Chapter 2

Adsorption in Liquid Phase

A process of adsorption involves separation of a substance from a fluid phase accompanied by the accumulation on the solid surface. The solid surface is called an adsorbent, and the substance concentrated or adsorbed on the surface is an adsorbate. Adsorption phenomenon is normally exothermic. The equilibrium capacity of adsorption for a given system is, therefore, found to increase with decreasing temperature. While, the rate of adsorption, which is generally controlled by diffusion mass transfer, normally increases with an increase in temperature(8).

2.1 Properties of Adsorbents

With utilization of adsorbent surface, an important characteristic of an adsorbent is specific surface area. For adsorption in liquid phase, pore size distribution is another important characteristic of an adsorbent since adsorption occurs on wetted surface only. Activated carbons, which are a type of porous adsorbents, are used widely for adsorption in liquid, because of high specific surface area, broad pore size distribution which is polymodal, and the capability for efficiently adsorption of a wide range of adsorbates.

The generic term "activated carbon" encompasses a broad range of amorphous carbon-based materials providing high degree of porosity and extensive surface areas. The large specific surface areas are associated with small pore size within the carbon granules by selective burning and oxidation of the raw material during an activation process. Commercial carbons typically provide total specific surface areas in the range from 450 to 1500 sq.m/g as assured by the nitrogen adsorption method. However, the actual surface area available for adsorption depends on the specific nature of the adsorbate, and can be considerably less than the total surface area. The pore volumes of commercial carbons range from 0.5 to 1.5 cc/g. For liquid adsorption, the average pore size is larger than 10 Å(9). The pore size distribution of a typical liquid phase activated carbon is trimodal (Figure 2.1)(9). These correspond to tiny micropores with radii between 5 and 50 Å., intermediate or transitionalpores with radii between 50 and 500 Å. and large micropores with radii 1000 Å. and larger pores, which often peak at 10000 Å. The large pores and the transitional pores permit the ready access of liquid with small capillary forces. In addition the effective capacity depends on molecular size of adsorbate.

Commercial available carbons are usually described by their characteristics. These characteristics cannot be used to predict how the carbon will perform on a given process; that can only be done through laboratory and pilot plant studies. The carbon characteristics which is usually reported by carbon suppliers are summarized in Table 2.1.

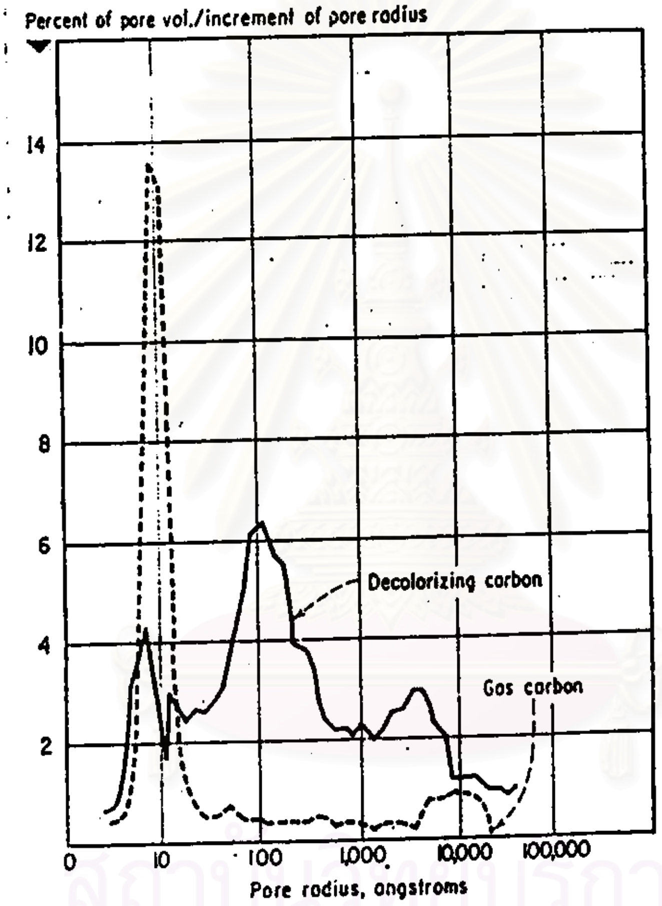

Figure 2.1 Comparison of pore volume distribution between liquid phase and gas phase activated carbon

