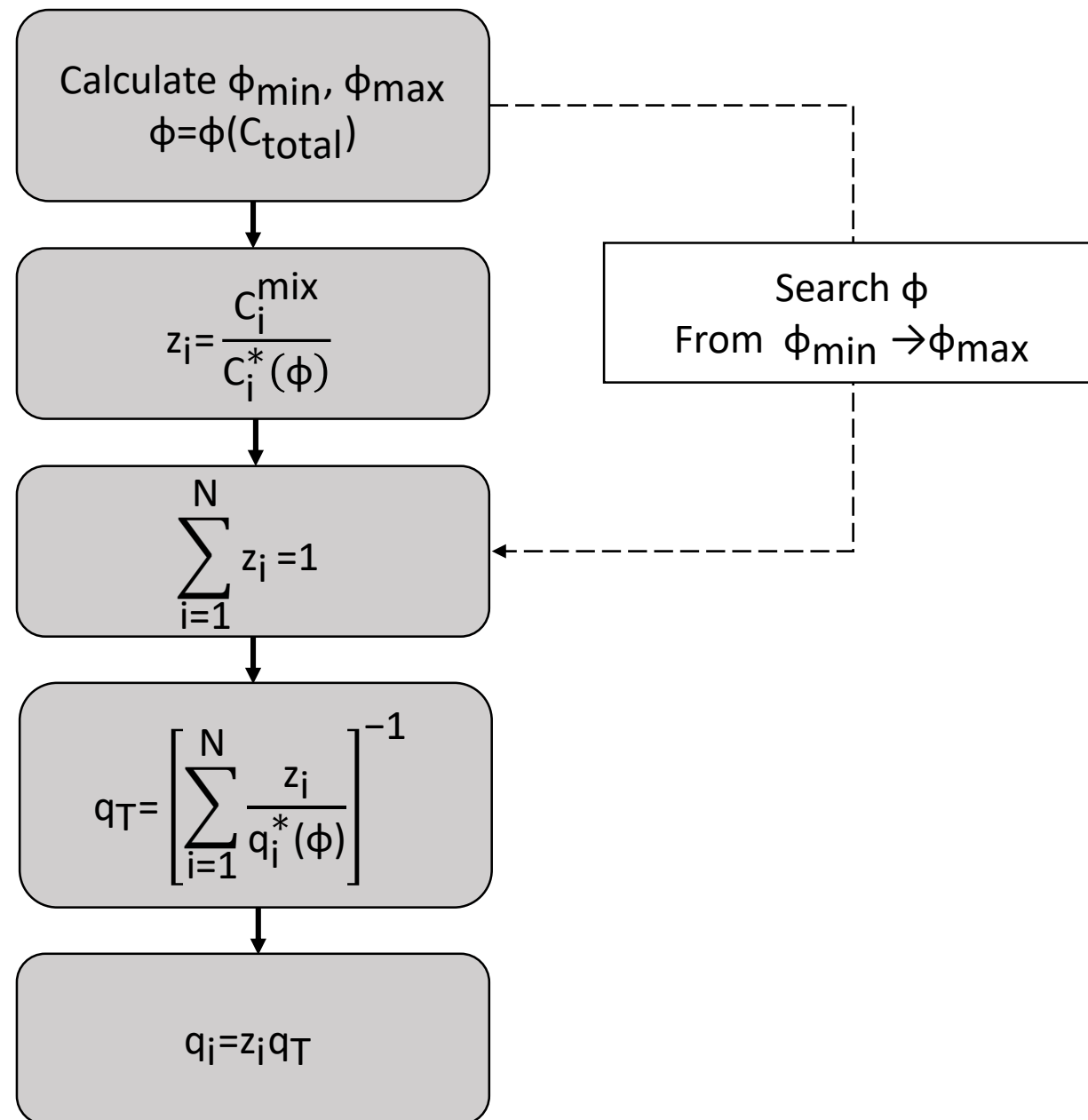

Calculate ϕ_{min}, ϕ_{max}
$\phi = \phi(C_{total})$

$$z_i = \frac{C_i^{mix}}{C_i^*(\phi)}$$

$$\sum_{i=1}^{N} z_i = 1$$

$$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{q_i^*(\phi)}\right]^{-1}$$

$$q_i = z_i q_T$$

Search ϕ
From $\phi_{min} \rightarrow \phi_{max}$

Figure 2.3 : IAST calculation scheme

To apply the scheme from previous slide, we need to solve for the spreading pressure (π_i). Here is some trivial solution for several commonly used isotherm.

Table 2.3 : Solutions to the spreading pressure integral
* mean single-solute parameter

Isotherm Equation	Φ_i	C_i^*	q_i^*
Henry $$q_i^*=H_iC_i^*$$	$$\Phi_i=H_iC_i^*$$	$$C_i^*=\frac{\Phi_i}{H_i}$$	$$q_i^*=\Phi_i$$
Freundlich $$q_i^*=K_i\left(C_i^*\right)^{n_i}$$	$$\Phi_i=\frac{K_i}{n_i}\left(C_i^*\right)^{n_i}$$	$$C_i^*=\left(\frac{\Phi_in_i}{K_i}\right)^{1/n_i}$$	$$q_i^*=\Phi_in_i$$
Langmuir $$q_i^*=\frac{q_{m_i}b_iC_i^*}{1+b_iC_i^*}$$	$$\Phi_i=q_{m_i}\ln(1+b_iC_i^*)$$	$$C_i^*=\frac{\exp\left(\frac{\Phi_i}{q_{m_i}}\right)-1}{b_i}$$	$$q_i^*=q_{m_i}\left[1-\exp\left(\frac{-\Phi_i}{q_{m_i}}\right)\right]$$
Langmuir-Freundlich $$q_i^0=\frac{q_{m_i}b_i\left(C_i^*\right)^{n_i}}{1+b_i\left(C_i^*\right)^{n_i}}$$	$$\Phi_i=q_{m_i}\ln\left(1+b_i\left(C_i^*\right)^{n_i}\right)$$	$$C_i^*=\left[\frac{\exp\left(\frac{\Phi_i}{q_{m_i}}\right)-1}{b_i}\right]^{1/n_i}$$	$$q_i^*=q_{m_i}\left[1-\exp\left(\frac{-n_i\Phi_i}{q_{m_i}}\right)\right]$$
General isotherm $$q_i^*=h(C_i^*)$$	$$\Phi_i=\int_0^{C_i^*}\frac{q_i^*}{C_i^*}dC_i^*=f\left(C_i^0\right)$$	$$C_i^*=g(\Phi_i)$$	$$q_i^*=h(C_i^*)=h\left(g(\Phi_i)\right)$$

Common error analysis models used as objective functions when fitting isotherm curves and used to validate simulations with experiments are listed below.

Table 2.4 : Error analysis statistical test.
O mean Observation (Experiment) and E mean Expected (Simulation)

Name	Abbreviation	Equation
Root-mean-square error	RMSE	$RMSE=\sqrt{\dfrac{1}{N}\sum\limits_{i=1}^{N}(O-E)_i^2}$
Sum of the squares error	ERRSQ	$ERRSQ=\sum\limits_{i=1}^{N}(O-E)_i^2$
Mean absolute percentage error	MAPE	$MAPE=\dfrac{100}{N}\sum\limits_{i=1}^{N}\left|\dfrac{O-E}{O}\right|_i$
Marquardt's percent standard deviation	MPSD	$MPSD=100\sqrt{\dfrac{1}{N-p}\sum\limits_{i=1}^{N}\dfrac{(O-E)_i^2}{O}}$
Chi-square analysis	χ^2	$\chi^2=\sum\limits_{i=1}^{N}\dfrac{(O-E)_i^2}{O}$

CHARACTERIZE COMPLEX MIXTURE FOR ADSORPTION PROCESSES

What is Sorption Analysis?

Since the mixture examined in this article is deemed too complex, isolating and identifying each component using contemporary analytical techniques is nearly impossible. Instead, the complex mixture is characterize by an experiment analysis set up that describes the most fundamental characteristics of the desired process. The ASTM D86 distillation apparatus, for example, is used as an analysis setup for the distillation process. Similar to ASTM D86, Sorption Analysis is a technique for characterizing complex mixtures for adsorption.

The Sorption Analysis includes the following steps:

- The total concentration of the to-be-characterized complex mixture is determined.

- The mixture is exposed to an increasing quantity of solid adsorbent. Then, create an isothermal curve for this mixture.

- Dilute the feed mixture in non adsorbed solvent and repeat the second step until we got **three** or **four** isotherms.
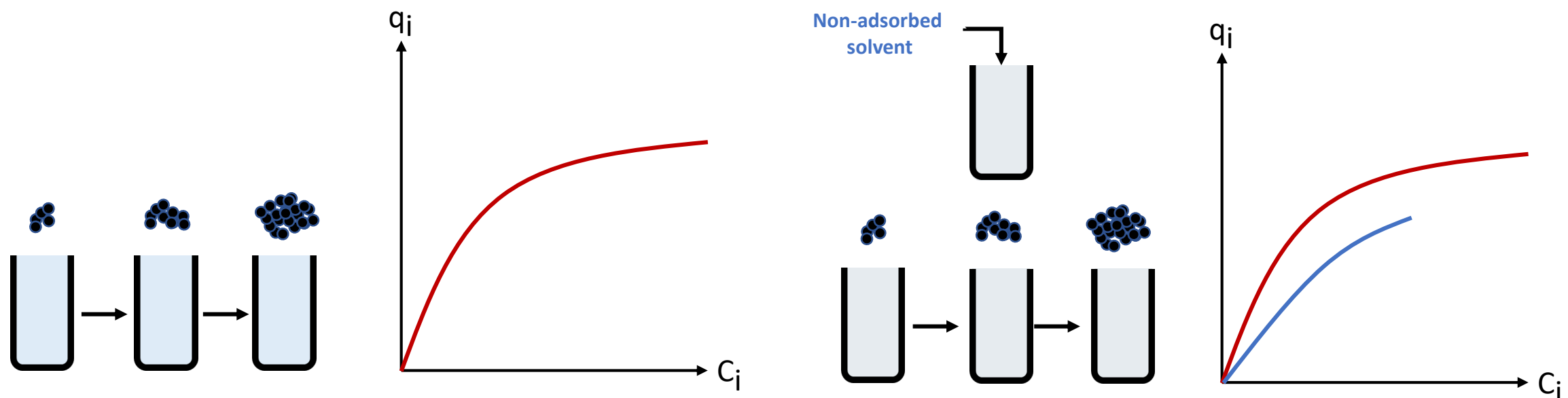

Figure 3.1 Sorption analysis workflow. Measure isotherm curve for non-dilute (left) and dilute feed (right)

Complex mixture behavior expressed through sorption analysis.

