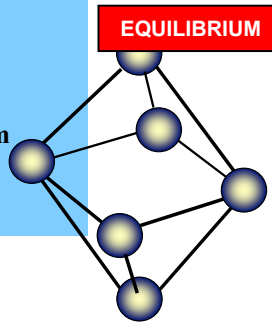


SECTION 6.1

- 6.1.1 Single-Sorbate Isotherms
- 6.1.2 Comparison of Sorption Performance
- 6.1.3 Equilibrium Constants
- 6.1.4 Experimental Sorption Isotherm
- 6.1.5 REFERENCES
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6

EQUILIBRIUM BIOSORPTION PERFORMANCE

SORPTION EQUILIBRIUM

6.1

The case of a sorption process considered here involves a solid phase (sorbent) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, e.g. metal ions). Due to the higher ‘affinity’ of the sorbent for the sorbate species the latter is attracted into the solid and bound there by different mechanisms. This process takes place until an equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in solution (at a residual, final or equilibrium concentration C_f). The degree of the sorbent ‘affinity’ for the sorbate determines its distribution between the solid and liquid phases.

The quality of the sorbent material is judged according to how much sorbate it can attract and retain in an ‘immobilized’ form. For this purpose it is customary to determine the metal uptake (q) by the biosorbent as the amount of sorbate bound by the unit of solid phase (by weight, volume, etc.).

The calculation of the metal uptake [mgMet /g (dry!) sorbent] is based on the material balance of the sorption system:

sorbate which ‘disappeared’ from the solution must be in the solid.

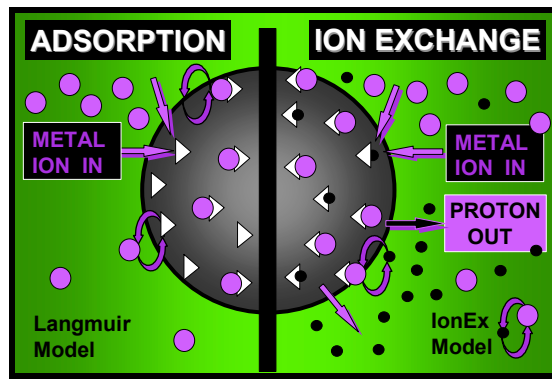


Figure 6.1-1

Adsorption is different from ion exchange

Correspondingly, the amount of metal bound by the sorbent which 'disappeared' from the solution can be calculated based on the mass balance for the sorbate in the system:

$V [L] (C_i) [mg/L]$ = all the sorbate in the system [mg]

$V [L] (C_f) [mg/L]$ = the sorbate left over in the solution [mg]

The **uptake** (sorbate in the solid phase) will be the difference:

$$q = V [L] (C_i - C_f) [mg/L] / S [g] \quad [\text{in weight units mg/g}]$$

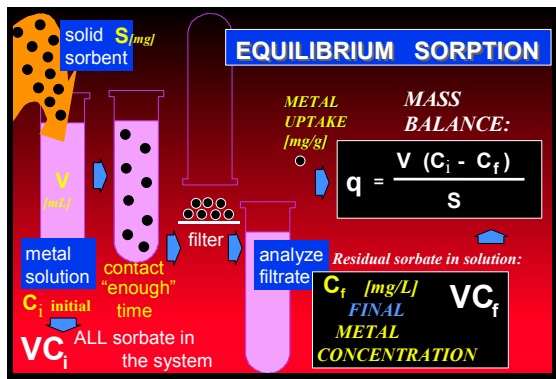


Figure 6.1-2

The sorbate uptake is obtained from its mass balance

where (metal sorbate example):

V is the volume of the metal-bearing solution contacted (batch) with the sorbent [L];

C_i and C_f are the initial and equilibrium (residual) concentrations of the metal in the solution, respectively. They have to be analytically determined [mg/L];

S is the amount of the added (bio)sorbent on the **dry** basis [g].

The sorption uptake q can be expressed in different units depending on the purpose of the exercise:

1) For practical and engineering process evaluation purposes which are eventually concerned with process mass balances it is customary to use *weight per (dry) weight* [e.g. **mg** of metal sorbed per **gram** of the (dry) sorbent material].

2) Ultimately, mainly because of the reactor volume considerations (e.g. a packed-bed column), the uptake may also be expressed on a *per volume* basis [e.g. **mg/L**]. However, the volume porosity (voids) may present a complication in quantitative comparison of biosorption performance.

3) Only when working on the stoichiometry of the process and when studying the functional groups and metal-binding mechanisms it may be useful to express q on a *molar* or *charge equivalent* basis - again, per unit weight or volume of the sorbent [e.g. **mmol/g** or **meq/g**].

All these units are relatively easily interconvertible. The only problem may arise with the sorbent weight-volume conversions. For scientific interpretations, the sorbent material dry weight basis is thus preferred.

The use of "wet biomass weight", unless the (wet-weight / dry-weight) conversion well specified should be discouraged. Different biomass types are likely to retain different moisture contents, intracellular as well as that trapped in the interstitial space between the cells or tissue particles (e.g. seaweed particles). Different types of biomass obviously compact in a different way.

SORPTION UPTAKE :

$$\text{mmol/g} = \frac{\text{Sorption Uptake [mg / g]}}{\text{Molecular (Atomic) Weight}}$$

$$\text{meq/g} = \frac{\text{Sorption Uptake [mmol / g]}}{\text{Ion Valence}}$$

When centrifuging the biomass, the g-force and time need to be specified and even then any comparison is difficult to make. All this makes the “wet biomass weight” citation very approximate at best and generally undesirable.