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2.2 Adsorption Equilibrium

Adsorption of a substance (adsorbate) from one phase to the surface of a selected solid (adsorbent) in a specific system leads to a thermodynamically defined distribution of that substance between the phases, i.e. fluid and adsorbed phase, when the system reaches equilibrium. The common manner in which to depict this distribution is to express the amount of the substance adsorbed per unit mass of adsorbent, q_e, as a function of the residual equilibrium concentration, C_e, of the substance remaining in the fluid phase. An expression of this type, termed an adsorption isotherm, defines the functional equilibrium distribution of the amount of adsorbate in the solution phase and in the adsorbed phase at a given temperature. Commonly the amount of adsorbed material per unit mass of adsorbent increases with increasing concentration. Equilibrium isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application and for preliminary determination of adsorbent dosage requirements. Several equilibrium models have been developed to describe adsorption isotherm relationships. Any particular one may fit experimental data accurately under one set of conditions, but may fail entirely under another.

Langmuir Model

This model, originally developed for adsorption of gases onto solids, is predicated on the assumption that adsorption energy is constant and independent of surface coverage; that adsorption occurs on localized sites with no interaction between adsorbate molecules, and that maximum adsorption occurs when the surface is covered entirely by a monolayer of adsorbate. For solid-liquid systems the equation is usually written(8):

$$q_e = Q^o bC_e/(1+bC_e) \qquad \text{..(2.1)}$$

Where q_e is the amount of solute adsorbed per unit mass of adsorbent, Q^0 is the solid phase concentration corresponding to complete coverage of available sites, or the limiting adsorption capacity, C_e is the residual liquid phase concentration at equilibrium.

Freundlich Model

Adsorption equilibrium data are often better described by the relationship(8)

$$q_e = K_F C_e^{1/n} \quad \text{.........(2.2)}$$

Where K_F and 1/n are characteristic constants.

Linear Model

The simplest isotherm model is a linear isotherm, expressed as(8)

$$q_e = K_p C_e \quad \text{.........(2.3)}$$

Where K_p is adsorption equilibrium constant. This model has an advantage of describing a given set of adsorption data in terms of a single parameter, K_p, and of simplicity for modeling purposes. However the linear partitioning model is not solely a mathematical convenience without basis in theory. It may be noted that all of the models, discussed above reduce either directly or indirectly to linear relationships under special conditions. For example, the denominator of the Langmuir isotherm in equation 2.1 approaches a value of unity dilute solutions, and $Q^o b$ then becomes the adsorption equilibrium constant for a linear isotherm. This corresponds to such low values of surface concentration ($q_e << Q^o$) that additional adsorption changes the available surface area insignificantly and the adsorption is dependent only on the solution phase concentration. Similarly, the Freundlich isotherm is linear when n = 1.0, a condition not infrequently found for adsorption of organic pollutants on soils at low solution concentrations(8). This indicates that all of these adsorption isotherm models tend to predict linear sorption at low solution concentrations.

2.3 Types of Adsorption Systems

Carbon adsorption processes can be operated on either a batch or a continuous - flow system. In batch processes the carbon and wastewater are mixed together in a suitable vessel until the concentration of solute has been reduced to the desired level. Most continuous - flow adsorption systems are operated in fixed - bed adsorption columns. These systems are capable of treating large volume of wastewater and are widely used for both municipal and industrial applications. Fixed bed adsorbers may be operated as a single column or as multiple columns in series. Continuous - flow operations have advantages over batch type operation because the rates of adsorption is almost constant as flowing through the column.