To see the importance of sorption analysis in characterizing multi component mixtures, let's consider an example. We have a mixture of components "1," "2," "3" and "4" that are distinguished by the adsorption strength between them, which is expressed by two parameters q_m and b of the Langmuir isotherm. The extended Langmuir model is utilized to simplify multicomponent adsorption.

$$q_i = \frac{q_{m_i} b_i C_i}{1 + \sum_{k=1}^{N} b_k C_k} \tag{3.1}$$

Component "1" is considered the least effective absorbent, followed by "2", "3" and "4". Thus, q_m and b are represented as follows, where α and β are coefficients greater than 1.

$$q_{mi} = q_{m1} \times \alpha^{i-1} \tag{3.2}$$

$$b_i = b_1 \times \beta^{i-1} \tag{3.3}$$

The mixture of the same concentration of "1", "2", "3", "4" is then diluted in solvent (assuming non-adsorbent, $q_m = 0$) in different proportions. Dilution ratios include 0.5% (0.5% solute - 99.5% solvent), 1%, 2% and 5%. The isotherm curve of each mixture is then measured by placing a feed solution of in contact with an increasing amount of adsorbent solid. The following 4 cases are investigated:
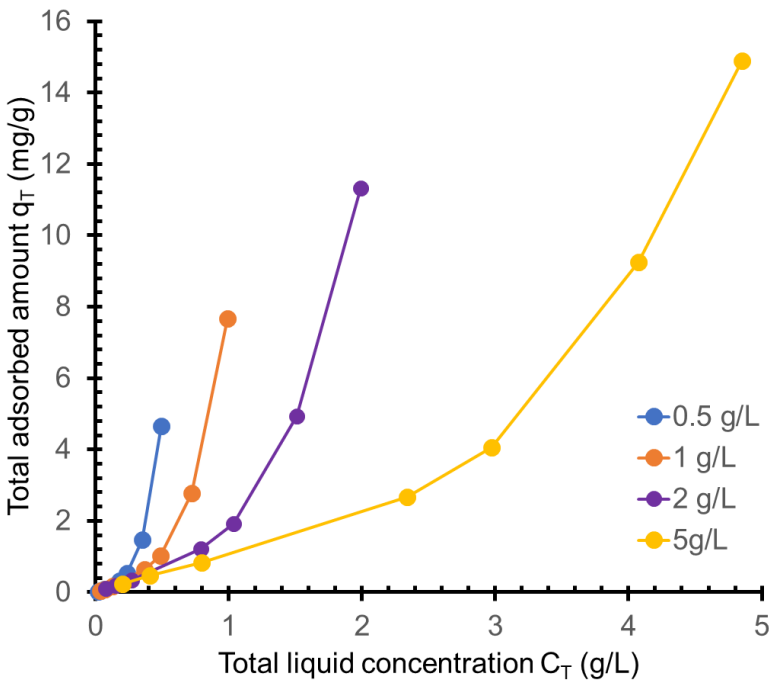
- **CASE A:** "1", "2", "3", "4" have similar properties ($\alpha = \beta = 1.05$)

- **CASE B:** "1", "2", "3", "4" have similar q_m ($\alpha = 2, \ \beta = 1.05$)

- **CASE C:** "1", "2", "3", "4" have similar b ($\alpha = 1.05, \ \beta = 2$)

- **CASE D:** "1", "2", "3", "4" are very different ($\alpha = 2, \ \beta = 2$)

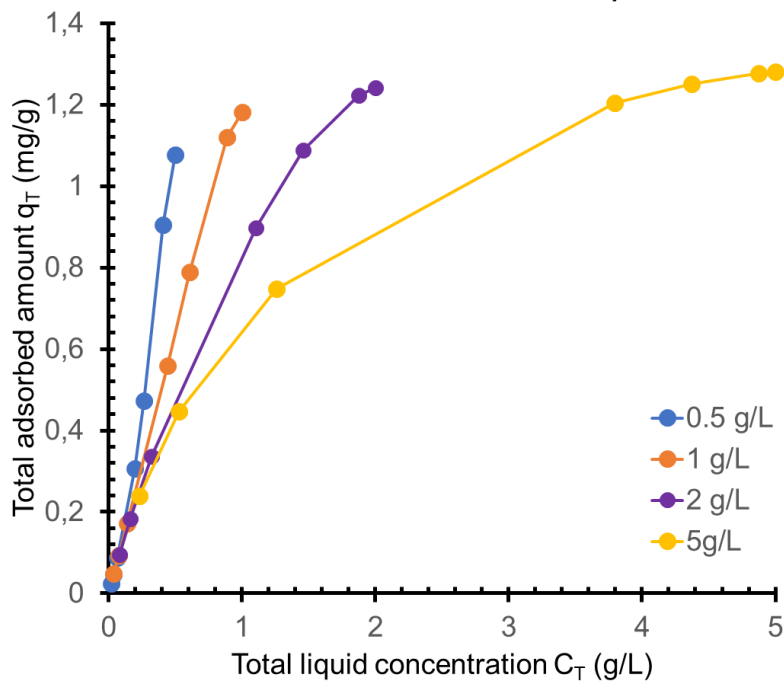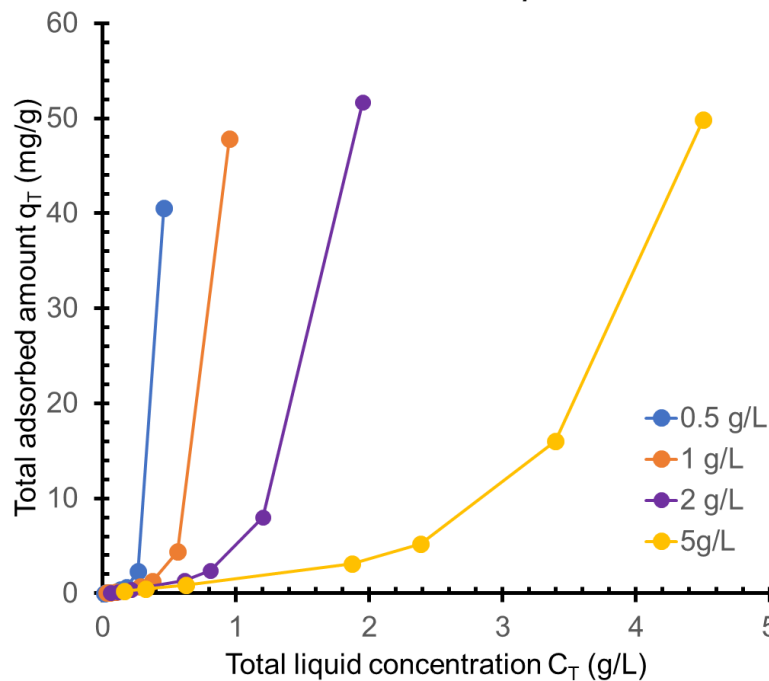**Complex mixture behavior expressed through sorption analysis.**
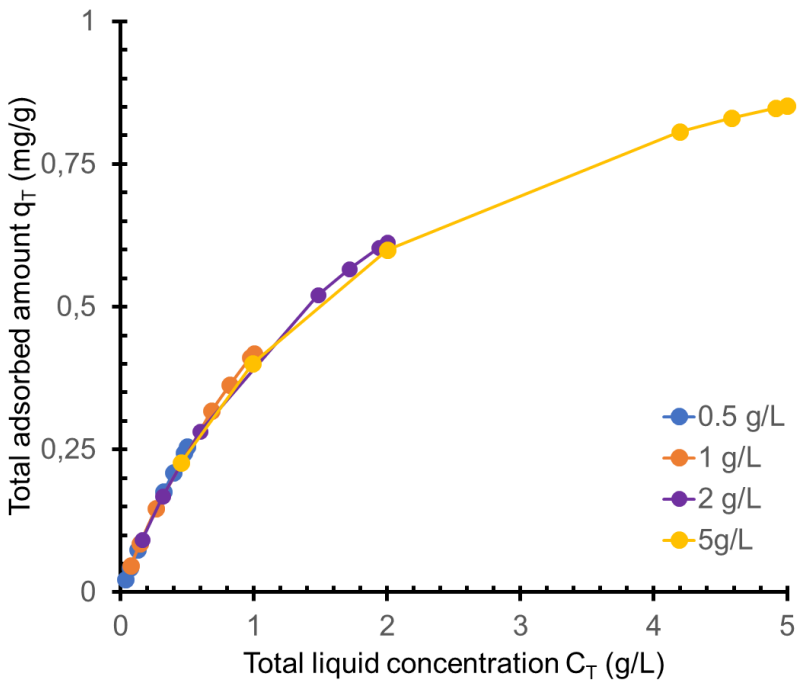
Figure 3.2. The sorption analysis illustrate the various behaviors of mixtures from **CASE I** to **CASE IV**. Here, it is assumed that the concentrations of "1", "2", "3", and "4" cannot be analyzed separately and must be measured as a whole (similar to Total Organic Carbon analysis in water). As we can see, when the adsorption strength is similar, **CASE I**, the whole mixture react like a single component. In **CASE II - IV**, however, each isotherm path is extremely distinct, despite the fact that the proportions of the components in the mixtures are identical and only the dilution ratio has been altered.

What is the definition of characterize mixture ?

In order to characterize the feed mixture, the total feed concentration of solutes in the feed solution, C_{tot}, are defined as follows:

$$C_{tot} = \sum_{i=1}^{N} C_i \qquad (3.4)$$

The mixture is completely defined when we known all the necessary properties of **"i"** and all C_i value. Where index **"i"** is the name of each component identified by modern analytical methods (e.g. GC-MS, HPLC). For instance, in membrane-based biogas upgrading, the mixture consists primarily of CH4, CO2, and saturated water vapor. Then "C_i" is the concentration of CH_4, CO_2, and H_2O, and necessary properties of **"i"** can be experimentally measured as pure gas permeability or heat capacity.

When dealing with poorly specified mixtures, index **"i"** as opposed to simply the component names, is directly associated with the property necessary to simulate that component during decomposition. As is evident from the distillation of complex mixtures, pseudo components are distinguished by their boiling point. In the adsorption processes, index **"i"** is defined as the adsorption rank in which i = 1 indicates that the component (or class of component) is the least adsorbed in the mixture.

This is the characteristic shared by all the characterizing models we are about to present. The most significant difference between the models is the amount of **"i"** used to describe the complex mixture. The quantity of **"i"** used ranges from one or a few (lump) to infinity (continuous mixture). As **"i"** increases, the mathematics underlying each method becomes significantly complex.

