ADSORPTION PROCESSES

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ABSTRACT

Adsorption is a fundamental process in the physicochemical treatment of municipal wastewaters, a treatment which can economically meet today's higher effluent standards and water reuse requirements. Activated carbon is the most effective adsorbent for this application. Expanded-bed contact systems permit most efficient use of granular carbon for waste treatment. The adsorption process is enhanced by *in-situ* partial regeneration effected by biological growth on the surfaces of the carbon. Physicochemical systems using adsorption with activated carbon consistently produce high levels of treatment and have a high degree of stability and reliability. Advantages over biological treatment systems include: lower land area requirements; lower sensitivity to diurnal flow and concentration variations and to toxic substances; potential for significant heavy metal removal; greater flexibility in design and operation; and, superior removal of organic wastes.

INTRODUCTION

Adsorption is integral to a broad spectrum of physical, biological, and chemical processes and operations in the environmental field. Purification of gases by adsorption has played a major role in air pollution control, and adsorption of dissolved impurities from solution has been widely employed for water purification. Adsorption is now viewed as a superior method for wastewater treatment and water reclamation.

Applications of adsorption for chemical processing, air pollution control, and water treatment are well known; applications in wastewater treatment and water pollution control are generally not as well recognized, nor as well understood. The process has been demonstrated to be widely effective for removing dissolved organic substances from wastewaters, but it should not be viewed as a catholicon for waste treatment, nor should its application be made in an empirical fashion. The purpose of this paper is to develop the details of this application, highlighting advantages over other wastewater purification processes, and defining major factors and considerations involved in its design and use.

ADSORPTION PROCESSES

Adsorption occurs at least partly as a result of—and likewise influences and alters—forces active within phase boundaries, or surface boundaries:

these forces result in characteristic boundary energies. Classical chemistry defines a system by the properties of its mass: for surface phenomena the significant properties are those of the surface or boundary.

A pure liquid reduces its free surface energy through the action of surface tension, which is quantitatively equal to the amount of work necessary to compensate the natural reduction in free surface energy. A large number of soluble materials can effectively alter the surface tension of a liquid. Detergents, for example, lower surface tension dramatically. If a material which is active at surfaces is present in a liquid system, a decrease in the tension at the surface will occur upon movement of the solute to the surface. Migration of the substance to the surface or boundary results in a reduction of the work required to enlarge the surface area, the reduction being proportional to the concentration of adsorbate at the surface. The energy balance of the system thus favours adsorptive concentration of such surface-active substances at the phase interface. The tendency of an impurity to lower the surface tension of water is referred to as hydrophobicity; that is, the impurity 'dislikes' water.

Adsorption of an impurity from water on to activated carbon may result from solute hydrophobicity, or it may be caused by a high affinity of the solute for the carbon. For most systems encountered in waste treatment, adsorption results from a combination of these factors.

The solubility of a substance in water is significant: solubility in the sense of the chemical compatibility between the water and the solute. The more hydrophilic a substance the less likely it is to be adsorbed. Conversely, a hydrophobic substance will more likely be adsorbed.

In the context of solute affinity for the solid, it is common to distinguish between three types of adsorption. The affinity may be predominantly due to: (1) electrical attraction of the solute to the adsorbent (exchange adsorption); (2) van der Waals attraction (physical or ideal adsorption); or, (3) chemical reaction (chemisorption or chemical adsorption).

Many adsorptions of organic substances by activated carbon result from specific interactions between functional groups on the sorbate and on the surface of the sorbent. These interactions may be designated as 'specific adsorptions'. It is possible for specific adsorptions to exhibit a large range of binding energies, from values commonly associated with 'physical' adsorption to higher energies associated with 'chemisorption'. The adsorptive interactions of aromatic hydroxyl and nitro-substituted compounds with active carbon, for example, are specific adsorption processes resulting from formation of donor–acceptor complexes with surface carbonyl oxygen groups, with adsorption continuing after these sites are exhausted by complexation with the rings of the basal planes of the carbon microcrystallite[1].

