Chapter 8

Adsorption

8.1 INTRODUCTION

Physical adsorption is a process in which solute molecules (adsorbate) become attached to a solid surface under the attracting influence of surface forces (van der Waals force). This is primarily a surface phenomenon. Good adsorbents have a very high specific surface area, which is relatively free of adsorbed materials (it is said to be 'active' or 'activated'). Many organic materials found in water and wastewaters can be removed by adsorption including detergents, which have a particularly high surface affinity (surface-active agents). Hydrophilic substances and ions are not amenable to removal by adsorption.

The adsorbent of choice in water and wastewater treatment is activated carbon, which may be used in a dispersed powder form (PAC) of in a fixed-bed granular form (GAC). Its main uses are the removal of taste and odour-causing trace organics and toxic trace organic residues from drinking water and as a final polishing process in advanced wastewater treatment systems.

8.2 ACTIVATED CARBON

Activated carbons suitable for water process applications are produced (Sontheimer et al., 1988) from a variety of raw materials, including bituminous coal, lignite, peat, petrol coke, wood and coconut shells. The production process involves the pyrolytic carbonisation of the raw material during which the volatile components are released and the carbon realigns to form a pore structure that is developed during the activation process. The activation process selectively removes carbon, resulting in an opening of closed pores and an increase in the size of micropores. Activation may be carried out by chemical or physical processes. Chemical activation is normally used for raw materials that contain cellulose and combines both carbonisation and activation. It involves pyrolytical heating in the presence of dehydrating chemicals such as zinc chloride or phosphoric acid. Physical activation is more commonly used for the carbons produced for water treatment applications. It involves contact of the carbonised char with steam (carbon dioxide or air are sometimes used) at a temperature in the range 850-1000 ^{o}C. A maximum surface area per unit mass of original char is found at an activation burn-off in the range 40-50%. Some of the key physical properties of activated carbon particles are summarised in Table 8.1.

Table 8.1 Physical properties of activated carbon particles

Raw material	Solid fraction density (kg m$^{-3)}$	Particle density (kg m^{-3})	Particle porosity
Bituminous coal	1945	491	0.75
Peat/coal	1864	561	0.70
Peat	1981	626	0.68
Coke	1767	783	0.45

Source: Sontheimer et al. (1988)

The solid fraction of the carbon matrix is approximately equal to the density of graphite. The particle density is much lower than the matrix density owing to the space occupied by the pore volume. The particle porosity is the ratio of the pore volume to the total volume. The pores vary in size and may be classified (Greg and Sing, 1982) in size ranges as follows:

micropores: $r_p < 1$ nm
mesopores: 1 nm $< r_p <$ 25 nm
macropores: 25 nm $< r_p$

where r_p is the pore radius.

Perhaps the most important physical characteristic of activated carbon is the very large specific surface area associated with their pore structure (range 600-1500 $m^2\ g^{-1}$). It is important to bear in mind that most of this active surface is contained within the pores of the material, over 99.9% in the case of GAC and obviously less in the case of PAC.

PACs are finely ground, resulting in very small particles with correspondingly large surface areas. The AWWA (1978) standard for the maximum particle size distribution for PAC is as follows:

$$99\% < 149\ \mu m$$
$$95\% < 74\ \mu m$$
$$90\% < 44\ \mu m$$

The grain size distribution for GAC applications may be specified in the same manner as filter sands (see section 6.8), using effective size (d_{10}) and uniformity coefficient (d_{60}/d_{10}) parameters. The effective GAC grain size may be in the range 0.6-1.2 mm and the uniformity coefficient should be less than 2.1 (AWWA, 1974).

8.3 ADSORPTION PROCESS

In the adsorption process there is a mass transfer of solute from a solvent on to the surface of a solid adsorbant. The driving force may be the lyophobic (i.e. solvent-rejecting) character of the solute or the affinity of the solute for the solid, or a combination of both. Thus, the substances that are removed from waters and wastewaters by adsorption on to activated carbon are typically organic contaminants which may have a molecular structure comprised of both hydrophobic and hydrophilic parts. In such cases the hydrophobic part tends to be active at the surface and undergoes adsorption. Surfactants are the prime examples of this category of substance. The second driving force element referred to above, namely the affinity of the solute for the solid may be due to a surface charge effect, a mass attraction effect or a chemical reaction effect.