The ultimate goal of each model is to determine "C_i" and the isotherm parameters of **"i"** through sorption analysis.
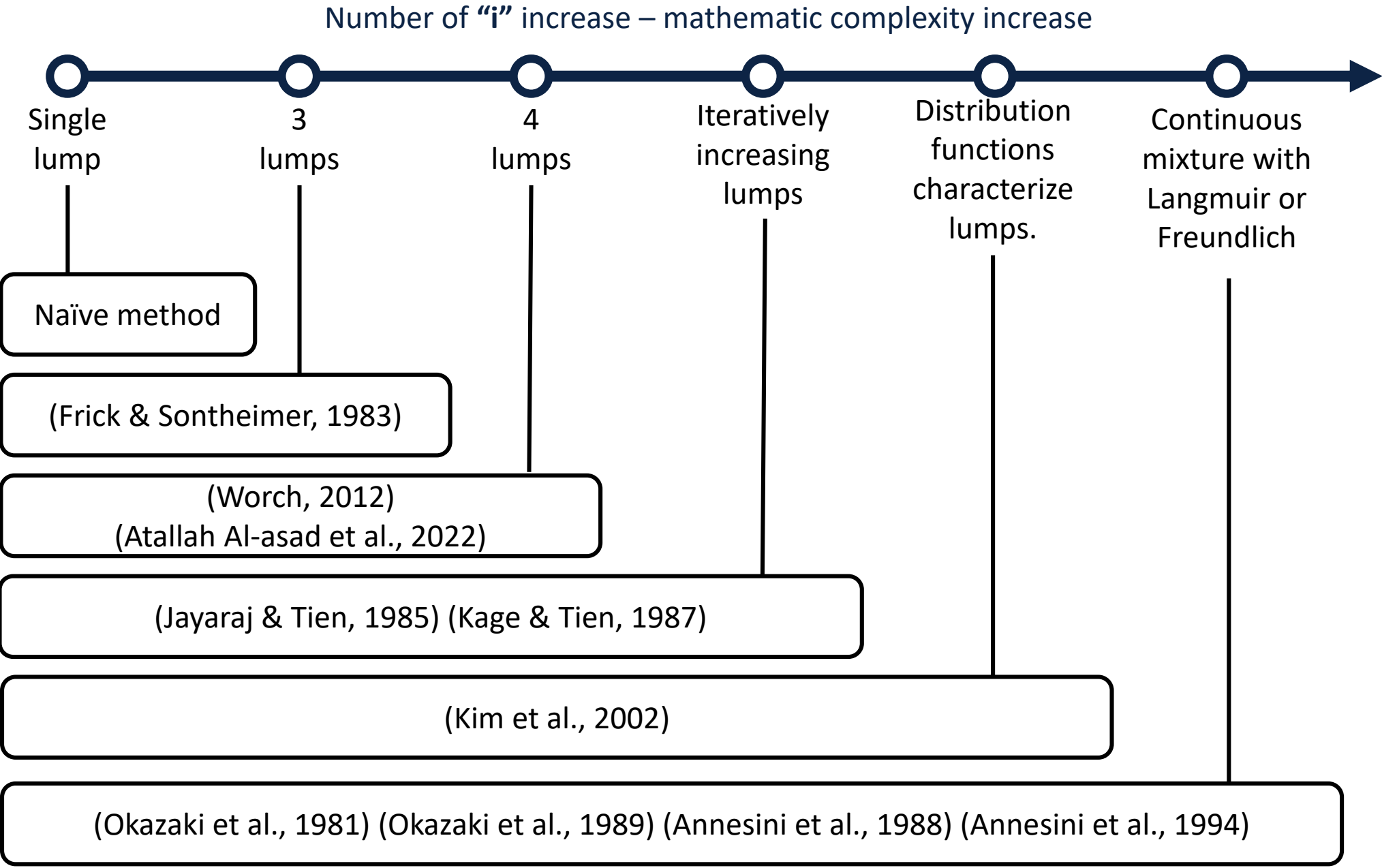
Figure 3.3 : Introduction of all characterizing model in this research

In absent of any information concerning the identities of the adsorbates in a solution, the logical starting point is to group all the adsorbate into a single species.

$$c_{tot} = \sum_{i=1}^{N} c_i, \qquad q_{tot} = \sum_{i=1}^{N} q_i \qquad\qquad (3.5)$$

The isotherm was fit with characterization curve, the isotherm model can be any single-solute isotherm model. It's a naïve approach and usually not yield a good prediction. The approach is only correct when the validate mixture is close to the characterizing mixture or all the adsorbates have the same adsorption strength (**Figure 3.2**)
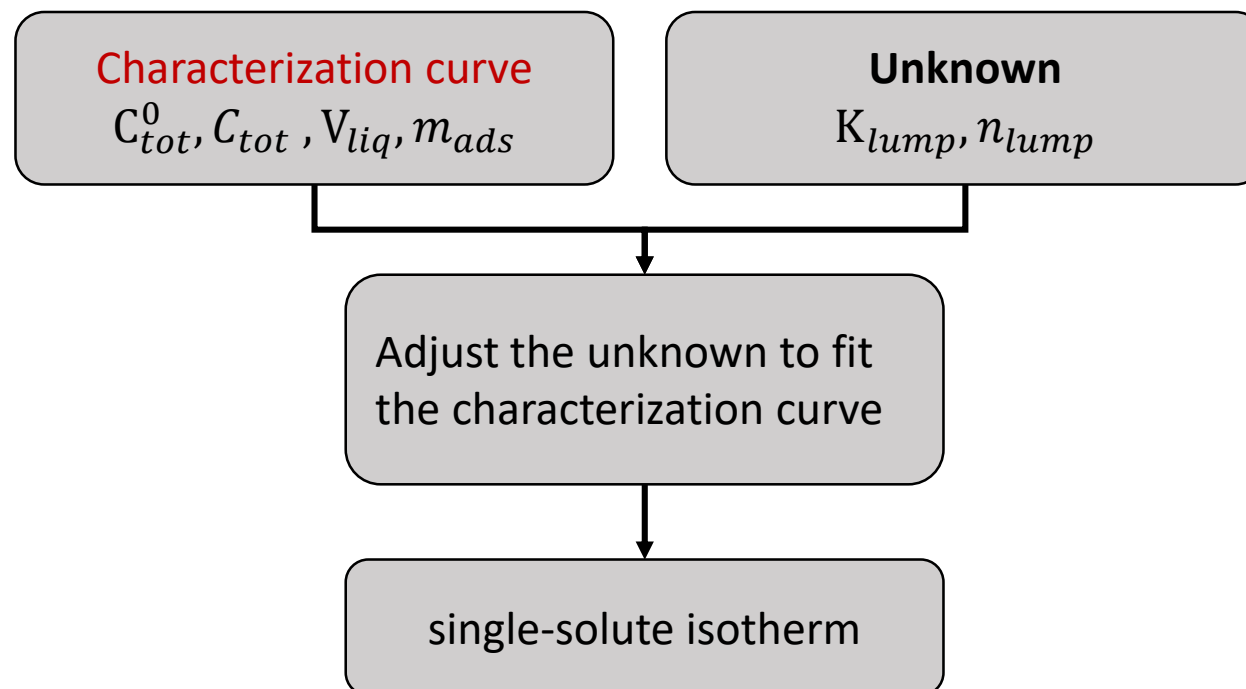

Figure 3.4 : Workflow of Single Lump method

The complex mixture was approximated into a simpler mixture with 3 lumps (or pseudo components/ or fictive component depends on the paper). The lumps is classified as follow, the properties of each lump is adopted from Freundlich isotherm parameters.

Table 3.1 : 3 Lumps model properties

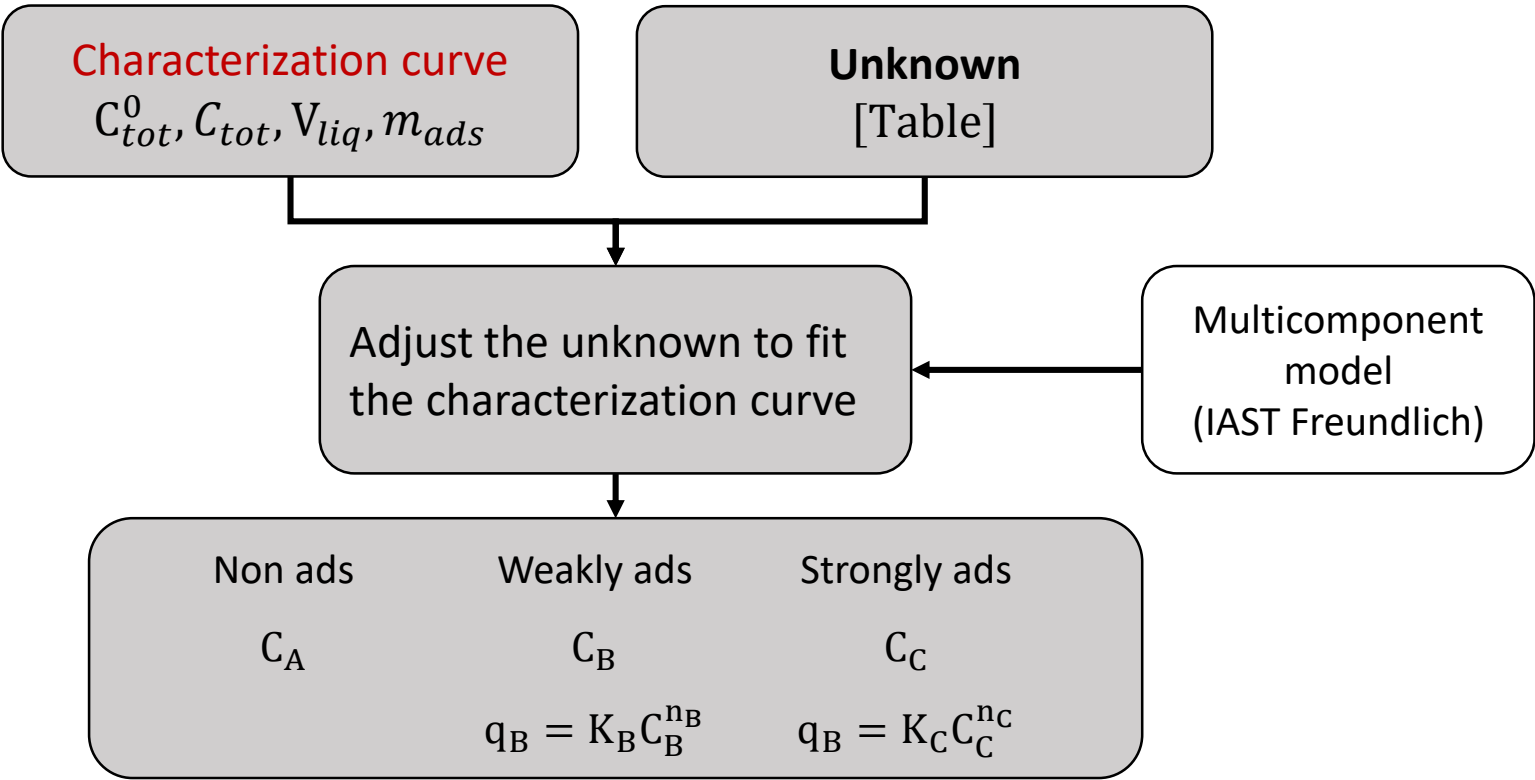| Name of "i"	Concentration	$q_i = K_f C_i^{n_i}$	
No Adsorbability	C_A	Determined with excess AC	
Weakly Adsorbability	C_B	K_B	n_B
Strongly Adsorbability	C_C	K_C	n_C

Figure 3.5 : Workflow of 3 Lump method proposed by **Frick & Sontheimer (1983)**

This slide introduces these lumps in the same manner as the previous one. This time, however, due to the larger lump, we cannot fit every variable. Instead, we manually assign the lump properties and then adjust the concentration.