Adsorption results in the removal of solutes from solution and their concentration at a surface, until the amount of solute remaining in solution is in equilibrium with that at the surface. This equilibrium is described by expressing the amount of solute absorbed per unit weight of adsorbent q_e, as a function of C, the concentration of solute remaining in solution. An expression of this type is termed an adsorption isotherm. Two equations, the Langmuir equation and the Freundlich equation, find common use for describing adsorption isotherms for water and wastewater treatment appli-

cations. The Langmuir isotherm is

$$q_e = QbC/(1 + bC) \tag{1}$$

in which b is a constant related to the energy or net enthalpy of adsorption, and Q is the ultimate adsorption capacity (maximum value of q_e).

The Freundlich equation has the general form

$$q_e = K_F C^{1/n} \tag{2}$$

where K_F and n are constants and $n > 1$. Data are usually fitted to the logarithmic form of the equation, which gives a straight line with a slope of $1/n$ and an intercept equal to the value of log K_F for $C = 1$ (log $C = 0$). The intercept is roughly an indicator of sorption capacity and the slope, $1/n$, of adsorption intensity. The Freundlich equation generally agrees well with the Langmuir equation and experimental data over moderate ranges of concentration, C. Unlike the Langmuir equation however, it does not reduce to a linear adsorption expression at very low concentrations, nor does it agree well with the Langmuir equation at very high concentrations, since n must reach some limit when the surface is fully covered.

The adsorption isotherm is useful for representing the capacity of an activated carbon for adsorbing organics from a waste, and in providing description of the functional dependence of capacity on the concentration of pollutant. The steeper the isotherm, the more effective is the activated carbon; that is, the sharper the rise of the isotherm to a given ultimate capacity as concentration increases, the higher will be the effective capacity at the concentration level desired for the treated water. Experimental determination of the isotherm is routine practice in evaluating the feasibility of adsorption for treatment, in selecting a carbon, and in estimating carbon dosage requirements. The Langmuir and Freundlich equations provide means for mathematical description of the experimentally observed dependence of capacity on concentration. The adsorption isotherm relates to an equilibrium condition, however, and practical detention times used in most treatment applications do not provide sufficient time for true equilibrium to obtain.

Rates of adsorption are thus significant, for the more rapid the approach to equilibrium, the greater is the fraction of equilibrium capacity utilized in a given contact time. There are three primary rate steps in the adsorption of materials from solution by granular activated carbon. First is the transport of the adsorbate through a surface film to the exterior of the adsorbent ('film diffusion'); second is the diffusion of the adsorbate within the pores of the adsorbent ('pore diffusion'); third is adsorption of the solute on the interior surfaces bounding pore and capillary spaces. For most operating conditions, transport of adsorbate through the 'surface film' or boundary layer is rate-limiting. If sufficient turbulence is provided, transport of the adsorbate within the porous carbon may control the rate of uptake.

The method by which the carbon is contacted with the water determines in large part which of the transport or reaction steps is rate-limiting. For a completely and vigorously mixed batch reactor, pore diffusion may be rate-limiting. For continuous flow systems (e.g. beds of granular carbon)

film diffusion is usually rate-limiting for normal flowrates of 2–10 gpm/ft^2 (81–408 l/min·m^2).

COMPONENTS AND CONDITIONS

Surface area

Extent of adsorption is generally proportional to specific surface area, specific surface area being that portion of the total surface available for adsorption. If the mechanism of uptake is one of adsorption on external sites of a non-porous adsorbent, the rate should vary reciprocally with the first power of the diameter. This holds also for porous adsorbents when the rate is controlled by an external resistance, i.e. 'film transport'. Conversely, for cases in which intraparticle transport controls, the variation should be with the reciprocal of a higher power of the particle diameter[1].

Solute properties

In general, an inverse relationship between extent of adsorption and water solubility can be anticipated. The water solubility of organic compounds within a particular chemical class decreases with increasing chain length, because the compound becomes more hydrocarbon-like as the number of carbon atoms becomes greater. Thus, adsorption from aqueous solution increases as an homologous series is ascended, largely because the expulsion of increasingly large hydrophobic molecules from water permits an increasing number of water–water bonds to reform.

Molecular size is of significance if the adsorption rate is controlled by intraparticle transport, in which case the reaction generally proceeds more rapidly the smaller the adsorbate molecule. It must be emphasized however, that rate dependence on molecular size can be generalized only within a particular chemical class or series of molecules. As shown by Weber and Morris[2] large molecules of one chemical class may adsorb more rapidly than smaller ones of another if higher energies (driving forces) are involved.