The rate at which adsorption proceeds is considered to be diffusion-controlled. Thus while adsorption equilibrium is quickly attained on exposed particle surfaces, the rate of equilibrium attainment on pore walls is slower, being governed by the rate of diffusion of adsorbate molecules through the capillary pore passages. Since virtually all the useful adsorptive surface area is within the pores the overall rate of adsorption is dependent on particle size – it varies reciprocally with the square of the particle diameter, increases with increasing concentration of solute, decreases with increase in temperature and decreases with decreasing molecular weight of solute (Eckenfelder, 1966). The rate of adsorption has been found to be proportional to the square root of the time of contact (Morris and Weber, 1964). In addition it is affected by pH, decreasing with an increase in pH and being very poor at pH values above 9.0 (Culp and Culp, 1971).

8.4 ADSORPTION EQUILIBRIUM RELATIONSHIPS

The mathematical formulation of relationships is usually expressed in terms of either Freundlich or Langmuir equations.

The Freundlich equation has the form:

$$\frac{X}{M} = kC^{1/n} \qquad (8.1)$$

where X is the mass of adsorbate, M is the mass of adsorbant, C is the equilibrium concentration of the substance remaining in solution, k and n are constants. The equation is more useful in logarithmic form:

$$\log\frac{X}{M} = \log k + \frac{1}{n}\log C$$

A plot of X/M versus C on log-log paper results in a straight line of slope 1/n. Such a graph is called an adsorption isotherm – it relates, for a particular temperature, the mass of substance adsorbed per unit mass of adsorbent with the concentration of substance in the effluent. An adsorption isotherm can be determined experimentally, using powdered activated carbon, which is separated out by filtration after a suitable contact time. A typical test result is shown in Fig 8.1. Such tests are a useful indication of the potential of the adsorption process for a particular application., but design data are preferably obtained from pilot plant operation.

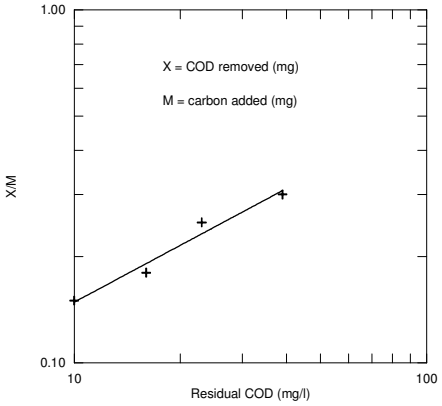

Fig 8.1 **Example of an adsorption isotherm**

The Langmuir equilibrium adsorption equation has the form:

$$\frac{X}{M} = \frac{abc}{(1+aC)} \qquad (8.3)$$

which may be written as

$$\frac{1}{X/M} = \frac{1}{b} + \frac{1}{ab}\cdot\frac{1}{C} \qquad (8.4)$$

where b is the amount of adsorbate required to form a complete monolayer on the adsorbent surface and is a constant that increases with molecular size. While a and b values have been reported for a number of organic substances, the usefulness of the Langmuir equation in water and wastewater applications is limited since many organic substances are adsorbed simultaneously.

8.5 DESIGN OF ADSORPTION SYSTEMS

8.5.1 PAC process design

While GAC has replaced PAC in many continuous applications, PAC processes offer considerable design flexibility and economy in situations where an adsorption step is required only on an intermittent basis, as may be the case in many drinking water treatment applications.

Powder activated carbon (PAC) may be used in a single-stage or multi-stage application mode. Because of the small particle size, adsorption equilibrium is reached rapidly. If it assumed that adsorption equilibrium is reached in each stage of a multi-stage process the specific removal (X/M) in each stage will, according to the Freundlich equation (8.1), be proportional to the (1/n)th power of the residual concentration ($C^{1/n}$). Thus, there will be a step reduction in the X/M value for each succeeding stage, the lowest value being in the final stage. If, however, only a single stage is used, its X/M value must be the same as that of the final stage of a multi-stage process if it to achieve the same final residual concentration as the multi-stage process. Hence, the average specific removal rate (average X/M) will be much higher for a multi-stage process than for a single stage process. Despite the process advantage of using more than a single stage, most practical applications are single-stage processes.