6.1-1 Single-Sorbate Isotherms

Since sorption processes tend to be exothermic and since the sorption performance may vary with temperature, constant temperature during the sorption process is a basic requirement. Sorption isotherms are plots between the sorption uptake (q) and the final equilibrium concentration of the residual sorbate remaining in the solution (C_f). This simple relationship can be expressed in slightly different variations.

Biosorption is not necessarily so strongly exothermic as other physical adsorption reactions. The temperature range for biosorption applications is considered relatively narrow, roughly between (10 - 70)°C, diminishing thus the temperature sensitivity issue to a large degree.

Simple Sorption Models

The (q) vs (C_f) sorption isotherm relationship can also be mathematically expressed. This was done already in the early 1900's in the classical work of Langmuir [9] and Freundlich [5] who studied activated carbon adsorption.

a The *Langmuir* isotherm relationship is of a hyperbolic form:

$$\text{Langmuir: } q = q_{\max} \frac{bC_f}{1 + bC_f}$$

The Langmuir relationship can be linearized by plotting either ($1/q$) vs ($1/C_f$)
or (C_f/q) vs C_f

where: q_{\max} is the maximum sorbate uptake under the given conditions; e.g. [mg/g];

b is a coefficient related to the affinity between the sorbent and sorbate (the relationship between b and the affinity constant K is developed later in this section).

The *Scatchard* linearization of Langmuir is:

$$(q/C_f) = b q_{\max} - b q$$

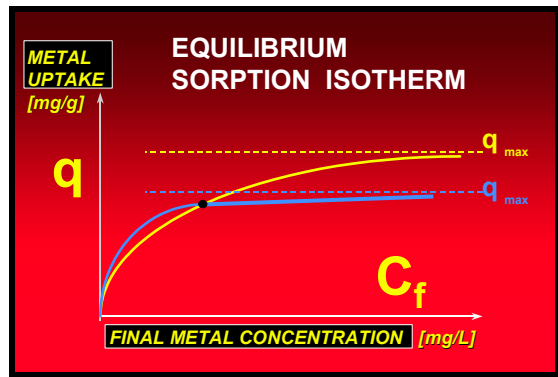


Figure 6.1-3
Typical single-sorbate isotherms.
Which sorbent here is “better”? Yellow or blue ?

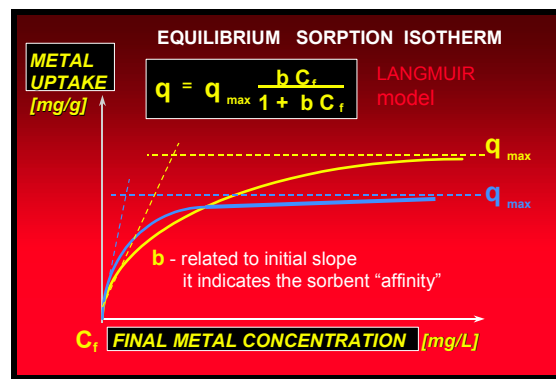


Figure 6.1-4
Langmuir model for the sorption isotherm

The **Langmuir isotherm** (1918) considers sorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. Langmuir constant $b = 1/K$ which is related to the energy of adsorption through the Arrhenius equation. The higher b and the smaller K , the higher is the affinity of the sorbent for the sorbate. q_{max} can also be interpreted as the total number of binding sites that are available for biosorption, and q as the number of binding sites that are in fact occupied by the sorbate at the concentration C_f .

Although the Langmuir model sheds no light on the mechanistic aspects of sorption, it provides information on uptake capabilities and is capable of reflecting the usual equilibrium sorption process behavior. Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and therefore sorption is restricted to a monolayer.

In the simplest case the following *assumptions* were made:

- fixed number of adsorption sites; at equilibrium, at any temperature and gas pressure a fraction of the surface sites θ is occupied by adsorbed molecules, and the fraction $1-\theta$ is free.
- all sorption sites are uniform (i.e. constant heat of adsorption)
- only one sorbate
- one sorbate molecule reacts with one active site
- no interaction between sorbed species

Assumption of a value for the surface area covered per molecule then could allow computation of the active specific surface area of the sorbent using Avogadro's number. However, the concept of "surface area" *cannot* be used in gel-like sorbents that most biosorbents may be.

As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems, or for varied conditions within any given system.

b

The **Freundlich** isotherm relationship is exponential:

Freundlich:

$$q = k C_f^{(1/n)}$$

where: k and n are Freundlich constants.

The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges (C_f !). However, it is easier to handle mathematically in more complex calculations (e.g. in modeling the dynamic column behavior) where it may appear quite frequently. Freundlich model can be easily linearized by plotting it in a (log-log) format.

The Langmuir model has eventually been empirically most often used since it contains the two useful and easily imaginable parameters (q_{max} and b) which are more easily understandable since they reflect the two important characteristics of the sorption system [6,7,12-14].

Note the assumptions taken for the development of these original relationships which originated from the work done with activated carbon as a solid-phase sorbent for molecular species. Monomolecular layer considered for deposition of sorbates implies the surface-based adsorption which is not the case for biosorption.