Many organic compounds exist, or have the potential of existing, as ionic species. Fatty acids, phenolic species, amines, and many pesticides are a few materials which ionize under appropriate conditions of pH. Activated carbon commonly has a net negative surface charge; further many of the physical and chemical properties of certain compounds undergo changes upon ionization. Most observations point to the generalization that as long as compounds are structurally simple, adsorption is at a minimum for neutral species. As compounds become more complex, the effect of ionization decreases. Studies of amphoteric compounds indicate an adsorption maximum at the isoelectric point, consistent with other observations that adsorption is at a maximum for neutral species. A polar solute will be strongly adsorbed from a non-polar solvent by a polar adsorbent, but will prefer a polar solvent to a non-polar adsorbent. Polarity of organic compounds is a function of charge separation within the molecule. Almost any asymmetric compound will be more or less polar, but several types of functional groups tend to produce fairly high polarities in compounds. Examples of these are hydroxyl, carboxyl, nitro, nitrile, carbonyl, sulphonate, and amine. Thus ethanol, C_2H_5OH, is polar, having an incremental negative charge on the

hydroxyl group and a corresponding positive charge on the ethyl group. Because solvation by water involves formation of a hydrogen bond from one of the positively charged hydrogens of the water to a group bearing more or less of a negative charge, along with some bonding in the reverse direction to the water oxygen, water solubility is expected to increase with increasing polarity. It therefore follows that adsorption decreases as polarity increases, even though active carbon is a polar adsorbent.

Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. Further, to the extent to which ionization of an acidic or basic compound affects its adsorption, pH affects adsorption in that it governs the degree of ionization. In general, adsorption of typical organic pollutants from water is increased with decreasing pH.

The organic components of a waste mixture may mutually enhance adsorption, may act relatively independently, or may interfere with one another. Mutual inhibition can be expected if the adsorption affinities of the solutes do not differ by several orders of magnitude and there is no specific interaction between solutes enhancing adsorption. Similarly, because the adsorption of one substance will tend to reduce the number of open sites and, hence, the 'concentration' of adsorbent available, mutually depressing effects on rates of adsorption may be predicted.

It should be apparent from the foregoing discussion of the effects of solute character on adsorption that an analytical characterization of the impurities present in a waste is helpful to a thoughtful prediction of the effectiveness of carbon in water purification.

Temperature

Adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature. Changes in enthalpy for adsorption are usually of the order of those for condensation or crystallization reactions, thus small variations in temperature tend not to alter the adsorption process in waste treatment to a significant extent.

Adsorbent properties

The properties of different carbons can have profound effects on both rate and capacity for adsorption. The surface chemistry of active carbon has been a subject of much interest for more than a century, yet surprisingly little is known about the nature of the surface functional groups of this material. Recent work has provided an examination of the character of functional groups formed on active carbon under different conditions of activation, using the technique of multiple internal reflectance spectroscopy (MIRS), as a means for characterizing surface functional groups[1].

Commercial carbons can be prepared from a variety of raw materials, including wood, lignite, coal, bone, petroleum residues, and nut shells. The raw material is generally activated in an atmosphere of carbon dioxide, carbon monoxide, oxygen, water vapour, air or other selected gases, at a temperature between 300° and 1000°C, often followed by quenching in air or water. Because of the 'impure' nature of the raw materials used in the production of commercial carbons, and because of the concentration and

temperature gradients that develop within the beds of carbon during activation, very heterogeneous or, at best, difficult to characterize surfaces result.

Oxygen is known to react to a significant extent with activated carbons. It has been shown that carbons activated in an atmosphere of pure carbon dioxide, or in a vacuum, react with molecular oxygen at room temperature and below. This affinity for irreversibly 'chemisorbed' oxygen strongly suggests the formation of organic oxygen functional groups on the carbon surface.

Several types of oxygen surface groups have been postulated to explain these phenomena. It is generally thought that two principal types of oxygen functional groups are present on an active carbon surface: those which desorb as CO, and those which desorb as CO_2. Several investigators have shown experimentally that carbons activated at higher temperatures are 'basic carbons'. 'Acidic' carbons are defined as carbons which are capable of lowering the pH of neutral or alkaline distilled water, and which are relatively hydrophilic. 'Basic' carbons are not really basic in the acid–base sense, as they interact with acidic solutions in a specific anion adsorption manner, but they are characterized by the ability to raise the pH of a neutral or acidic solution, and by relative hydrophobicity.