Table 3.2 : 4 Lumps (Worch, 2012) model properties

Name of "i"	Concentration	$q_i = K_f C_i^{n_i}$	
No Adsorbability	C_A	Determined with excess AC	
Poor Adsorbability	C_B	10	0.2
Medium Adsorbability	C_C	50	0.2
Strong Adsorbability	C_D	80	0.2

Characterization curve
$C_{tot}^0, C_{tot}, V_{liq}, m_{ads}$

Unknown
Concentration

Adjust the unknown to fit the characterization curve

Multicomponent model
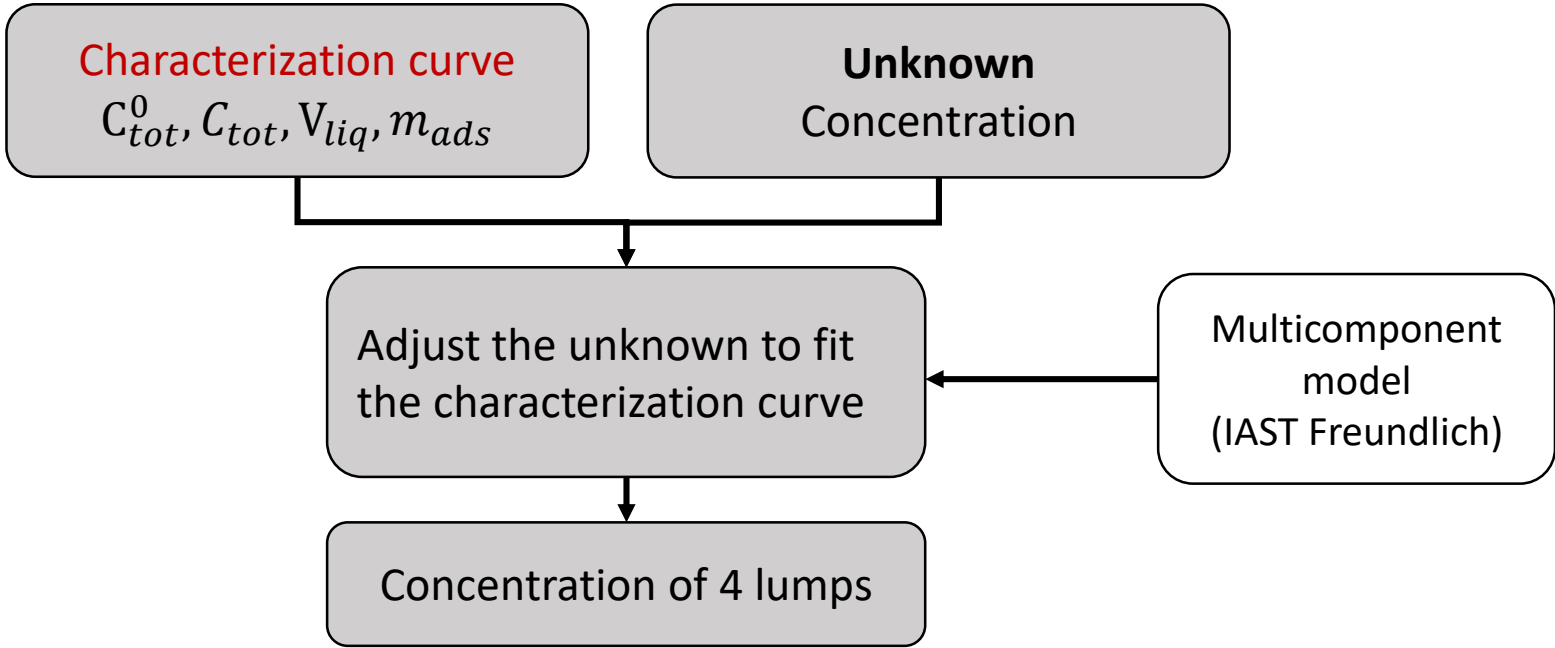(IAST Freundlich)

Concentration of 4 lumps

Figure 3.6 : Workflow of 4 Lump method proposed by **Worch (2012)**

Atallah Al-asad et al. (2022) also determines the number of lumps to be four, but this time he assigns the concentration based on the assumption that each lump's concentration is equal and the lump's properties were fitted.

Table 3.3 : 4 Lumps (Worch, 2012) model properties

Name of "i"	Concentration	$q_i = K_f C_i^{n_i}$	
No Adsorbability	C_A	Determined with excess AC	
Poor Adsorbability	$(C_{tot} - C_A)/3$	$0.5 K_f$	n_f
Medium Adsorbability	$(C_{tot} - C_A)/3$	K_f	n_f
Strong Adsorbability	$(C_{tot} - C_A)/3$	$2 K_f$	n_f
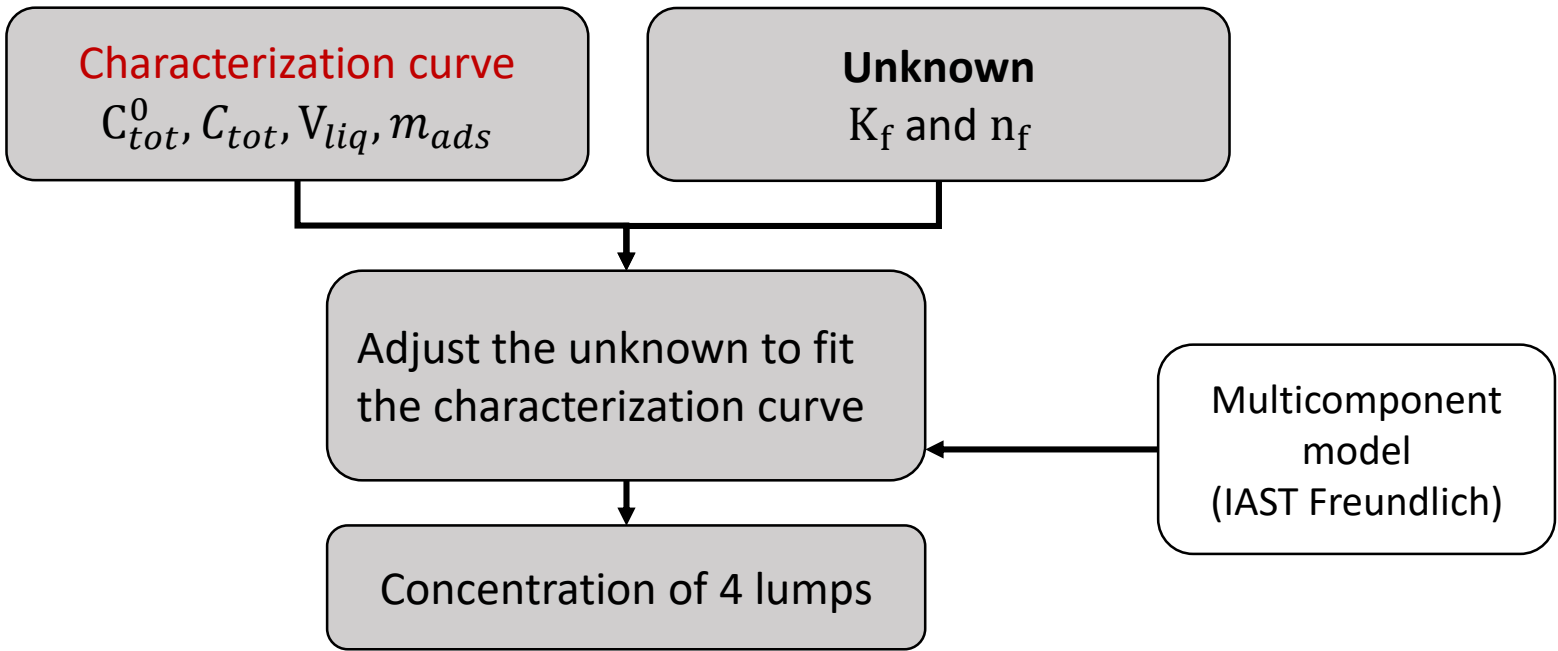
Figure 3.7 : Workflow for 4 Lump method proposed by **Atallah Al-asad et al. (2022)**

This method is similar to the previously described lumping method, with the exception that the properties of the lump are derived from the isotherm curve under the assumption of a single component. The principle of this method based on that the adsorbate with similar affinities can be grouped as a single entity (**Figure 3.2**). Instead of fixing one parameter in isotherm, this method varies both. This method requires two step: (a) Find the appropriate properties of pseudo components. (b) Assign concentration value for each pseudo species.

The adsorption mixture can be calculated by following method: (a) Freundlich with IAST (b) Langmuir with IAST (c) Extended Langmuir. Usually, the isotherm with two parameter were chosen. **Kage & Tien (1987)** assumed that all the pseudo component obey the Freundlich expression and the IAST is valid in describing multicomponent adsorption equilibrium
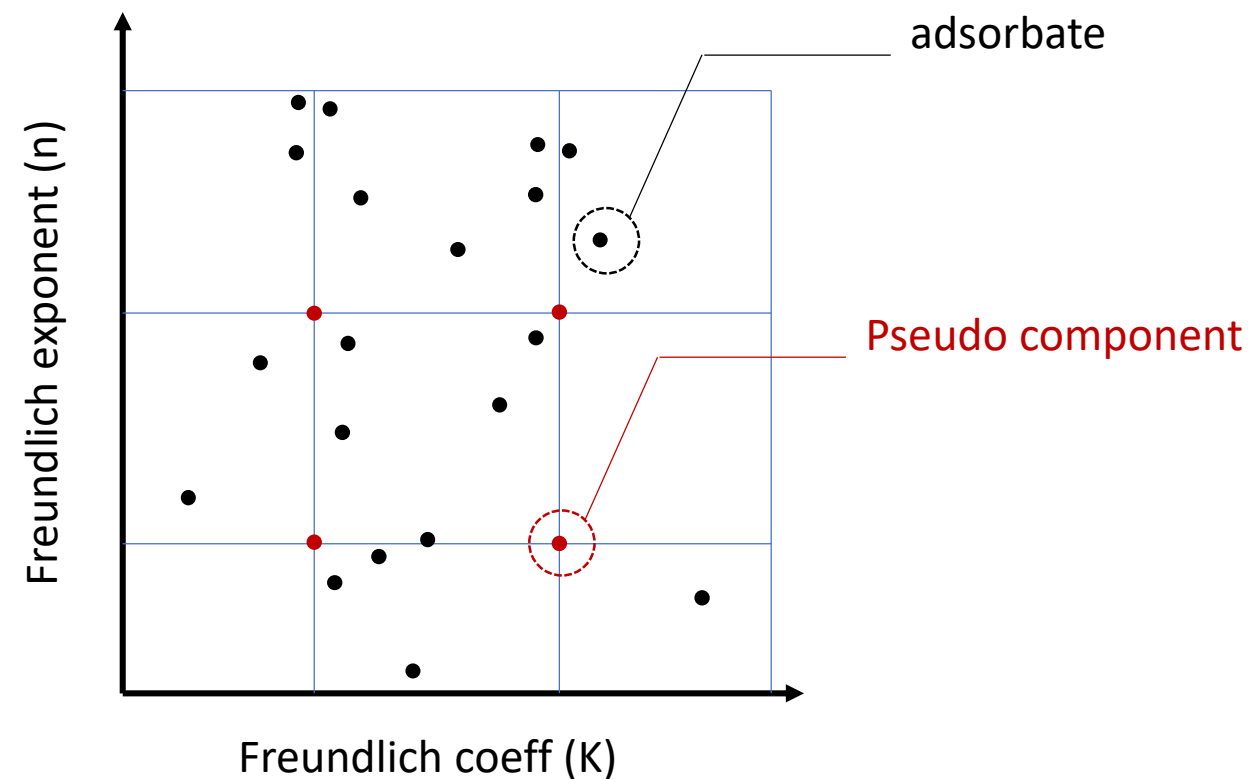

Figure 3.8 : Representation of a solution of large numbers of adsorbates by pseudo species. Each point corresponding to a given adsorbate.