Other sorption isotherm relationships :

Other sorption isotherm relationships listed in *Table 6-1* are commonly appearing in the biosorption literature. It is necessary to realize that these relationships basically do not reflect the physico-chemical underlying principles of the sorption process which, in most cases, may not even be well understood. For all practical purposes they are just mathematical models of the phenomenon capable of describing the (q) vs (C_f) relationship as experimentally observed. In this capacity, neither can any of these models offer any important clues as to the sorption mechanism nor could they be sensitive to external process variables (such as e.g. pH, ionic strength, etc.).

While the Langmuir adsorption model is valid for a single-layer adsorption, the **BET** model represents sorption isotherms reflecting apparent multi-layer adsorption (*Figure 6.1-5*). Both equations are limited by the assumption of uniform energies of adsorption on the surface. The **BET** isotherm, the more generally applicable of the two, reduces to the Langmuir model when the limit of adsorption is a mono-layer. Both models may be deduced from either kinetic considerations or the thermodynamics of adsorption [9,2,1]. The latter derivations are somewhat more sophisticated, though less intuitive, than the kinetic treatments since fewer assumptions are involved (e.g. the balancing of forward and reverse rate processes according to some assumed mechanism).

The **BET** model assumes that a number of layers of adsorbate molecules form at the surface and that the Langmuir equations applies to each layer. A further assumption of the **BET** model is that a given layer need not complete formation prior to initiation of subsequent layers; the equilibrium condition will therefore involve several types of surfaces in the sense of number of layers of molecules on each surface site. For adsorption from solution with the additional assumption that layers beyond the first have equal energies of adsorption, the **BET** equation takes the simplified form as in *Table 6-1*.

Table 6-1

Some sorption isotherm relationships

Brunauer-Emmett-Teller (BET) [1938]:

$$q = \frac{BQC_f}{(C_s - C_f)[1 + (B-1)(C_f/C_s)]}$$

C_s is the saturation constant of the solute;

B is a constant relating to the energy of interaction with the surface;

Q is the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface;

Dubinin-Radushkevich (DR) [1947]:

$$\ln q = \ln q_m - B E^2$$

B is a constant related to the sorption energy

E is Polanyi potential

$$E = RT \ln(1 + 1/C_f)$$

Radke-Prausnitz [1972]:

$$\frac{1}{q} = \frac{1}{aC_f} + \frac{1}{bC_f^{\beta}}$$

Redlich-Peterson [Jossens et al., 1978]:

$$q = \frac{aC_f}{1 + bC_f^n}$$

Combination:

$$q = \frac{bq_m C_f^{(1/n)}}{1 + bC_f^{(1/n)}}$$

(Langmuir-Freundlich) [Sips, 1948]

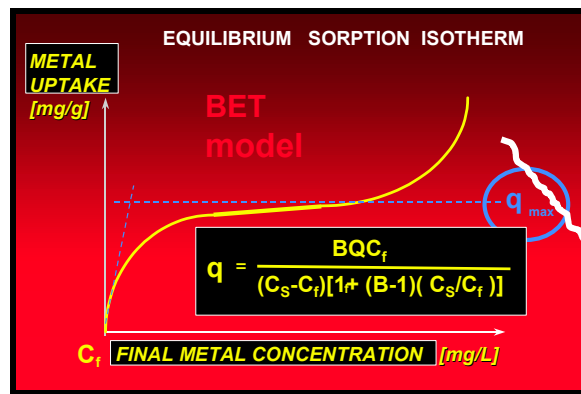


Figure 6.1-5

Brunauer-Emmett-Teller sorption isotherm model

The use of simple isotherm models is not much more than “curve fitting”

The “surface area” concept is NOT applicable for gel-like biosorbents

Needless to say, for different sorption systems and mechanisms outside of the scope of these assumptions the application and fit of the model equations is a matter of chance. They become just mathematical relationships which happen to be capable of following the experimental data. The problem with biosorption is that usually not very much specific information is available on the sorption mechanism(s) involved.

The usual concept of the solid-phase sorbent with physical pores and ‘surface area’ etc. may not be so close to the real structure, appearance and behavior of biosorbent materials. Particularly in conjunction with metallic ions as sorbate species, biosorbents may appear as gels, very transparent for the minute ions and protons. Actually, when it comes to an ion exchange process, which apparently plays a very important role in biosorption, at least one ion from within the molecular structure of the sorbent is exchanged for another one coming from outside. This leads to ever-changing conditions in the sorption system due to the stream of ‘exchanged’ ions also leaving the sorbent into the liquid environment. That is until the sorption equilibrium is established.

6.1-2 Comparison of Sorption Performance

Performance of sorbing materials often needs to be compared. The simplest case is when there is only one sorbate species in the system. The comparison of single-sorbate sorption performance is best based on a complete single-sorbate sorption isotherm curve.

In order for the comparison of two or more sorbents to be ‘fair’ it must always be done under the same conditions. These may be restricted by the environmental factors under which sorption may have to take place (pH, temperature, ionic strength, etc.). They may not necessarily be widely adjustable. It is important to compare sorption performance e.g. under the same pH since isotherms could vary with pH.

By ‘performance’ of the sorbent is usually meant its uptake (q). The sorbents can be compared by their respective q_{max} values which are calculated e.g. from fitting the Langmuir isotherm model to the actual experimental data (if it fits). This approach is feasible if there exists the characteristic q_{max} sorption performance plateau (the maximum sorbent saturation). A ‘good’ sorbent that one always looks for would feature a high sorption uptake capacity q_{max} .