We have determined with MIRS techniques the presence of significant amounts of carbonyl and carboxyl groups on activated carbon surfaces, directly substantiating what had long been speculated. The behaviour of active carbon as an adsorbent has to be related to its surface chemistry: the evidence for chemical interaction at the surface between carbonyl and carboxyl groups and organic adsorbates is convincing. Enhancement of the adsorption capacity of active carbon may well be accomplished by increasing the concentration of appropriate surface functional groups[1].

The most characteristic physical property of activated carbon is its extremely large surface area, which is comprised mainly of surfaces bordering inner pore spaces. The surface area of active carbon is approximately 1000 m^2/g. Relative to the small geometric area of the granules or particles of this material, the large total area requires the existence of a considerable internal surface which can be provided only by small capillaries. In explaining many observed relationships associated with adsorption of materials from solution by carbon, it is essential to consider the physical structure of the adsorbent because the size and arrangement of the capillaries (micropores: 10–30 Å) and channels or interstices (macropores: 30–100000 Å) appear to play a significant role in adsorption processes.

In general, the system of macropores contributes little to the total surface area and adsorptive capacity of active carbons. A high percentage of macropore volume in an active carbon is often a distinct disadvantage because of loss of density to extraneous pore volume. On the other hand, for those instances in which intraparticle transport processes control the kinetics of uptake by porous carbon, an extensive system of larger macropores may be of considerable benefit in that full utilization of the capacity will be attained more rapidly because of the relative ease and speed of transport in larger pores. The total pore volume of an active carbon may be measured by displacement of an inert gas such as helium to account for the micropore volume and by displacement of mercury to account for the macropore volume. At

atmospheric pressure, however, mercury will not penetrate pores less than about 10 Å in diameter, hence simple mercury and helium displacement measurements will not yield sufficiently accurate information regarding pore size distribution. For characterization of the distribution of micropores in active carbons, the water desorption method of Juhola and Wiig is often employed[1].

Regeneration is an important consideration in the use of active carbon for wastewater treatment. Detailed discussion of this aspect of activated carbon lies beyond the scope of this paper. It should be noted, however, that it is currently feasible to regenerate granular carbon by conventional thermal techniques for at least 15 cycles of successive saturation and regeneration. The results of attempts to develop efficient and economical means for chemical regeneration of carbon have thus far been disappointing.

CONTACT SYSTEMS AND REACTORS

The manner in which to contact carbon most effectively with the solution to be treated is of particular significance for large-scale treatment of water. Rates of adsorption from solution on granular adsorbents have been found to be dependent upon the particle size of the adsorbent. It is therefore desirable to employ particles of as small a diameter as conditions of efficient operation allow, so that high rates of adsorption may be obtained.

In batch-type contact processes a quantity of carbon is mixed continuously with a specific volume of water until the contaminants have been decreased to a desired level. The carbon is then removed and either discarded or regenerated for use with another volume of solution. If finely powdered carbon is used in this type of system, separation of the spent adsorbent from the water may be difficult. Conversely, the use of large particles of carbon, which are removed more rapidly when exhausted, requires longer periods of contact between solution and adsorbent, necessitating larger basins or tanks in which to retain the water during treatment.

Column-type continuous-flow operations have an advantage over batch-type operations because rates of adsorption depend on the concentration of solute in the solution being treated. For column operation the carbon is continuously in contact with a fresh solution. Consequently, the concentration in the solution in contact with a given layer of carbon in a column changes very slowly. For batch treatment, the concentration of solute in contact with a specific quantity of carbon decreases much more rapidly as adsorption proceeds, thereby decreasing the effectiveness of the adsorbent for removing the solute.