The following diagram illustrates the iterative process of the method, beginning with a single lump and gradually increasing the lumps with each iteration until the model accurately reflects the experimental results.
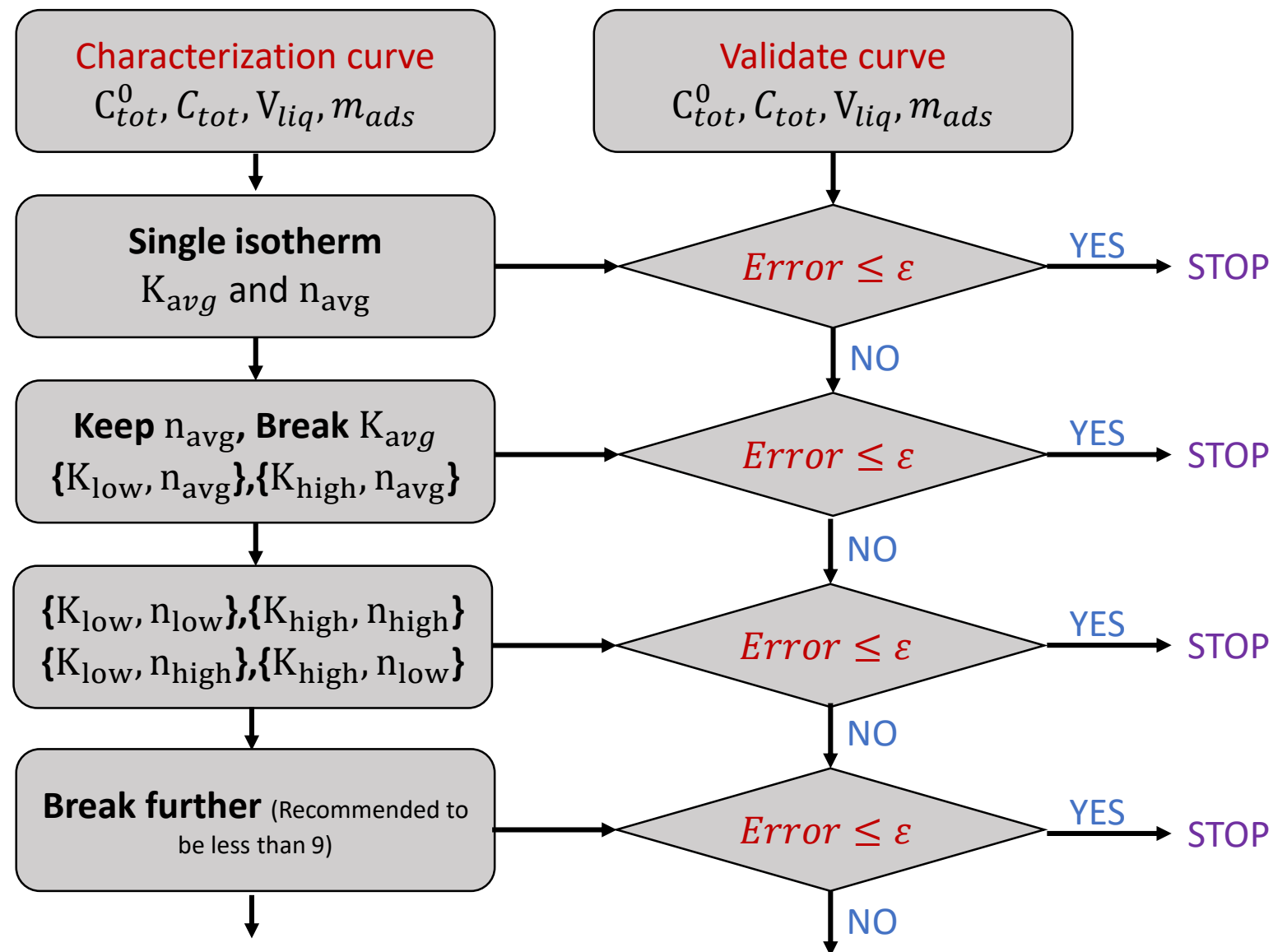

Figure 3.9 : Workflow for iteratively increasing lump method proposed by **Tien et al. (1987)**

Distribution functions characterize lumps (Kim et al., 2002)

When increasing the number of pseudo-constructors to nine, **Kage & Tien (1987)** were confronted with different results with every search. This issue arises when the number of variables in the equation exceeds the number of experimental points, resulting in an infinite set of pseudo component concentrations that all satisfy the sorption analysis results. **Kim et al. (2002)** used a binomial distribution to relate the concentration of each pseudo component to their properties in order to solve this problem. From there, the problem transitions from finding each concentration to determining the parameter of distribution function. Concentration of each pseudo component is expressed in molar fraction.

$$C_i = x_i C_T \tag{3.6}$$

In which

$$x_i = \frac{N!}{i!(N-i)!}(s)^i(1-s)^i, \qquad \text{for } i=1,2,3\ldots,N \tag{3.6}$$

N is the total pseudo component, "i" is the component index, s determines the skewness of the pseudo component concentration distribution and is within the range $0 < s < 1$ with $s = 0.5$ corresponding to a normal distribution type.
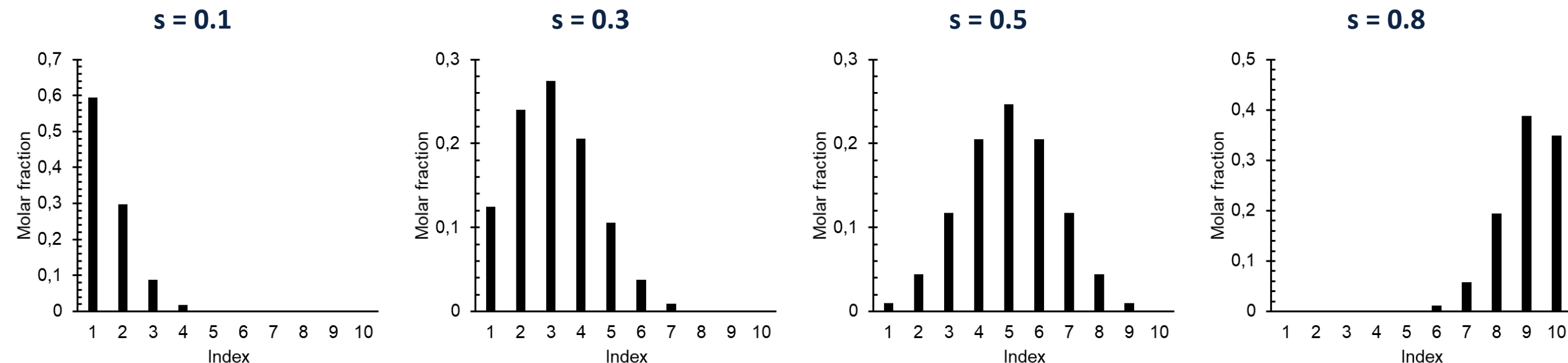

Figure 3.9 : Binomial distribution for 10 pseudo with different skewness **s**

As mentioned before, to avoid the infinite solution, the concentration of pseudo component must be related to their properties. Since the binomial distribution already associated the concentration of "i" and the index itself. The next step is relate the index "i" to the properties that represent by isotherm parameters.

Kim et al. (2002) assumes that the pseudo component obey the Freundlich isotherm and IAST as multicomponent model. Therefore, the Freundlich isotherm parameters is related to the index "i" as follow:

$$K_f = K_{ref} \times j^2 \tag{3.6}$$

$$n_f = n_{ref} \times j^0 \tag{3.7}$$

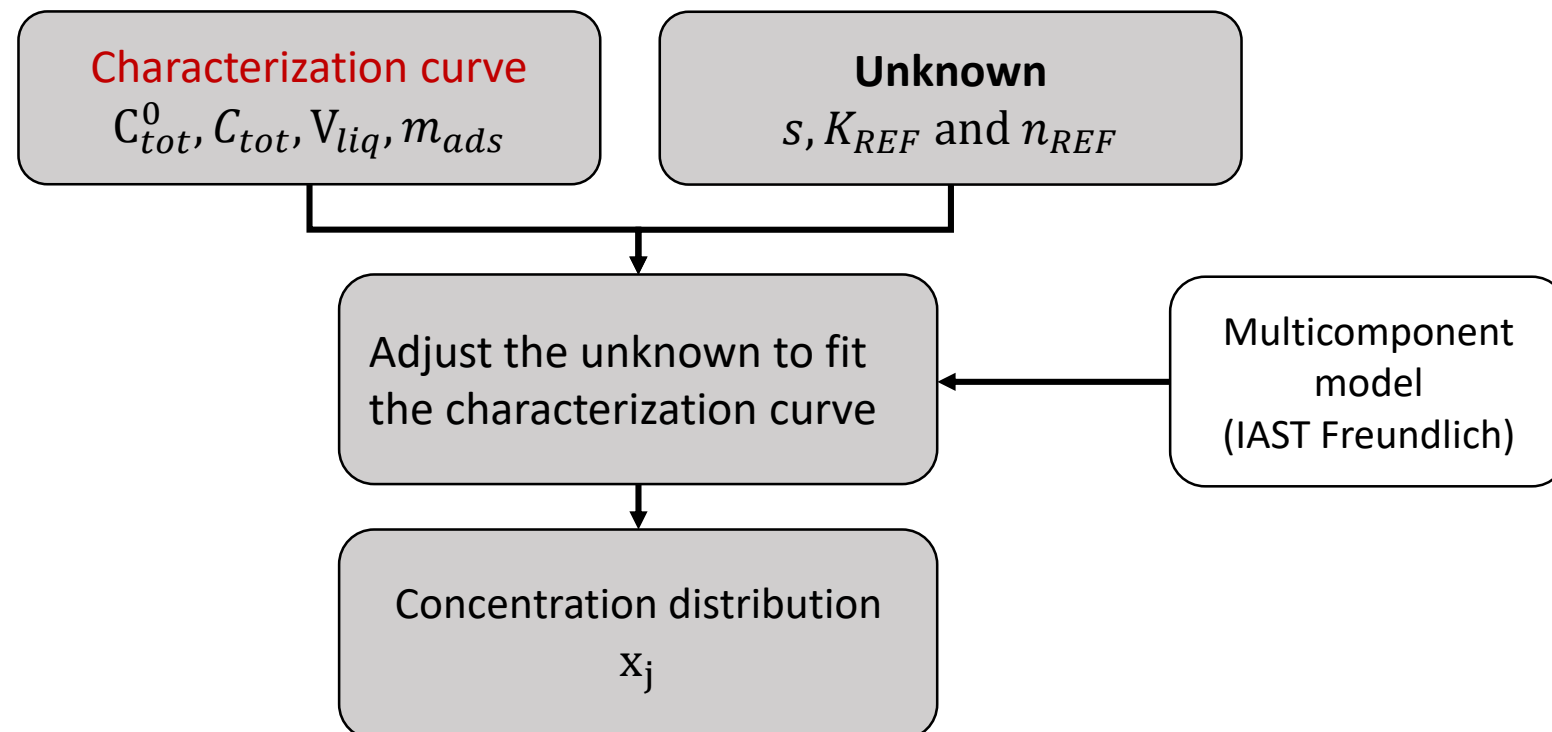Then the further calculation can follow the below guild.

Figure 3.10 : Workflow for distribution functions characterize lumps proposed by **Kim et al. (2002)**

As stated previously, the only distinction among characterization methods is the number of pseudo components considered when characterizing a complex mixture. Now that we have entered the realm of continuous mixture, the considered number of pseudo components here is infinite. **Okazaki et al. (1989)** proposed the method that utilize the infinite amount of pseudo component in which the individual adsorbates are described by their Langmuir constants, q_m and b. That's so call the characteristic distribution curve (CDC), it's a concentration frequency distribution function $c(q_m,b)$, the total liquid concentration is calculated by:

$$C_T = \int_0^{q_m} \left(\int_0^b c(q_m,b) \ db \right) dq_m \qquad (3.8)$$

To simplify the problem, **Okazaki et al. (1989)** assume that one of these coefficients is much more controlling than the other. He choose q_m to be the controlling one, while b is constant for all solute. The extended Langmuir is then written for such a mixture. The left is the extended Langmuir for discrete mixture while the right equation is for continuous mixture. For easy notation, here $q_m \equiv x$

$$q_i = \frac{q_{m_i} b_i C_i}{1 + \sum_k b_k C_k} \qquad q(x) = \frac{xbc(x)}{1 + b \int_{x_{min}}^{x_{max}} c(x)dx} \qquad (3.9)$$

Total concentration of all solute is

$$C_T = \int_{x_{min}}^{x_{max}} c(x)dx \qquad (3.10)$$

The objective of this method is to find the CDC of initial feed, when we known the $c^0(x)$ → equilibria under any condition can be easily determined.