2.4 Adsorption Isotherm by Batch Test

An adsorption isotherm is the initial experimental test step for determining feasibility of adsorption treatment. A batch adsorption isotherm is a batch equilibrium test which provides data relating adsorbed adsorbate per unit mass of adsorbent to the amount of adsorbate remaining in solution. While any particle size of same carbon should reach the same equilibrium capacity, the rate at which the carbon reaches equilibrium is dependent on particle sizes. Small particles simply reach equilibrium faster than the large ones. Adequate contact time between the carbon and the fluid is essential to allow the carbon to approach the adsorption equilibrium. Enough time must be allowed for the low carbon dosage to yield valid data points. Measuring the concentration change over time in this system will show the effect of contact time. The data presented in Figure 2.2(8) show that for the system tested, 45-60 minutes will achieve a resonable approach to equilibrium.

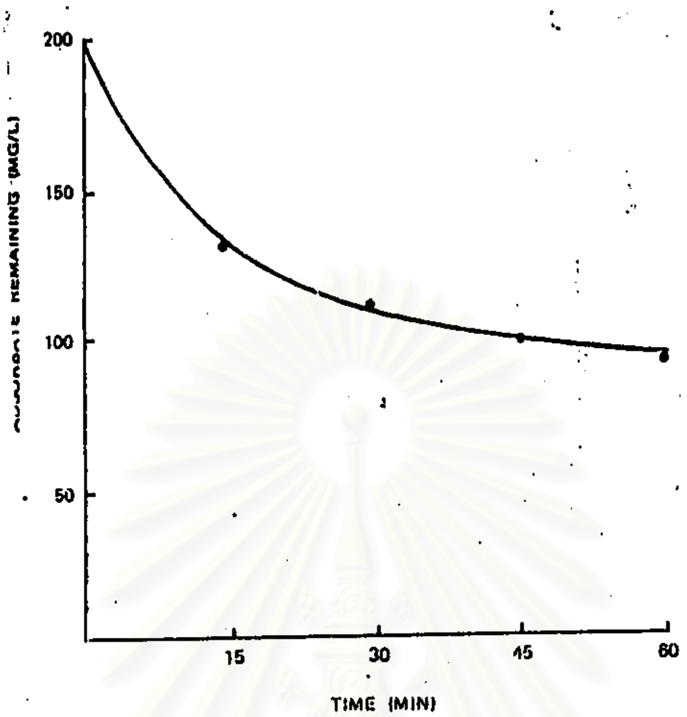

Figure 2.2 Plot of time versus residual adsorbate concentration for determination of isotherm contact time

2.4.1 Interpretation of Adsorption Isotherm

The data generated from an adsorption isotherm depends on the measurement of residual adsorbate remaining in the solution. Typical data which might be obtained from an adsorption test for removal of phenol from water by activated carbon is presented in Figure 2.3. The values of the carbon dosage designated 'm' are recorded and the values 'c' are measured specifically in this case for residual phenol concentration. Values of 'x' and 'x/m' are calculated from the laboratory data. The isotherm data is plotted on log-scale paper as 'x/m' on the ordinate versus 'c' on the abscissa.

For a single component system, the plot of concentration versus adsorption capacity should produce a straight line plot. In some instances, a fluid may contain a few components which have similar adsorption potential and the adsorption plot for such a fluid would be linear and would resemble a single component system. The phenol isotherm plot in Figure 2.3 is an example of these type systems.

Useful information can be obtained by inspecting the slope of an isotherm plot. An example of an isotherm having a flat or shallow slope is shown by line A in Figure 2.4(8). In this case, the adsorbate removal per mass of carbon is nearly equal at all equilibrium concentrations along the isotherm plot. This adsorbate shows a high affinity for the carbon independent of equilibrium concentration. From a practical standpoint , this type of systems could be treated either in a batch or follow-through system. Steep isotherms such as that of line B of Figure 2.4 indicate that the adsorption capacity is highly dependent on the equilibrium concentration. A batch treatment system is not usually suitable in this case.