The rate of exhaustion of carbon in most waste treatment applications is usually not high enough to justify moving-bed adsorbers for column or bed type systems. Thus a fixed-bed adsorber is generally preferred. Upflow expanded operation of fixed beds of activated carbon permits the use of small particles for faster adsorption rates without the associated problems of excessive head-loss, air-binding, and fouling with particulate matter common to packed-bed operation with fine media. In expanded-bed operation, the water flows upward through a column of relatively fine granular carbon at a velocity sufficient to suspend the carbon. Packed-bed adsorption techniques have conventionally been used for water treatment. Expanded-bed

technology is relatively new. The advantages of expanded-bed adsorbers over packed-bed adsorbers have been demonstrated and discussed by Weber[1].

For fixed-bed (either packed or expanded) adsorption operations with activated carbon the water or wastewater to be treated is passed through a stationary bed. Nonsteady-state conditions prevail in that the carbon continues to remove increasing amounts of impurities from solution over the entire period of useful operation.

Figure 1 is a plot of the adsorption pattern which normally obtains for a fixed-bed nonsteady-state adsorber. The impurity is adsorbed most rapidly and effectively by the first few layers of fresh carbon during the initial stages

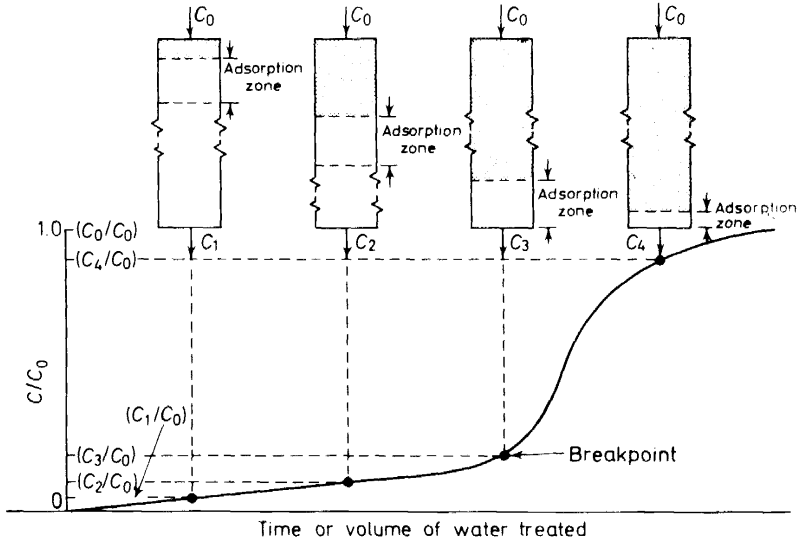

Figure 1. Schematic representation of the movement of the adsorption zone and the resulting breakthrough curve (after Weber[1]).

of operation. These first layers are in contact with the solution at its highest concentration level, C_0. The small amounts of solute which escape adsorption in the first few layers of adsorbent are then removed from solution in subsequent strata, and essentially no solute escapes from the adsorber initially ($C = 0$). The primary adsorption zone is concentrated near the influent end of the column. As the polluted feedwater continues to flow into the column, the first few layers of carbon become practically saturated with solute and less effective for further adsorption. Thus, the primary adsorption zone moves through the column to regions of fresher adsorbent. The wavelike movement of this zone, accompanied by a movement of the C_0 concentration front, occurs at a rate much slower than the linear velocity of the water or wastewater. As the primary adsorption zone moves through the column, more and more solute tends to escape in the effluent, as indicated in the sequence of schematic drawings in *Figure 1*. The plot of C/C_0 versus time (for a constant flowrate) or volume of water treated depicts the increase

in the ratio of effluent to influent concentrations as the zone moves through the column. The breakpoint on this curve represents that point in operation where—for all practical purposes—the column is in equilibrium with the influent water, and beyond which little additional removal of solute will occur. At this point it is desirable to reactivate or replace the carbon.

The method chosen for operation of a fixed-bed adsorber depends to a large extent on the shape of the curve given by plotting C/C_0 versus time or volume. As noted previously, this curve is referred to as a breakthrough curve. For most adsorption operations in water and wastewater treatment, breakthrough curves exhibit a characteristic S shape, but with varying degrees of steepness and position of breakpoint. Factors which affect the actual shape of the curve include all of the parameters discussed earlier (shape of the adsorption isotherm, solute concentration, pH, rate-limiting mechanism for adsorption and nature of the equilibrium conditions, particle size, etc.) and, in addition, the depth of the column of carbon and the velocity of flow. As a general rule, the time to breakpoint is decreased by: (1) increased particle size of the carbon; (2) increased concentration of solute in the influent; (3) increased pH of the water; (4) increased flowrate; and, (5) decreased bed depth. If the total bed depth is smaller than the length of the primary adsorption zone required for effective removal of solute from solution, then the concentration of solute in the effluent will rise sharply from the time the effluent is first discharged from the adsorber. Thus, for each type of adsorption operation there exists a critical minimum carbon depth.