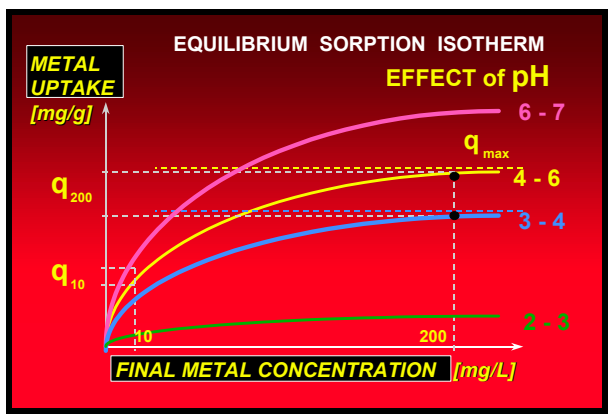


Figure 6.1-6

As an “external factor”, pH has to become a “parameter” for the conventional sorption isotherm plot

However, also desirable is a high affinity between the sorbent and sorbate reflected in good uptake values at low concentrations (C_f). This is characterized by a steep rise of the isotherm curve close to its origin. Performance in this region is reflected in the Langmuir coefficient b .

Which sorbent is “better”??

There is no direct answer to that until this question is qualified: under what conditions? The sorption isotherm diagram depicts the experimentally determined performance of sorbents “A” and “B”. Given the same experimental (environmental) conditions, as required for comparison, the independent variable in the sorption system is the C_f . Both curves intersect - obviously, at that point the performance of both sorbents is the same (in terms of q).

However, sorbent “A” would exhibit higher q 's for the same C_f 's in the range of lower C_f values (left from the curve intersect): sorbent “A” is ‘better’ than sorbent “B” in that range. This is important, for instance, when the sorbent is supposed to work at low residual sorbate concentrations as may be the case e.g. the when regulatory agency limits the maximum concentration of a pollutant (sorbate, toxic metal, etc.) allowable in the discharged effluent.

When the limitation of the maximum residual sorbate concentration is not of a concern and the purpose is to saturate the sorbent as much as possible (no matter how much of the sorbate may still be ‘left over’ in the solution), sorbent “B” is ‘better’ because it accumulates more sorbate at higher residual sorbate concentrations (higher C_f range). This may be of importance when the eventual recovery of the sorbate from the biosorbent is desired. A biosorbent “better” at low concentrations may be “inferior” at higher ones, and vice versa.

This is the reason why one comparison at “low” C_f (e.g. 10 mg/L) and also another one at “high” C_f (e.g. 200 mg/L) was made in some biosorption screening work [6,7]. Another aspect of a ‘fair’ comparison is to compare, for instance, ‘the best’ with ‘the best’: the optimal pH value for the best performance of one sorbent may not be the same one as for the best performance of another sorbent. If the operating parameter is as simple as pH, which can perhaps easily be adjusted in the process, the feasibility of

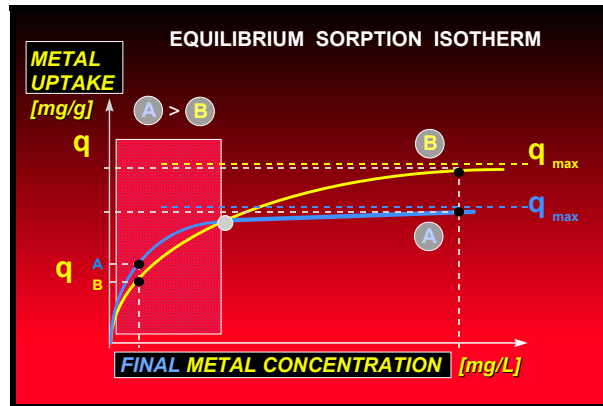


Figure 6.1-7

At low C_f 's “A” is better than “B”

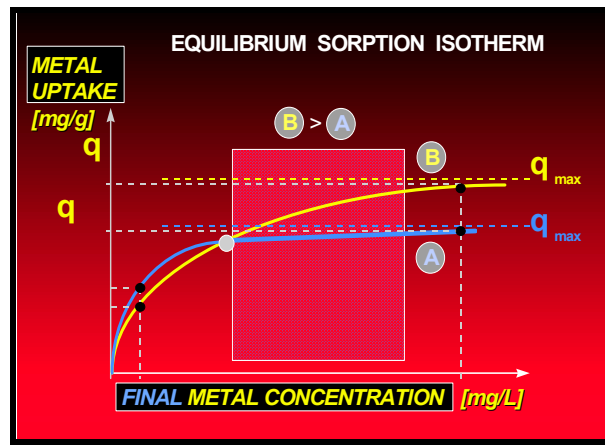


Figure 6.1-8

At high C_f 's “B” is better than “A”