PAC is applied at many waterworks on an occasional basis for taste and odour control, typically at a dose rate in the range 5-10 g m^{-3}. If more than 25 g m^{-3} has to be added for long periods of time, GAC columns are likely to be more economical. Carbon powder is generally added at the rapid mix stage of the chemical coagulation process and removed in the downstream sedimentation and sand filtration processes. This mode of application provides the essential process components of particle wetting, adsorption contact time and particle separation. It should be noted that PAC use in this manner is likely to increase filter head loss and reduce filter run time. PAC may also be separated by membrane filtration processes.

PAC has been applied in wastewater treatment in conjunction with the activated sludge process (Schultz and Keinath, 1984), where it is added to the influent in the aeration basin at concentrations in the range 50-300 g m-3. Its observed positive effects (Sontheimer et al., 1988) include improved process stability, increased mixed liquor suspended solids concentration (i.e. increased microbial biomass) and improvements in the settling and dewatering characteristics of the activated sludge. In the case of wastewaters containing toxic components, some of the enhanced removal efficiency can be attributed to the adsorption of the toxic compounds by the PAC.

8.5.2 GAC process design

Granular activated carbon (GAC) in fixed beds is generally preferred to its use in powdered form, where continuous application is required. GAC allows a more complete use of the adsorption capacity of the carbon, thus reducing make-up costs. GAC columns provide a filtration capacity as well as an adsorption function. GAC is easier to handle than PAC, requiring only to be replaced when its adsorption capacity is reached, typically after three months to one year of operation.

GAC columns may be designed to operate in a conventional down-flow filtration mode or in an up-flow mode. The residence time in GAC columns is usually expressed in terms of the empty bed contact time EBCT, which is generally in the range 5-20 min. Most economic use of granular carbon can be made in up-flow columns operated on a counter-current principle (Culp and Culp, 1971). Spent carbon is removed from the bottom of the bed periodically and a corresponding quantity of fresh carbon is added to the top of the bed. With this system, optimum removal is effected and maximum use is made of the adsorptive capacity of the carbon at the same time. Packed-bed and expanded-bed systems are used. Packed beds can only be used for waters of low turbidity (<50 NTU) owing to their susceptibility to clogging. The up-flow velocity of turbid waters in expanded-bed systems must be sufficient to provide a self-cleansing action. For grain size of 0.8-1.0 mm this can be achieved at a velocity of about 15 m h^{-1} with a corresponding bed expansion of about 10% (Hager and Flentje, 1965). Up-flow operation has the advantage that the spent carbon is always at the bottom where it can be easily removed. This remains true in expanded bed operation owing to the fact that the effective density of the grains increases with the quantity of adsorbate attached and hence, owing to its increased density, there is a tendency for saturated material to migrate towards the bottom of the bed.

A batch-operated fixed bed system, in which all the carbon is replaced when breakthrough occurs, may also be used. Saturation of the carbon moves progressively down through the bed until finally breakthrough occurs as shown in Fig 8.2. When the carbon has to serve as filter and adsorbent, the bed is cleaned by backwashing as in ordinary rapid sand filtration. However, backwashing of a down-flow filter systems tends to upset bed stratification and the advantages of counter-current operation are lost.

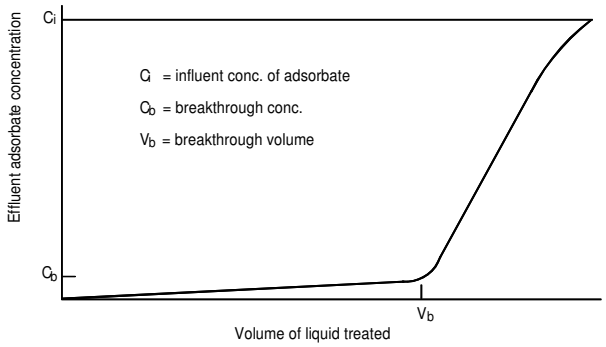

Fig 8.2 Illustration of carbon breakthrough

Two important considerations should be borne in mind in relation to the design of adsorption systems: (a) adsorption is a process for removing dissolved solids, and for best results the influent turbidity should be as low as possible; and (b) reliable values for design parameters – volume of carbon required to secure the desired effluent quality, rate of carbon saturation – can only be reliably obtained through pilot plant investigation.

Spent or saturated carbon can be re-activated by a number of methods, including solvent washing, acid or caustic washing, steam treatment and thermal regeneration. The latter method is the most widely used.

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