PREDICTION AND DESIGN

Quantitative prediction of the performance of fixed-bed adsorbers involves prediction of the shape and position of the breakthrough curve, representing the movement of the adsorption front through an adsorber. If the breakthrough curves for adsorber systems can be reliably predicted on the basis of some easily determined laboratory measurements, extensive pilot plant scale studies can be obviated, and considerable savings in time and money can be realized. This requires application of appropriate mathematical modeling techniques for operation on information developed from component and condition analysis. Modeling procedures can take several levels of sophistication. A simple mass transfer model and a second-order kinetics model have been described by Weber[1]. Usinowicz and Weber[3] have examined the use of the second-order model for mixtures of contaminants exhibiting markedly different adsorption characteristics. *Figure 2* is representative of the results obtained. The use of second-order kinetics facilitates analytical solution of the resulting partial differential modeling equations, but for multiple solute systems does not provide a true prediction of the entire breakthrough curve. As may be noted from *Figure 2*, however, the prediction is generally good for the first 50–60 per cent of the operational period of the adsorber; this suffices for most practical purposes, since adsorbers are normally not operated to more than 15–30 per cent breakthrough in wastewater treatment. Nonetheless, models amenable to analytical solution must employ relatively simple types of rate expressions describing the uptake of adsorbates (e.g. second-order kinetics or film transport). The

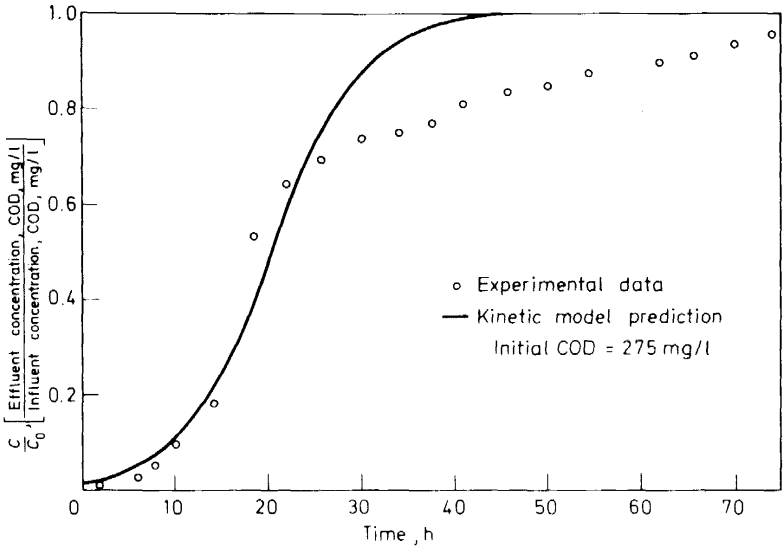

Figure 2. Experimental and predicted COD breakthrough curves for a complex mixture of organic substances (after Usinowicz and Weber[3]).

models are similarly limited to linear or Langmuir type adsorption isotherms: both of these analyses are inadequate for describing adsorption behaviour at the high concentrations found in many wastewaters. Usinowicz and Weber[3] applied the mathematical technique of Thomas (1944) to mixtures of compounds exhibiting a broad spectrum of adsorption behaviour: since this method was developed for a homogeneous single sorbate system, the systems studied were necessarily treated in terms of one lumped-parameter quantity, COD (Chemical Oxygen Demand). The data presented by Usinowicz and Weber could be predicted for only the first half of the effluent breakthrough profile by the analytical solution of Thomas. Models of this type predict symmetrical breakthrough curves, hence, although they are often adequate for dilute single-solute or dominant-solute solutions, or similarly simple systems, their use for complex heterogeneous systems is limited. Other shortcomings are the lack of flexibility to permit inclusion of multicomponent interactions, biological activity, solids mixing, dispersion, and multicomponent equilibrium hysteresis. To eliminate these handicaps Weber and Crittenden[5] have developed several numerical techniques which can include these factors.