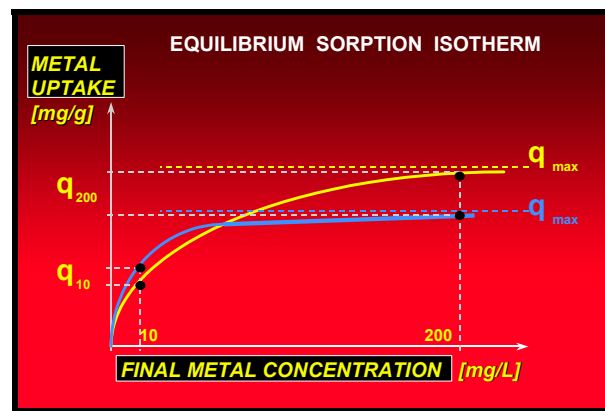


Figure 6.1-9

q_{max} indicates the ‘ultimate’ performance

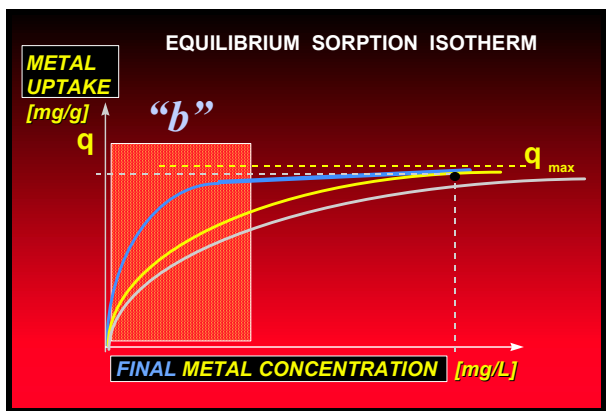


Figure 6.1-10
Langmuirian “*b*” relates to affinity between the sorbent and the sorbate (often metal ion considered here)

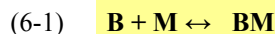
this adjustment should be considered. In all comparisons it is extremely important to make certain that all the external sorption system parameters remain indeed comparable.

The above consideration leads to another important characteristic of the sorption isotherm curve and this is its initial slope. A curve with a steep initial slope indicates a sorbent which has a capacity for the sorbate in the low residual (final, C_f) concentration range. That means that the sorbent has a high affinity for the sorbed species. This affinity is indicated by the coefficient b in the Langmuir equation. The lower the value of b the higher the affinity.

In conclusion, for ‘good’ sorbents in general, one is looking for a high q_{max} and a steep initial sorption isotherm slope as indicated by low values of Langmuir parameter b [9,13]. It is advisable to base the comparison of sorption performance on whole sorption isotherm plots which are in turn derived experimentally.

6.1-3 Equilibrium Constants

Langmuir model assumes that all the binding sites on the sorbent are free sites, ready to accept the sorbate from solution. Therefore, an adsorption reaction is taking place that can be described as :



\mathbf{B} represents the free binding sites, \mathbf{M} is the sorbate in the solution (metal), and \mathbf{BM} denotes the adsorbed sorbate \mathbf{M} bound on \mathbf{B} .

The adsorption equilibrium constant is defined from the mass conservation law:

$$K = \frac{[\mathbf{BM}]}{[\mathbf{B}][\mathbf{M}]} \quad (6-2)$$

it represents the affinity of sorbate for the binding site.

[] denotes the concentration.

According to the mass conservation of binding sites, the total binding capacity B^T is:

$$[\mathbf{B}^T] = [\mathbf{B}] + [\mathbf{BM}] \quad (6-3)$$

By combining equations (2) and (3) the following is obtained:

$$[\mathbf{BM}] = \frac{[\mathbf{B}^T] K [\mathbf{M}]}{1 + K [\mathbf{M}]} \quad (6-4)$$

where $[\mathbf{BM}]$ also represents the sorbate uptake q , then:

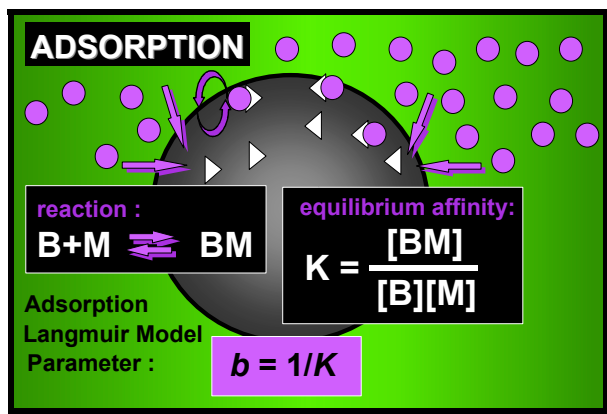


Figure 6.1-11
Relationship between Langmuirian b and the equilibrium affinity constant K

$$q = \frac{[B^T] K [C]}{1 + K [C]} \quad (6-5)$$

Equation (6-5) is one of the conventional forms of Langmuir equation. K represents the affinity of sorbate M to site B .

Another form of Langmuir equation could be derived from the above equation (6-5) by dividing the whole fraction in equation (6-5) with K and we obtain:

$$q = \frac{[B^T] [C]}{(1/K) + [C]} \quad (6-6)$$

Making $b = 1/K$ (6-7)

then $K = 1/b$ (6-8)

Replacing K in equation (6-6) with equation (6-8) we obtain:

$$q = \frac{[B^T] [C]}{b + [C]} \quad (6-9)$$

Equation (6-9) is another form of Langmuir equation where b is a constant.

Its physical meaning could be illustrated by combining equations (6-2) and (6-7):

$$b = 1/K = \frac{[B][C]}{[BC]} \quad (6-10)$$

Therefore, b represents the reverse of the affinity.