How to determine the CDC (Characteristic distribution curve) ?

The material balance between, before and after an integral adsorption analysis is

$$c(x,0) - c(x,y_I) = y_I q(x,y_I) \tag{3.11}$$

With y_I is the amount of absorbent per unit volume. Then we substitute (3.11) to (3.9b)

$$(x,0) - c(x,y_I) = \frac{xby_I c(x,y_I)}{1 + b \int_{x_{min}}^{x_{max}} c(x,y_I) dx} \tag{3.12}$$

We also have

$$C_T(y_I) = \int_{x_{min}}^{x_{max}} c(x,y_I) dx \tag{3.13}$$

From (3.11) and (3.12) we obtain

$$c(x,y_I) = c(x,0) \frac{1 + bC_T(y_I)}{1 + C_T(y_I) + bxy_I} \tag{3.14}$$

Integrating equation (3.14)

$$C_T(y_I) = \int_{x_{min}}^{x_{max}} c(x,0) \frac{1 + bC_T(y_I)}{1 + C_T(y_I) + bxy_I} dx \tag{3.15}$$

From that, c(x,0) is the CDC of initial feed. With $C_T(y_I)$ is the data we could obtain from the sorption analysis, the problem now become the fitting problem for c(x,0) and b

$$C_T(y_I) = F(c(x,0), b) \tag{3.16}$$

How to determine the CDC (Characteristic distribution curve) ?

To perform a fitting, the CDC need to adopt a distribution curve. **Okazaki et al. (1989)** chose a following function:

$$c(x,0)=\frac{1}{2}\sum_{i=1}^{n}(f_i(x)+|f_i(x)|) \quad \text{with } i=1,2,3,\dots,n \qquad (3.17)$$

Where the $f_i(x)$ have the quadratic shape

$$f_i(x)=A_i(x-B_i)(x-D_i) \qquad (3.18)$$

The coefficient A_i,B_i,D_i have following rule:

- $A_i<0$

- $\min(B_i)\leq x_{min}<x_{max}\leq\max(D_i)$

The fitting function becomes

$$C_T(y_l)=F(A_i,B_i,D_i,b,x_{min},x_{max}) \qquad (3.19)$$

Number of unknowns is: A_i, B_i, D_i, x_{min}, x_{max}, b → 3i+3 → we already knew $C_T(0)$ → 3i+2

```
┌─────────────────────────┐   ┌─────────────────────────────┐
│  Characterization curve │   │      3i + 2 Unknown         │
│  C⁰_tot, C_tot, V_liq, m_ads │   │  A_i, B_i, D_i, x_min, x_max, b │
└─────────────────────────┘   └─────────────────────────────┘
              │                             │
              └──────────────┬──────────────┘
                             ▼
                ┌────────────────────────┐
                │  Fitting to find c(x,0) │
                └────────────────────────┘
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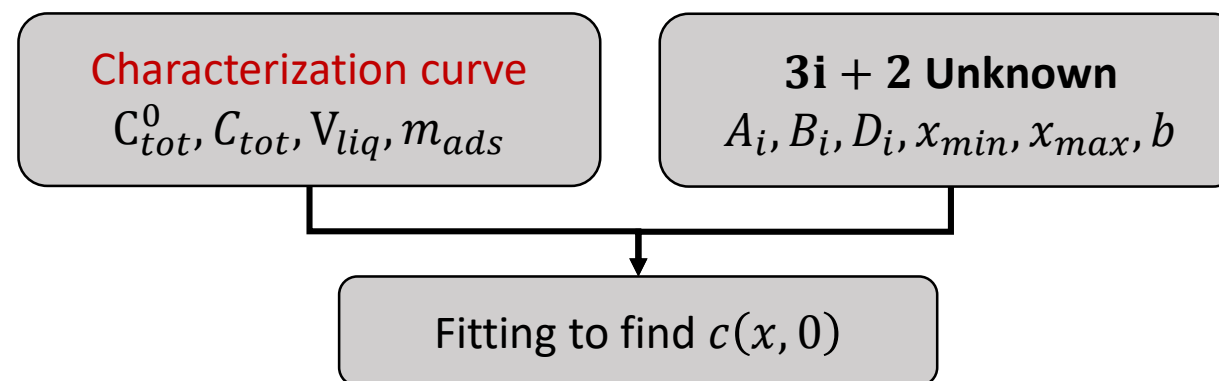
Figure 3.11 : Workflow for continuous mixture Extended Langmuir proposed by **Okazaki et al. (1989)**

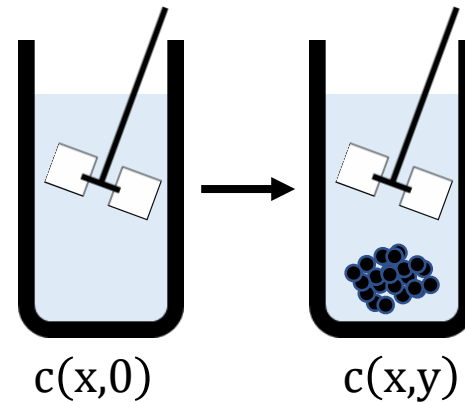**How to determine the equilibrium (flash calculation) when we known c($x,0$)?**

c(x,0)   c(x,y)

Figure 3.12 : Flash calculation when c(x,0) is known

The flash calculation is very straightforward if we already knew c(x,0). We only need to solve a non-linear equation below (Remember the equation (3.15) ?)

$$C_T(y_I)= \int_{x_{min}}^{x_{max}} c(x,0) \frac{1+bC_T(y_I)}{1+C_T(y_I)+bxy_I} dx \qquad (3.20)$$

Because $C_T(y_I)$ is not depended on x, there for the function is easy to integrate. $C_T(y_I)$ can be found by try-and-error method. The amount of solute in solid phase can be easily determined by mass balance

$$q_T = \frac{C_T(0) - C_T(y)}{y} \qquad (3.21)$$

Compared with other methods, the method proposed by Cristina Annesini et al (1988,1994) is mathematically the most complex. A theoretical framework is given by the ideal adsorbed solution model, and adsorption equilibrium equations are rewritten in a continuous form.

This method is presented in the following order:

- First, the IAST model's framework was rewritten in continuous form. In addition, a comparison discrete form and continuous form is provided.

- Then, the relationship between the characteristic distribution curve and the degree of solute removal is investigated so that, given the characteristic distribution curve of the feed and the solute removal rate, we can predict the liquid concentration and adsorbed amount at equilibrium.

- Next two distribution function for feed is explored: gamma distribution function and log-normal distribution function

- Finally, the behavior of the continuous mixture is studied, thereby discovering that all the isotherm curves of the complex mixture lie within a region bounded by two curves: (a) the isotherm curve when the feed consists of a single component and (b) the isotherm curve limiting at a high degree of solute removal.

Framework of IAST in continuous mixture

The difference between continuous and traditional mixture is the usage of distribution function. We will convert some parameter to continuous form.

<p align="center">**Table 3.4** : Compare discrete mixture and continuous mixture</p>

Discrete form	Continuous form	Meaning
c_i	$C(K_1,K_2)=\int_{K_1}^{K_2} w_L(K)dK$	Concentration of component have properties between K_1 and K_2
$C_T=\sum_i^N c_i$	$C_T=\int_K w_L(K)dK$	Total concentration
-	$W_L(K)=w_L(K)/C_T$	Intensive distribution in liquid phase
x_i	$x(K_1,K_2)=\int_{K_1}^{K_2} W_L(K)dK$	Fraction of component have properties between K_1 and K_2
q_i	$q(K_1,K_2)=\int_{K_1}^{K_2} w_S(K)dK$	Concentration in solid phase from K_1 to K_2
-	$W_S(K)=w_S(K)/\int_K w_S(K)dK$	Intensive distribution in solid phase
z_i	$z(K_1,K_2)=\int_{K_1}^{K_2} W_S(K)dK$	Fraction in solid phase of component have properties between K_1 and K_2
$q_i=\dfrac{V_{liq}(c_i^0-c_i)}{m_{ads}}$	$w_S(K)=\dfrac{V_{liq}(w_L^0(K)-w_L(K))}{m_{ads}}$	Invariant Adsorption

Framework of IAST in continuous mixture

We assume the ideality of the adsorbed phase and of the liquid dilute solution, the star (*) mean that the parameter obtained from single solute adsorption condition

$$C_i = C_i^*(\pi)z_i \qquad\qquad w_L(K) = C^*(K,\pi)W_S(K) \qquad (3.22)$$

Molar/mass fraction in the solid (z_i) must satisfy the following condition:

$$\sum z_i = 1 \qquad\qquad \int W_S(K)dK = 1 \qquad (3.23)$$

According to thermodynamic, Gibbs adsorption isotherm is written as follow

$$\phi = \frac{\pi A}{RT} = \int_0^{C_i^*} \frac{q_i^*}{C_i^*} dC_i^* \qquad\qquad \phi = \frac{\pi A}{RT} = \int_0^{C_i^*} \frac{q^*(K)}{C^*(K)} dC^*(K) \qquad (3.24)$$

Further, the total adsorbed amount in multi solute adsorption is related to the adsorbed amounts of the mixture components during single-solute adsorption at the given spreading pressure, π, by

$$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{q_i^*(\pi)}\right]^{-1} \qquad\qquad \int_M w_S(K)dK = \left[\int_M \frac{W_S(K)}{q^*(K,\pi)}\right]^{-1} \qquad (3.25)$$

The partial adsorbent loading of each component, q_i, in multi-solute adsorption can be found from

$$q_i = z_i q_T \qquad\qquad - \qquad (3.26)$$

Framework of IAST in continuous mixture $\{w_L(M) \Rightarrow q_T\}$

The procedure for the calculation of φ consists of the following steps:

- Adsorption isotherm is obtained or assumed beforehand to assign the dependence on $C^*(K)$ of the invariant adsorption $q^*(K)$
- The integration is carried out,

$$\phi = \frac{\pi A}{RT} = \int_0^{C_i^*} \frac{q^*(K)}{C^*(K)} dC^*(K) \tag{3.27}$$

- The function $f(K)$ is obtained for each value of φ:

$$\phi(\pi) = f(C^*(K),K) \Rightarrow C^*(K) = f(K,\phi) \tag{3.28}$$

- Substituting $C^*(K)$ to intensive distribution in solid phase $W_S(K)$

$$\int_M W_S(K)dM = \int_M \frac{w_L(K)}{C^*(K)} dK = \int_M \frac{w_L(K)}{f(K,\phi)} dK \tag{3.29}$$

- Find ϕ in order to satisfy the condition from equation (3.23):

$$\int_M \frac{w_L(K)}{f(K,\phi)} dK = 1 \tag{3.30}$$

- With the correct φ we can find $C^*(K) \rightarrow q^*(K) \rightarrow$ total q_T

$$q_T = \int_M w_S(K)dK = \left[\int_M \frac{W_S(K)dK}{q^*(K,\pi)}\right]^{-1} = \left[\int_M \frac{w_L(K)dK}{C^*(K) \, q^*(K,\pi)}\right]^{-1} \tag{3.31}$$

Relationship between characteristic distribution function and degree of solute removal

Mass balance for adsorption single stage (Adsorption Invariant)

$$w_L^0(K) - w_L(K) = \frac{m_{ads}}{V_{liq}} q(K) = y_I q(K) \qquad (3.32)$$

Integrating the equation (3.32)

$$C_T^0 - C_T = y_I q_T \qquad (3.33)$$

Dividing equation (3.x) to (3.1)

$$\frac{w_L^0(K) - w_L(K)}{C_T^0 - C_T} = \frac{q(K)}{q_T} = \frac{q_T \frac{K w_L(K)}{\bar{K} C_T}}{q_T} = \frac{K w_L(K)}{\bar{K} C_T} \qquad (3.34)$$

Introduce the solute removal $\chi = C_T / C_T^0 \in (0,1)$

$$w_L(K) = \frac{\bar{K} w_L^0(K) \chi}{\chi \bar{K} + (1-\chi)K} = \frac{w_L^0(K)}{1 + (1-\chi)\frac{K}{\chi \bar{K}}} = \frac{w_L^0(K)}{1 + (1-\chi)\frac{K C_T^0}{\int K\, w_L(K)dK}} = F[w_L(K), K] \qquad (3.35)$$

From equation (3.35)

$$\frac{w_L^0(K) - w_L(K)}{C_T^0 - C_T} = \frac{K w_L(K)}{\bar{K} C_T} \Leftrightarrow \frac{K^n w_L^0(K) - K^n w_L(K)}{C_T^0(1-\chi)} = \frac{K^{n+1} w_L(K)}{\frac{M_1}{C_T} C_T} \Leftrightarrow M_{n+1} = \frac{M_1(M_n^0 - M_n)}{C_T^0(1-\chi)} \qquad (3.36)$$

Relationship between characteristic distribution function and degree of solute removal

The equation (3.36) shows that the moment $\{M_n\}$ can be directly evaluate from $\{M_n^0\}$ once χ and M_1 are known. The first-order moment M_1 is the solution of the implicit nonlinear equation (3.35)

$$M_1 = \int_0^\infty \frac{K w_L^0(K)}{1+\dfrac{(1-\chi)KC_T^0}{M_1}}\, dK = g(\chi, M_1) \tag{3.37}$$