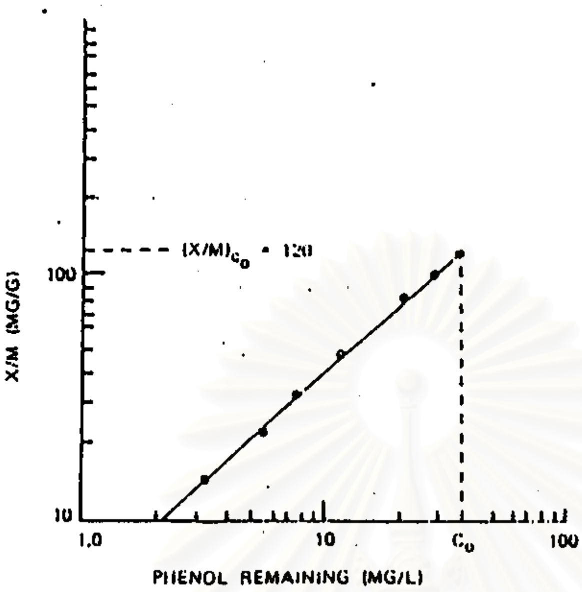

Figure 2.3 Adsorption isotherm of phenol on activated carbon

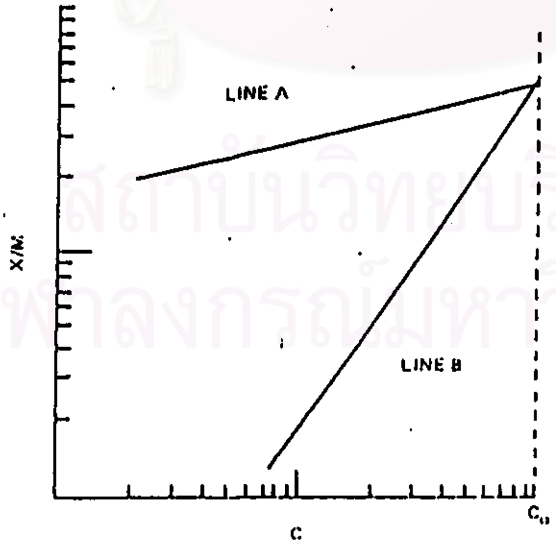

Figure 2.4 Adsorption isotherms with different types of carbons

The adsorption isotherm is excellent for comparison of candidate adsorbents in a particular fluid system. Selection of the superior adsorbent is simple where parallel lines are produced; the upper line describes better capacity and therefore the corresponding adsorbent can be selected. However, the selection is more complicated when isotherm lines are intersecting lines. An example of such a system is shown in Figure 2.5(8). By inspection it is obvious that adsorbent A has a higher x/m value at the residual concentrations, approaching to C_0. However the steepness of the isotherm line for adsorbent A indicates high sensitivity to the concentration. Adsorbent B on the other hand, has a smaller x/m value than that of the adsorbent A at high residual concentration, but has less steep slope and higher x/m than that of the adsorbent A at low concentration, such as C_e, adsorbent B may be an economical choice.

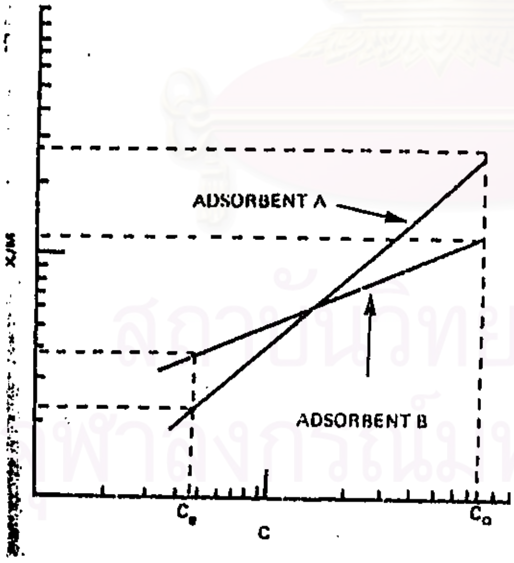

Figure 2.5 Adsorption isotherm of two different adsorbents.