Langmuir or Freundlich type binding assumes free sites, not an (ion) exchange. In the mathematical modeling of the phenomenon the Langmuir equation and the ion exchange constant for the binding of a metal ion M (for simplicity here a monovalent ion) replacing a proton H on a complexing site B are related as seen in the relationships in the left column:

The differences between the two models may be especially pronounced at low metal ion concentrations [3].

The ion exchange approach is probably somewhat closer to the reality than the simple Langmuir model, but it is not completely satisfying either. The

assumption of the constant number of free sites may be reasonable for a constant pH system. It may not hold for systems with changing pH values. The cation exchange capacity tends to increase with increasing pH above the isoelectric point. Modeling the competitive binding of metals and protons using only a metal-proton ion exchange constant is simplistic. It should include at least one reaction where a cation reacts with a free site.

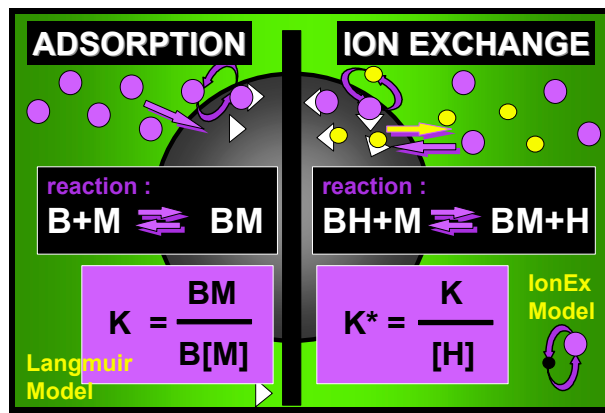


Figure 6.1-12 Relationship of Langmuirian and Ion-Exchange equilibrium constants (affinities)



$${}^{BM}K = \frac{BM[H]}{BH[M]} \quad \text{and} \quad [B]_t = [BH] + [BM]$$

therefore: ${}^{BM}K^* = {}^{BM}K / [H]$ (6-12)

6.1-4 Experimental Sorption Isotherm

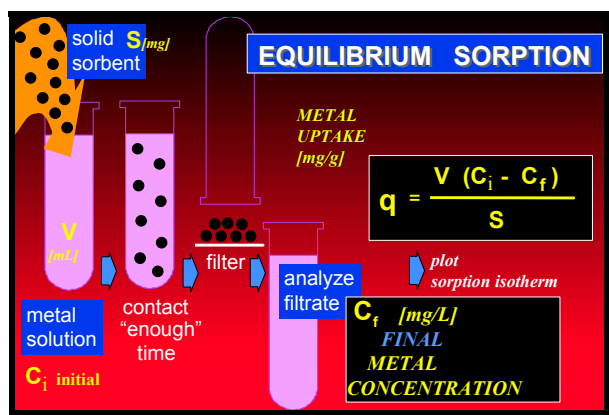


Figure 6.1-13

Experimental procedure for deriving the sorption isotherm

Preliminary dynamics of the sorption process (uptake-time relationship) must be approximately

It is convenient to vary C_i

The sorbent weight S can fluctuate but must be precisely known for each sample

It is relatively simple and easy to obtain laboratory equilibrium sorption data for a single sorbate. A small amount of the sorbent tested is brought into contact with solution containing the given sorbate. However, the ‘environmental’ parameters in the sorption system (particularly pH) have to be carefully controlled at the given value over the entire period of contact until the sorption equilibrium is reached. It may take a few hours or much longer depending on the size of sorption particles and the time it takes until they attain sorption equilibrium. A simple preliminary sorption kinetics test will establish the exposure time

necessary for the given sorbent particles to reach the equilibrium state characterized by the unchanging sorbate concentration in the solution. That is determined by time-based analyses.

Safely ‘enough’ time will be allowed for the sorption system to reach equilibrium. The following procedure provides an example for obtaining the experimental sorption equilibrium data points for the isotherm as seen also in the procedure schematic flowchart:

- 1) Prepare the sorbate in solution at the highest concentration of interest.
- 2) Make dilutions to cover the entire concentration range (from 0 -blank, to the max.).
- 3) Adjust the ‘environmental parameters’ (e.g. pH, ionic strength, etc.).
- 4) Determine the sorbate initial concentrations (C_i in all the liquid samples).
- 5) Distribute the samples into appropriate-volume containers (record $V = 30\text{-}150$ mL of liquid) such as flasks or test tubes (in duplicate, triplicate or as required).
- 6) Weigh accurately each (approximate) amount of the (bio)sorbent solids to be used in each contact test and record each amount (S mg). It may help to be able to roughly estimate the anticipated sorption uptake so that there is a well detectable sorbate final concentration left in the solution at equilibrium in each sample. If there is too much solids added there may be virtually no sorbate left in the solution for a reliable analysis.
- 7) Add the sorbent solids into each sample solution and provide for rather gentle mixing over the contact period (‘enough’ time!).
- 8) Make sure the ‘environmental’ parameters (pH!) are controlled at a constant value during the contact period (use appropriate acid or base for the purpose; do not ‘dilute’ the sorption system by adding excessive volume).

- 9) At the end of the contact period, separate the solids from the liquid (decantation, filtration, centrifugation, etc.)
- 10) Analyze the liquid portion for the residual, final, equilibrium sorbate concentration (C_f).
- 11) Calculate the sorbate uptake:

$$q = V[L] (C_i - C_f)[mg/L] / S [g]$$

Note that q could also be determined directly by analyzing the separated solids and thus closing the material balance on the sorbate in the system. However, this usually presents analytical difficulties (digestion-liquefaction of solids and/or very sophisticated analytical methods may be required).