A material balance on an adsorption results in two partial differential equations (PDEs), one for the liquid phase and one for the solid phase. Extending this to a multisolute system, a pair of PDEs is obtained for each solute. A suitable expression for the rate of uptake, an equation of equilibrium, and information on the mixing of the solids is needed before the solution of the PDEs can be effected. Weber and Crittenden have used film transport, and Thomas's second order expression to describe the equilibrium behaviour of the solute and have treated the solid phase as both completely mixed and fixed. For multicomponent systems, the only difference is the means in which

the equilibrium positions is described. Extension of the Langmuir expression to multisolute systems as reported by Snoeyink and Jain[6] and by ideal solution and ideal adsorption theory developed by Radke and Prausnitz[7] were used to characterize the equilibrium behaviour in multisolute systems.

Four mathematical techniques were compared to each other by Weber and Crittenden[5] and to the data of Keinath and Weber[8], Usinowicz and Weber[3] and Valencia and Gloyna[9]. A list of the four mathematical techniques evaluated, including a brief description of the numerical techniques, follows:

(1) Thomas's analytical solution to the PDEs, the solid phase is fixed.

(2) Numerical techniques developed by the authors. An Implicit Backward Finite Difference Method (IBFDM) is utilized to solve the liquid phase PDE and a second-order Runge–Kutta is employed to solve the solid phase PDE. This technique is applied for both extremes of the solids mixing range, i.e. fixed and completely mixed. The authors demonstrated that the IBFDM used on the liquid phase PDE converged to the identical breakthrough curve that the Implicit Forward Finite Difference Method (IFFDM) used on the liquid phase PDE would predict for small time and distance steps, i.e. about 400 time steps and 400 distance steps. However, the IBFDM converges more rapidly than the IFFDM, hence requires fewer time steps and fewer distance steps.

(3) Michael's mass transfer model, in which the solid phase is taken to be fixed and the rate law used for the uptake of the adsorbate is film transport.

(4) The distributed parameter technique, in which the adsorber is divided into a series of completely mixed flow reactors (CMFRs). Two Ordinary Differential Equations (ODEs) per CMFR is the outcome of this analysis. The ODEs are solved by a 16th-order predictor–corrector method known as DVDQ. This method was chosen over the Continuous Systems Modeling Program (CSMP) since it is more economical and much more accurate. It will meet a local truncation error specified by the user.

For a multicomponent system methods 2–4 can be extended from the single solute case to incorporate multicomponent interactions, but not the analytical solution of Thomas. The reasons these can account for multicomponent behaviour in carbon column is that methods 2 and 4 are just marching time and distance problems for which the addition of more components produces additional algebraic equations at any given time step, while for method 3, additional equations in the numerical quadrature technique pose no difficulty.

Figure 3 is a plot of predicted breakthrough profiles for the numerical technique (number 2 above) of Weber and Crittenden. Film transport controls rate of uptake in this case. The Langmuir expression is used to describe the equilibrium position. Plots are given for fixed and completely mixed solid phase with several values for the film transfer coefficient.

DiGiano and Weber[10,11] have examined and discussed the kinetics of adsorption in, and performance characteristics of, completely mixed batch (CMB) and CMF reactors. The batch or CMB reactor requires consideration of nonsteady reaction conditions for both solution and solid (activated carbon) phases, while the CMF reactor is normally operated in a region of steady-state (constant concentration) for the solution phase. The types of modeling equations discussed by DiGiano and Weber for these systems