2.4.2 Predicting Performance

Using adsorption isotherm properly can provide preliminary information on the feasibility of treatment of the fluid tested.

High adsorbent dosages can be used in the isotherm test to indicate whether residual concentrations can be reduced to the desired level. Figures 2.6(8)A and 2.6(8)B illustrate systems in which a residual concentration below 20 mg/l is not attainable because of a nonadsorable component, or steepness of the isotherm. For both the adsorbates described in isotherm plots 2.6(8)C and 2.6(8)D, the effluent of 20 mg/l is attainable.

While the adsorption isotherm is a relationship between carbon capacity and residual concentration on an equilibrium batch basis, the data obtained can be used to roughly predict the carbon dosage or usage rate to be expected on a fixed column type system. The fixed bed adsorber can be considered to be an infinite number of series batch adsorption stages, each of which comes to equilibrium with a different concentration. Across the bed therefore can have concentrations ranging from C_0 to zero and a corresponding range of x/m values.

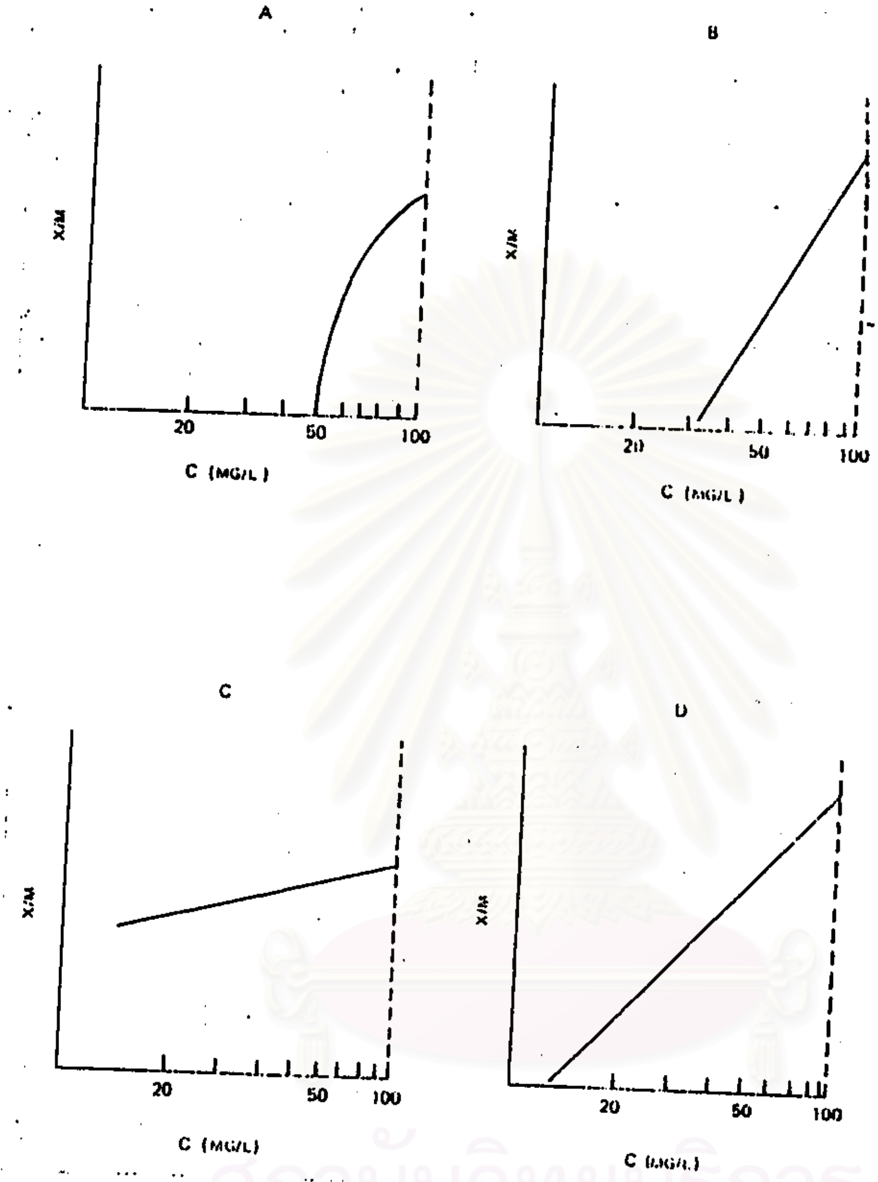

Figure 2.6 Adsorption isotherms of typical systems.

2.5 Fixed Bed Continuous Column Adsorption