A variation of this approach is the “tea-bag experiment”, described below, whereby $C_f = C_i$ and only the solids are analyzed. In either case, the C_f in the liquid must be known for the sorption isotherm plotting:

- 12) Plot the sorption isotherm q vs (C_f).

Note that for all practical purposes the choice of experimental variables narrows usually down to two: concentration C_i and the amount of sorbent solids S contacted. One or the other or both can be varied. In the above procedure it was the concentration of sorbate dilutions C_i . The key point is to obtain measurable and different values of C_f at the end of the contact experiment.

From the equilibrium principles it is easily seen that the initial concentration of sorbate (C_i) is of little relevance in these kinds of sorption tests. It can assist in identifying the final concentration range which, of course, depends on the amount of sorbent solids (S) in the system. Also note that one has no control over the value of C_f , it sort of “happens” during the experiment.

Metal depletion in the solution has to be avoided since it renders such samples useless (unreliable or impossible C_f determination)

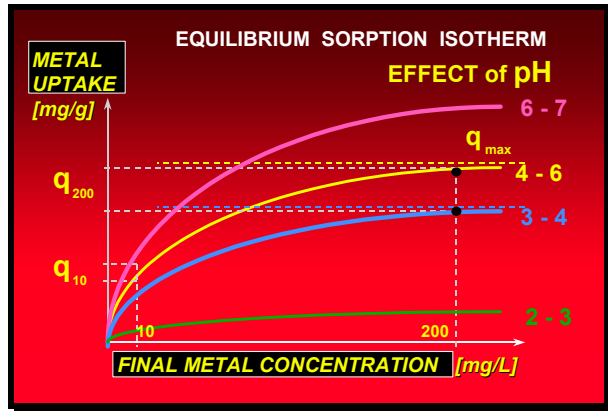


Figure 6.1-6 (repeated)
 pH is an external factor and it has to be controlled for standard isotherm experiments – the final, equilibrium pH is the one that matters !

There is no control over C_f , it ‘happens’ in the experiment

Experimental variables could be either C_i or S

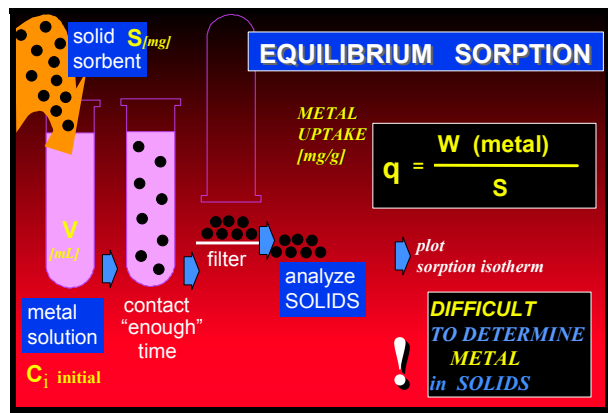


Figure 6.1-14
 For checking, the loaded sorbent solids can be analyzed too but it is usually more complicated. If they could be completely eluted, the desorption liquid could then be analyzed to make sure that the sorbate mass balance closes

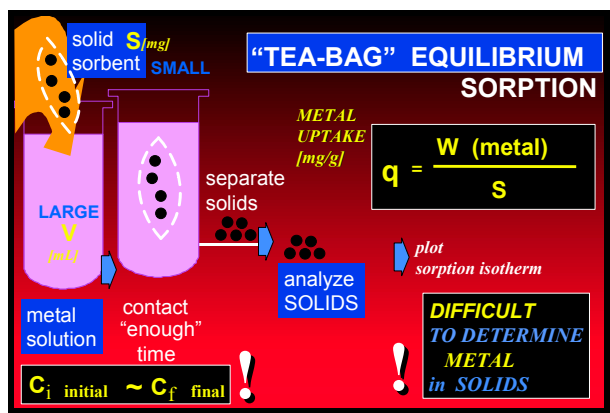


Figure 6.1-15

In the “tea-bag” experiment $C_i = C_f$

The “tea-bag” experiment

In this approach there is a possibility of choosing and maintaining the C_f . For this purpose the liquid volume is large and the amount of sorbent solids added to it so relatively small that there is practically no change in the sorbate concentration and thus $C_i = C_f$. When the solids are isolated from this special sorption system, they are analyzed for the sorbate content. This analysis of solids is usually much more demanding than the analysis of liquid. Consequently, this kind of approach may be used in special cases only.