The equation (3.37) can be solve if we explicitly know the characteristic curve distribution of feed $w_L^0(K)$. $w_L(K)$ could be solve iteratively by using $w_L^0(K)$ as starting point.

$$w_L^{(1)}(K)=F[w_L^0(K),K]$$
$$w_L^{(2)}(K)=F[w_L^{(1)}(K),K]$$
$$\vdots \tag{3.38}$$
$$w_L^{(n+1)}(K)=F[w_L^{(n)}(K),K]$$

The sequence of $w_L^{(n)}$ guarantees convergence at $w_L(K)$ (Appendix 3 at [Ref](#))

Relationship between characteristic distribution function and degree of solute removal

The It's convenient to normalize $w_L(K)$

$$W_L(K) = \frac{w_L(K)}{C_T} = \frac{w_L(K)}{\chi C_T^0} \tag{3.39}$$

With $M_n^* = M_n / \chi C_T^0$

$$W_L(K) = \frac{w_L^0(K)}{\chi C_T^0 + \dfrac{(1-\chi)KC_T^0}{M_1^*}} \tag{3.40}$$

With $M_1^* = M_n / \chi C_T^0 = \bar{K}$ and $\int_K W_L(K)dK = 1$ we obtain

$$1 = \int_0^\infty \frac{w_L^0(K)dK}{\chi C_T^0 + \dfrac{(1-\chi)KC_T^0}{\bar{K}}} \Rightarrow \frac{C_T^0}{\bar{K}} = \int_0^\infty \frac{w_L^0(K)dK}{\dfrac{\chi}{(1-\chi)}\bar{K}+(1-\chi)K} \tag{3.41}$$

The mean value of K, $\bar{K}$ then can be solve for a specific removal rate χ

Relationship between characteristic distribution function and degree of solute removal
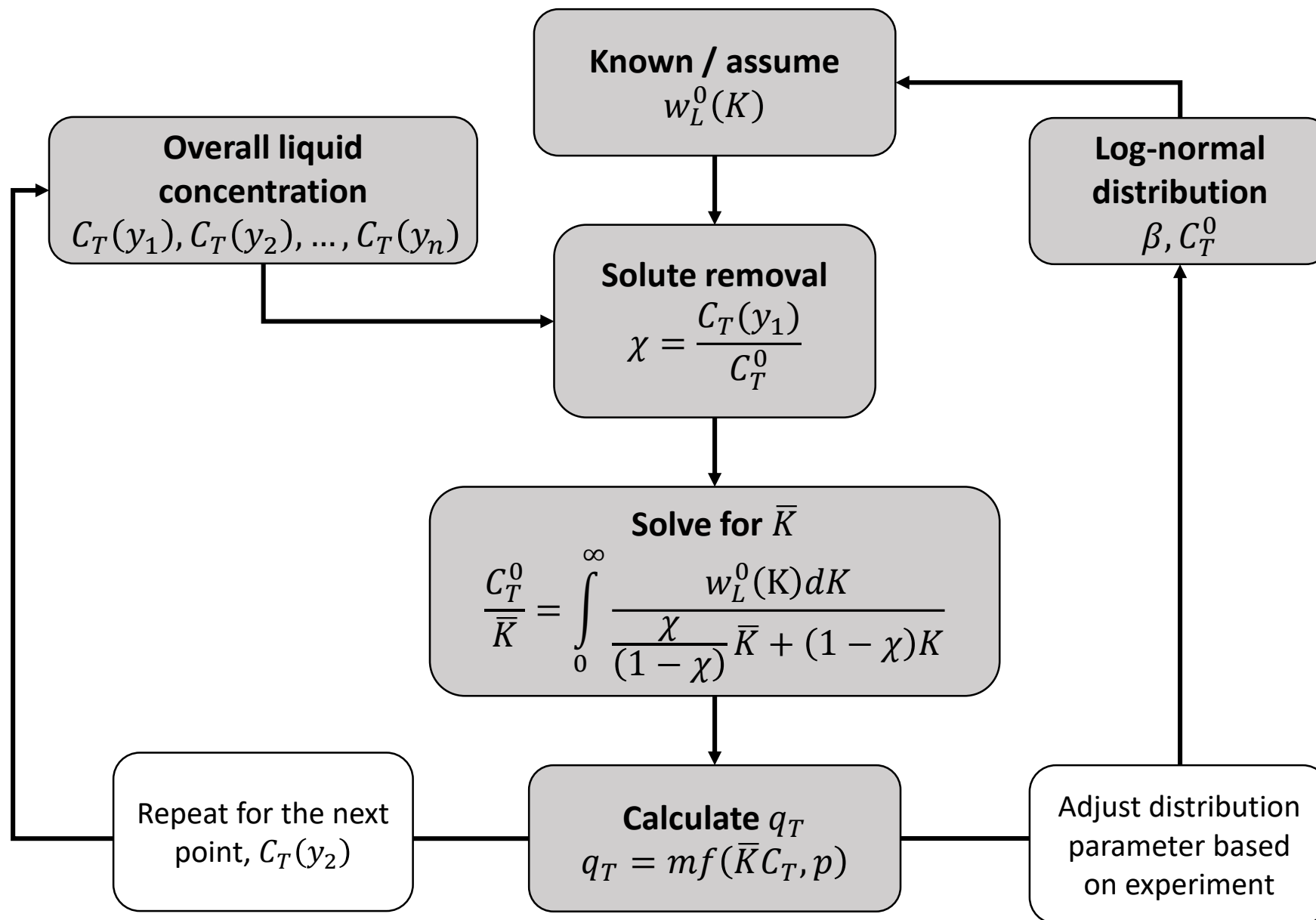

Figure 3.13 : Workflow for Continuous mixture IAST proposed by **Annesini et al. (1994)**

Typical distribution function for $w_L^0(K)$

Without loss of generality $w_L^0(K)$ is normalize so that $\bar{K}^0=1$ or $M_1^0=C_T^0$

Gamma distribution

$$w_L^0(K)=C_T^0\frac{\beta^\beta}{\Gamma(\beta)}\exp(-\beta K)\,K^{\beta-1} \tag{3.42}$$

$$\sigma_0^2=\beta^{-1} \tag{3.43}$$

- $\beta>1 \Rightarrow w_L^0(K)/K$ is summable $\Rightarrow \bar{K}^\infty = \beta/(\beta-1)$

- $0<\beta\leq1 \Rightarrow w_L^0(K)/K$ is not summable $\Rightarrow \bar{K}^\infty=0$

Log-normal distribution

$$w_L^0(K)=\frac{C_T^0}{\sqrt{2\pi}\beta e^{-\beta^2}}\exp\left[-\frac{\ln\left(K+\frac{3}{2}\beta^2\right)^2}{2\beta^2}\right] \tag{3.44}$$

$$\sigma_0^2=e^{\beta^2} \tag{3.45}$$

- The summable condition is always satisfy $\Rightarrow \bar{K}^\infty=e^{-\beta^2}$

Limiting Distribution for High Solute Removal

For high solute removal $\chi \to 0$, we look for the limiting distribution

$$W_L^\infty(K) = \lim_{\chi \to 0} \frac{w_L^0(K)}{\chi c_T^0 + \frac{(1-\chi)Kc_T^0}{\overline{K}}} \qquad (3.46)$$

And the limiting value of $\overline{K}$, we find that $\overline{K}$ is bounded and $\overline{K}^\infty$ is finite

$$\overline{K}^\infty = \lim_{\chi \to 0} \overline{K} \qquad (3.47)$$

$W_L^\infty(K)$ has some interesting properties:

- A mixture containing a finite or an infinitesimal amount of nonadsorbable compounds ($w_L^0(0) \neq 0$). The limiting distribution is $W_L^\infty(K) = C_{na}\delta(K)$ → obtain C_{na} from high loading experiment and use new distribution $w_L^0(K) - C_{na}\delta(K)$ which does not contain any nonadsorbable compounds.

- If $w_L^0(K)/K$ is summable (it physically should be) and $w_L^0(0) = 0$ (Contain no nonadsorbable compound), then we can find (follow the Appendix 4 of Ref)

$$\frac{1}{\overline{K}^\infty} = \int \frac{w_L^0(K)}{Kc_T^0} dK \qquad (3.48)$$

Once $\overline{K}^\infty$ is known, the entire moment hierarchy M_n^*, of the limiting distribution $W_L^\infty(K)$ is obtained

$$M_{n+1}^* = \overline{K}^\infty \left(M_n^0 / c_T^0 \right) \qquad \text{for} \quad \chi \to 0 \qquad (3.49)$$

Characterize initial distribution function by Adsorption analysis experiment

The initial distribution was characterized by overall adsorption isotherm experiment.

The experiment is conducted by placing a feed solution of known composition in contact with an increasing amount of adsorbent solid.

Different isotherms are obtained by diluting the feed. It means that changing C_T^0 but keeping $w_L^0(K)$.

All the isotherm with different C_T^0 start at $mf(\overline{K}^0 C_T, p)$ and collapse at $mf(\overline{K}^\infty C_T, p)$
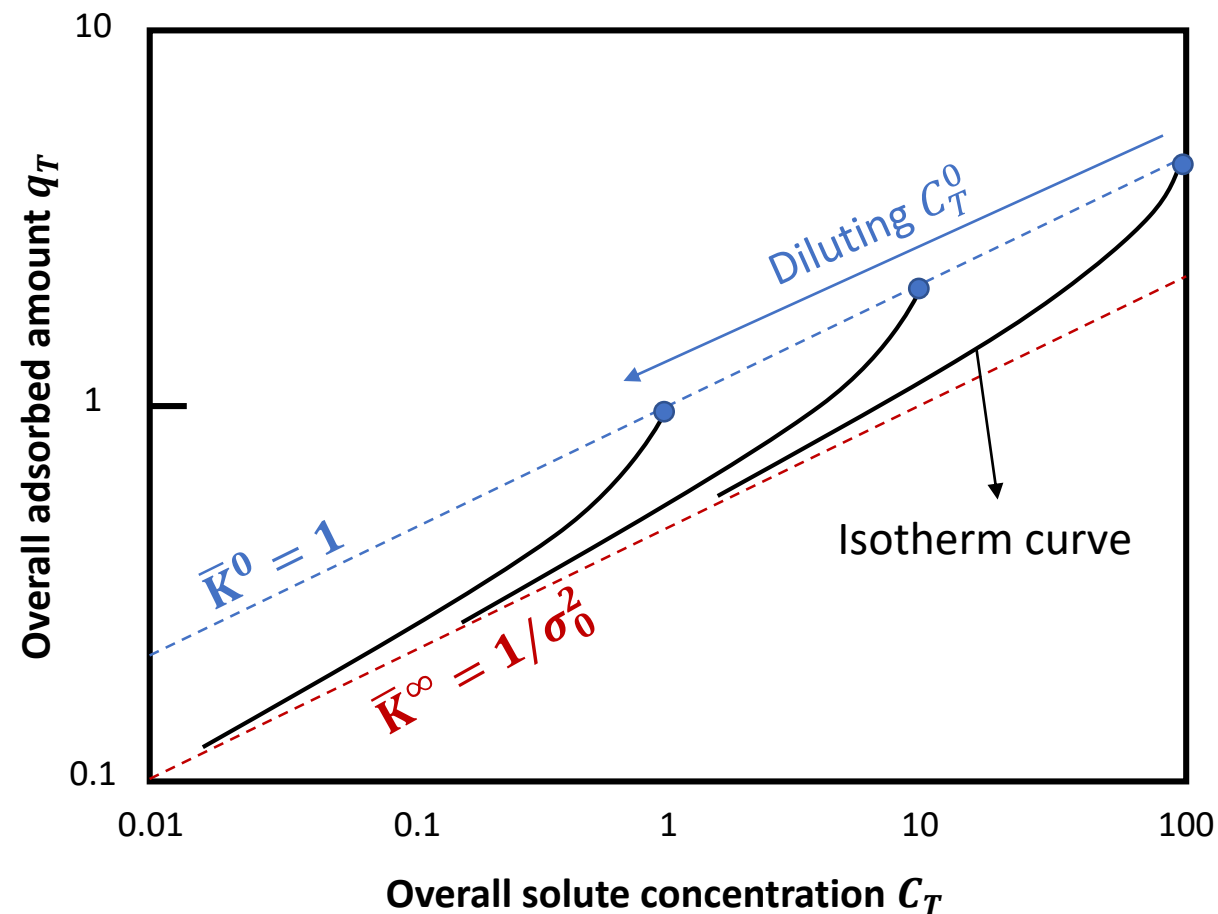

Figure 3.14 : Overall adsorption isotherms for a continuous mixture with a log-normal distribution function ($p = 1/3; \sigma_0^2/\overline{K}^{0^2} = 9.5$)

Characterize initial distribution function by Adsorption analysis experiment

The parameters $\bar{K}^0$, $\bar{K}^\infty$ and p,m can be obtained from the experimental data in the limiting of $C_T/C_T^0 \to 1$ and $C_T/C_T^0 \to 0$

- At $C_T/C_T^0 \to 1$

Slope deviate from single solute mixture with $K=\bar{K}^0$

$$\frac{dq_T}{dC_T} = m\frac{df(\bar{K}^0 C_T, p)}{dC_T}\left[1+\frac{\sigma_0^2}{\bar{K}^{0^2}}\right] \qquad (3.50)$$

- At $C_T/C_T^0 \to 0$

$$\frac{dq_T}{dC_T} = m\frac{df(\bar{K}^\infty C_T, p)}{dC_T} \qquad (3.51)$$

For example, with Freundlich isotherm, $q_T = (\bar{K}C_T)^p$

$$\frac{d\ln(q_T)}{d\ln(C_T)} = p\left[1+\frac{\sigma_0^2}{\bar{K}^{0^2}}\right] \qquad \text{at } C_T/C_T^0 \to 1 \qquad (3.52)$$

$$\frac{d\ln(q_T)}{d\ln(C_T)} = p \qquad \text{at } C_T/C_T^0 \to 0 \qquad (3.53)$$

For Langmuir isotherm, $q_T = q_m(\bar{K}C_T)/(1+\bar{K}C_T)$

$$\frac{dq_T}{dC_T} = \frac{q_m\bar{K}^0}{\left(\bar{K}^0 C_T^0+1\right)^2}\left[1+\frac{\sigma_0^2}{\bar{K}^{0^2}}\right] \qquad \text{at } C_T/C_T^0 \to 1 \qquad (3.54)$$

$$\frac{dq_T}{dC_T} = q_m\bar{K}^\infty \qquad \text{at } C_T/C_T^0 \to 0 \qquad (3.55)$$

EXPERIMENTAL DATA

A sorption analysis should be performed when:

- There are no available analytical methods that can analyze each component separately

- There are too many components, making it impractical to use all of them in the simulation.

- None of the components is more numerous or of greater significance than the others, making it impossible to select the proper key component.

- Total concentration of all component can be tracked by mean of a collective parameter (TOC or elemental analysis)

An easy way to understand sorption analysis is to think of it as a measurement of the isotherm for both the complex mixture and the mixtures that have been diluted from the complex mixture. When putting characterization methods to the test, it is common practice to first create complex mixtures, which typically consist of a mixture of ultra pure water and organic or inorganic compound to represent wastewater.

The synthetic mixture from **Kit et al. (2002)** is was prepared by dissolving several organic matters such as glucose, yeast extract, and peptone in addition to some typical inorganic com pounds that normally exist in domestic wastewater. Organic and inorganic wastewater constituents are listed in Table 4.1.

Table 4.1 : Synthetic wastewater constituents (Kim et al., 2002)

Compound	Weight (mg/L)	Species
Glucose	16.5	
Yeast extract	1.75	Organic compounds
Peptone	1.75	
$MnSO_4$	0.13	
$CaCl_2$	0.93	
$NaHCO_3$	0.88	
NaCl	2.5	Inorganic compounds
$MgSO_4.7H_2O$	3.75	
KH_2PO_4	1.25	
$(NH_4)_2SO_4$	3.5	

Experimental data from literature (Kim et al., 2002)
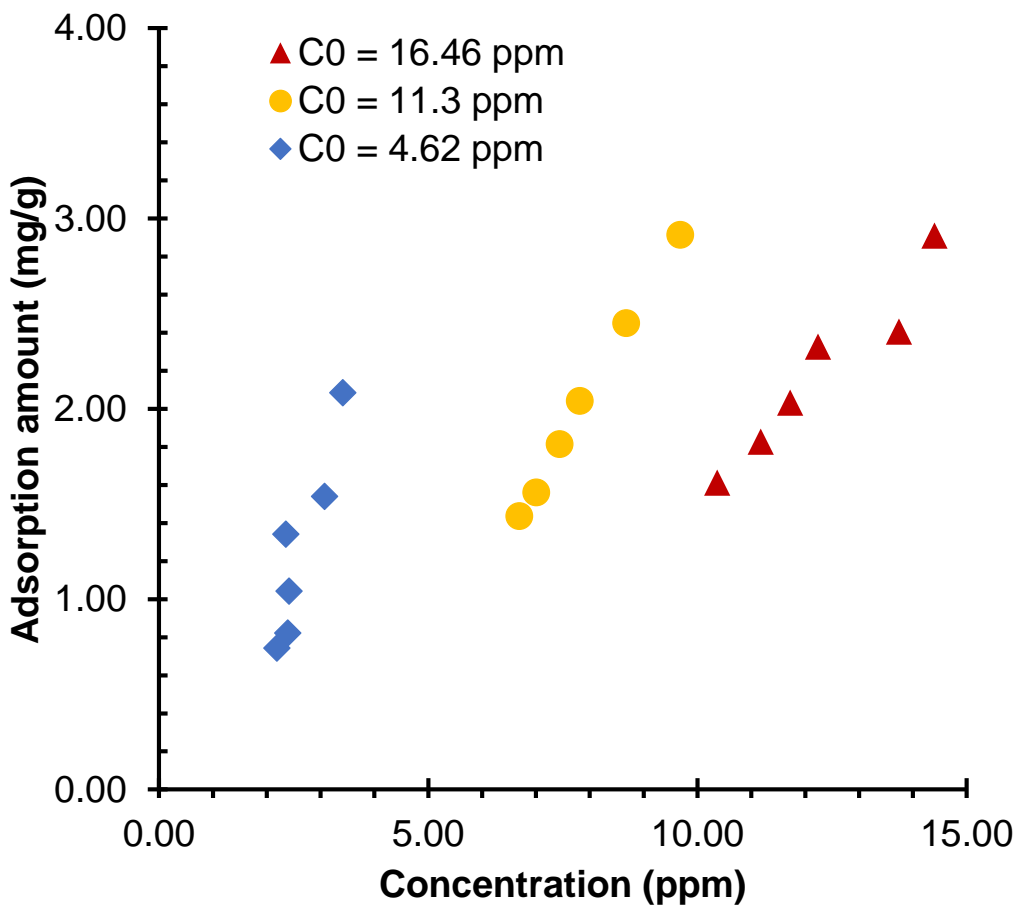
Figure 4.1 : Equilibrium data on GAC

Table 4.2 : Equilibrium data on GAC

C_0 = 16.46 ppm		C_0 = 11.3 ppm		C_0 = 4.62 ppm	
C_e(ppm)	q_e(mg/g)	C_e(ppm)	q_e(mg/g)	C_e(ppm)	q_e(mg/g)
10.37	1.61	6.69	1.44	2.19	0.74
11.17	1.83	7.01	1.56	2.39	0.82
11.72	2.03	7.44	1.81	2.42	1.04
12.24	2.33	7.81	2.04	2.35	1.34
13.74	2.41	8.68	2.45	3.07	1.54
14.40	2.91	9.68	2.91	3.41	2.08

Figure 4.2 : Equilibrium data on PAC

Table 4.3 : Equilibrium data on PAC

C_0 = 16.46 ppm		C_0 = 11.3 ppm		C_0 = 4.62 ppm	
C_e(ppm)	q_e(mg/g)	C_e(ppm)	q_e(mg/g)	C_e(ppm)	q_e(mg/g)
10.37	1.61	6.69	1.44	2.19	0.74
11.17	1.83	7.01	1.56	2.39	0.82
11.72	2.03	7.44	1.81	2.42	1.04
12.24	2.33	7.81	2.04	2.35	1.34
13.74	2.41	8.68	2.45	3.07	1.54
14.40	2.91	9.68	2.91	3.41	2.08

MODEL COMPARISION & DISCUSSION

(TO BE UPDATED)

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