The fixed bed is the most widely used arrangement for conducting adsorption operations. In the continuous percolation column, the uppermost portions of the bed are constantly being contacted by fresh feed solution, whereas the lower portions of the bed are contacted by solution containing solute not adsorbed by the upper portion. Thus, the bed becomes fully load (and in equilibrium with the feed) at the top of the column firstly and the equilibrium region expands towards the bottom, as shown in Figure 2.7(9). The height of the carbon bed is h; the height of the adsorption zone is h_a; and the column diameter is d_c. Carbon at the top of adsorption zone which is always contacted by fresh, full-strength feed liquor becomes exhausted (to degree permitted by the operating conditions). Accordingly, after the lower boundary of the adsorption zone has progressed through the full depth of the bed and reach its bottom, the breakthrough has begun. As the adsorption zone itself moves out of the column, the breakthrough curve rise sharply. After the zone has moved all the way out, the entire bed of carbon is spent, the impurity concentration (c_f) of the effluent liquor is now the same as that of the feed (c_0).

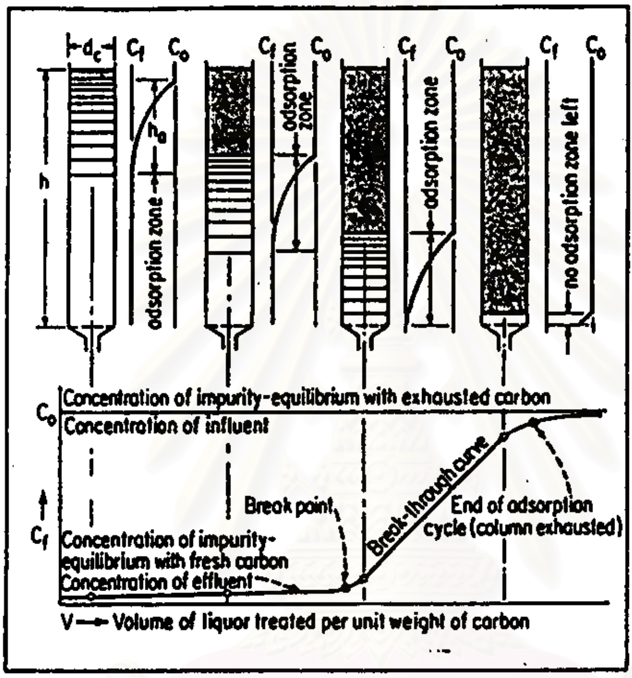

Figure 2.7 Adsorption zone depth and exhaustion-curve shape

2.5.1 Test Procedures

The three major parameters for designing granular activated carbon adsorption column systems are(8) : 1) contact time; 2) carbon usage rate; and 3) pretreatment requirements.