Sorbent

Comparison Based on “% Removal”

Another criterion for comparing sorbent materials found in the literature is based on % removal of the sorbate from the solution. This is a rather crude and somewhat inaccurate approach as will be demonstrated in this section. Using a specific example may perhaps best serve as a demonstration of the principle:

It is desirable to compare the sorption performance of (bio)sorbents A, B, C, and D. This could be done in a few equilibrium tests carried out by the same procedure using the same V (100mL), C_i (100mg/L), and S (30mg) for each of the contact samples

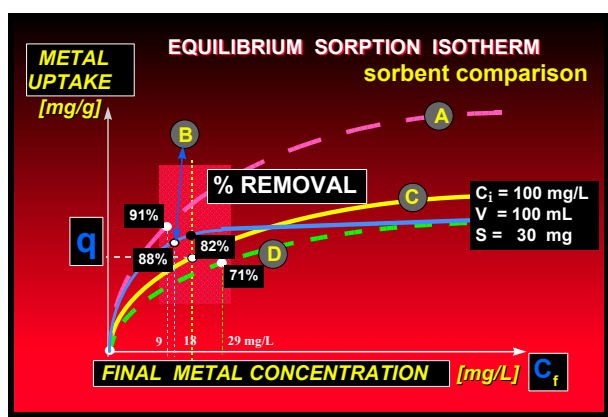


Figure 6.1-16

Example of “% Removal” screening

examined. The results recorded were as follows:

Biosorbent A:	experimental $C_f = 9 \text{ mg/L}$;	calculated sorbate removal = 91%.
Biosorbent B:	experimental $C_f = 12 \text{ mg/L}$;	calculated sorbate removal = 88%.
Biosorbent C:	experimental $C_f = 18 \text{ mg/L}$;	calculated sorbate removal = 82%.
Biosorbent D:	experimental $C_f = 29 \text{ mg/L}$;	calculated sorbate removal = 71%.

It is obvious that there exist four separate sorption isotherms each characterizing one of the sorbent materials. However, available is only one point for each curve.

For each of the C_f values obtained there is one (and different!) corresponding q which can serve as a basis for sorption performance comparison. The inaccuracy inherent in this approach is in the fact that the performance comparison is NOT done on the same basis since the C_f 's are different. In the first case seen in the Figure, the conclusion can be drawn that the sorbent performance follows this pattern: $A > B > C > D$.

That may be quite correct if the individual isotherms follow a similar (steadily rising) pattern. Of course, the correct comparison can only be done along the same line of the same C_f for all the materials. Obviously, this is not possible when the whole sorption isotherm plots are not available. The danger in using the simplistic methodology is that the full individual isotherm curves might follow quite different patterns outside of the range of the C_f 's experimentally obtained. This is seen in the next case Figure where the conclusion on the sorbent performance would suggest the same pattern: $A > B > C > D$.

However, in the higher C_f range, the isotherm for sorbent B is flat and another test conducted in the higher final concentration range would undoubtedly indicate a different sorbent performance pattern: $A > C > B > D$!

The original simple test would never reveal this fact. Indeed, in some cases, the simplistic “% Removal” method could lead to outright misleading conclusions on the relative sorption performance.

It can only serve the purpose of crude orientation, perhaps adequate only for quick and very approximate screening of (bio)sorbent materials. The “% Removal” values so often quoted in the literature also do not offer any information on the concentration range where the removal took place (e.g. range in the 1,000's, 100's or 10's of mg/L).

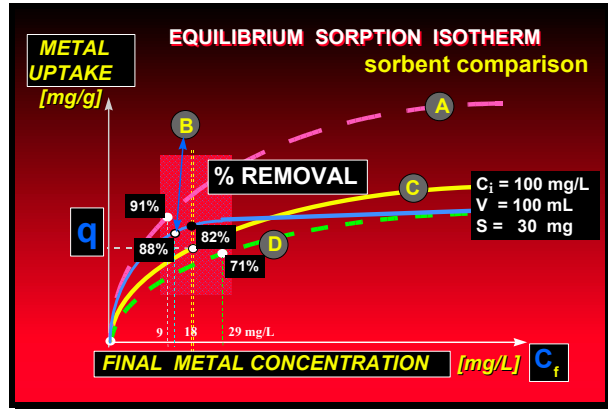


Figure 6.1-17

DANGER: The full isotherms do not follow a pattern

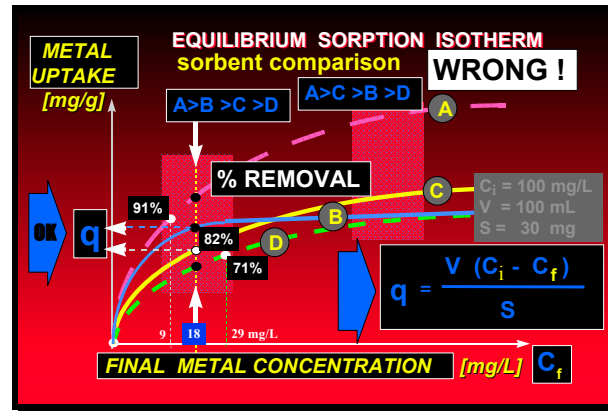


Figure 6.1-18

Wrong conclusion about the sorbents !

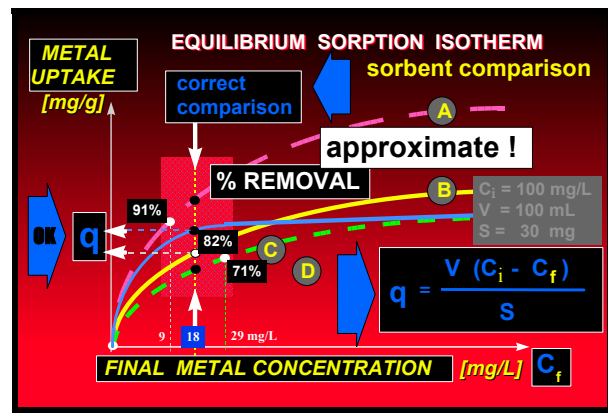


Figure 6.1-18

“% Removal” is only for crude judgement

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