The contact time indicates the amount of activated carbon required on stream at any given moment-thus the size of the equipment, and the capital cost. Carbon usage rate or exhaustion rate describes frequency with which the carbon must be replaced or reactivated and this defines the operating costs of the system. The pretreatment requirements, which are dependent on pH, suspended solids, oil, grease, etc. , relate directly to additional unit operations required for optimum treatment. These three parameter cannot be adequately described by batch equilibrium tests such as the adsorption isotherm, and so pilot column testing is required:

Adsorbent type and characteristics
Column diameter
Wastewater flow rate
Adsorbent bed depth
Weight of adsorbent/column
Contact time/column
Influent impurity concentration data
Effluent impurity concentration data
Desired effluent impurity concentration

Test results are most valid where the pilot system is scaled down version of the full scale indicating use of regenerate adsorbent. If virgin adsorbent is used for testing and regeneration is contemplated on full-scale, be aware that the pilot test data may produce greater efficiency than may be realized in the full-scale.

The length of mass transfer zone, an important design parameter, is usually directly affected by contact time. When water or other low viscosity fluid flows through a bed at a very rapid rate, decreasing contact time, the mass transfer zone can become long and drawn-out; this will result in a breakthrough curve which begins to leak contaminant very early and requires a long time until complete breakthrough is achieved. It is to our advantage, therefore, to use long contact time, as this will result in more complete utilization of the adsorbent to any point of effluent concentration.

2.5.2 Sizing of Adsorber

For an adsorption system, the key design parameter is flow rate, or its reciprocal, residence time. This parameter establishes a required adsorbent volume and dimension of the adsorption units which is a major factor in establishing capital costs. Flow rate is constrained by a number of other important parameters, such as leakage level, loading(capacity), column throughput and regeneration frequency.

2.6 Engineering Considerations

2.6.1 Scale Up of Fixed Bed Column Adsorbers

In choosing the operating conditions for the laboratory experiments to obtain design data for scale up, one should consider what the commercial size unit looks like. The laboratory adsorbent bed is normally considered a simulation of a small cylindrical portion of the commercial size adsorbent bed.

The critical scale up variables are(8) (1) the flow velocity which can be expressed as a superficial (based on an empty bed) velocity and (2) the liquid residence time expressed as an empty adsorbent bed volumes per unit time . Unpublished data suggest that pore diffusion is a significant resistance to mass transfer in adsorption onto both polymeric resins and activated carbon; therefore, the residence time is important.

2.6.2 Hydraulics

A minimum adsorbent height of two or three feet is usually required to take advantage of the multiple stage effect in a column adsorption operation. Therefore, means for distributing the flow of both the feed and regenerant fluids uniformly through the adsorbent bed is necessary. To ensure good flow distribution, the design of the flow distributors and collectors must be matched properly. Proper sizing of piping to control flow and back pressure must be considered to ensure the fluids contact all of the adsorbent uniformly at all times in the cycle, otherwise, the column adsorption capacity will decrease.

Although there are some exceptions, the linear flow rate range that is employed throughout the industry for most adsorbents is approximately 2-10 gal/min/ft^2. This range has been set for a variety of reasons. Various important reasons are as follows(8) :

1. Flow rates in excess of 10 gal/min/ft^2 can yield excessive pressure drops that may give rise to adsorbent breakage or flow channel formation in the bed. It is common practice to limit the pressure drop across a bed to less than 10 psi, although some adsorbents can tolerate higher pressure drops.
2. The 2-10 gal/min/ft^2 range takes into account the fact that the backwash and process flow rates cannot vary over too wide a range since it would be impossible to design a single set of flow distributors and collectors for an adsorption unit. Good flow distribution through the bed depends upon a minimum back pressure. If separate sets of distributors and collectors were required, the increased costs has to be considered.
3. The effect of hydraulic loading in this range is usually negligible.
4. Flow rates below this range cause difficulty in designing proper flow distribution devices in the adsorbent column.
5. Volumetric flow rates or residence time are sometimes used in discussion of flow through adsorbent columns. The range considered to be satisfactory is 30 minutes to 1.5 seconds. Rates below this range can cause problems in flow distribution, and above the range, pressure drop across the bed will be excessive