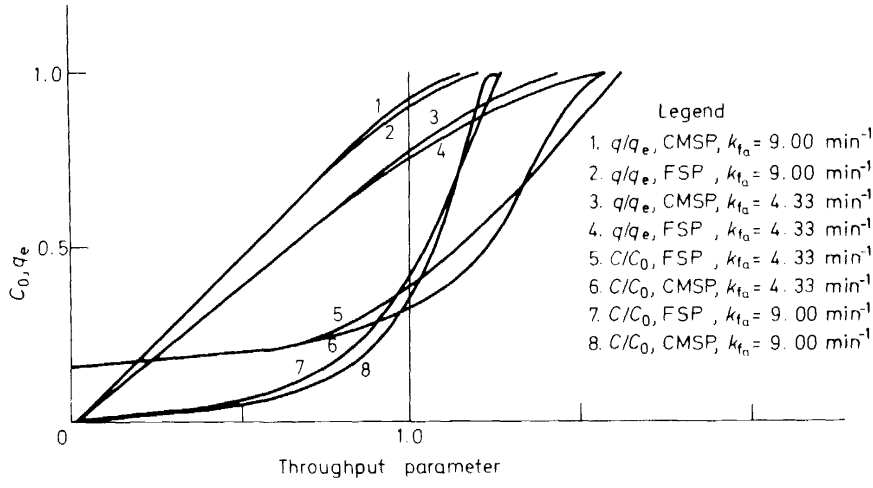

Figure 3. Effluent concentration influent concentration (C/C_0) and uptake of solute/equilibrium uptake of solute at the influent concentration (q/q_e) versus the throughput parameter for a completely mixed solid phase (CMSP) and a fixed solid phase (FSP). Overall film coefficient (k_{f_0}) given for each curve.

apply both for the distributed parameter simulation technique for fixed bed adsorbers and for single and/or multiple stage application of carbon in tank reactors. As noted earlier, granular carbon is normally applied in fixed-bed (PF or PFD) reactors while powdered carbon is generally applied in tank-type (CMB or CMF) reactors.

APPLICATIONS

As noted earlier, the most common type of adsorption system is one in which wastewater is passed through fixed beds of carbon. In such systems the waste is applied to the beds at rates generally ranging from 2 gpm/ft^2 to 10 gpm/ft^2 (81–408 l/min.m^2). In this flow range essentially equivalent adsorption efficiency is obtained for equivalent contact times. At flowrates below 2 gpm/ft^2 (81 l/min.m^2) adsorption efficiency is reduced, while at flowrates above 10 gpm/ft^2 (408 l/min.m^2) excessive pressure drop takes place in packed beds. Contact times employed are in the range of 30 minutes to 60 minutes. In general, increases in contact time up to 30 minutes yield proportionate increases in organic removal. Beyond 30 minutes the rate of increase falls off with increases in contact time, and at about 60 minutes the effects of additional contact time become negligible. Carbon beds operated at the lower end of the flow range are generally designed for gravity flow. Systems designed for higher flowrates must employ pressure vessels if packed beds are used. A pressure vessel is more expensive to construct than a gravity flow vessel, but commonly requires less land area, and provides greater ability to handle fluctuations in flow.

Provision must be made regularly to backwash packed-bed carbon systems because they collect suspended solids and attached biological growths

which tend to develop in this application. Backwashing alone generally relieves clogging due to suspended solids, but does not completely remove attached biological growth. It is advisable to include a surface wash and air scour to be assured of removal of gelatinous biological growth.

Attached growth can lead to development of anaerobic conditions in packed beds. Aeration of the feed is partially effective in preventing anaerobic conditions, but this also accelerates growth to the extent that excessive backwash is required; air-binding can also result.

Packed beds of granular carbon are well suited for treatment of solutions containing little or no suspended solids, and under such circumstances normally operate effectively for extended periods without clogging or excessive pressure loss. However, the suspended solids invariably present in municipal and industrial wastewaters and the potential for biological growth on the surfaces of the carbon present some problems for the use of packed beds as noted above. By passing wastewater upward through a bed of carbon at velocities sufficient to expand the bed, problems of fouling, plugging and increasing pressure drop are minimized. Effective operation over longer periods of time results, as has been demonstrated in comparative laboratory studies and in pilot field investigations in both 'tertiary' and direct physicochemical applications (Weber[12], Hopkins *et al.*[13], Weber *et al.*[14, 15]). Another advantage of the expanded bed is the relatively small dependence of pressure drop on particle size. It is possible to use carbon of smaller particle size in an expanded bed than is practicable in a packed bed, thus taking advantage of higher adsorption rates.

Perhaps the most significant potential benefit provided by expanded-bed adsorption systems is the extension of the operational capacity of activated carbon observed by Weber *et al.*[14, 15]. These researchers found that apparent sorption capacities in excess of 100 wt% as organic matter and 150 wt% as chemical oxygen demand (COD) could be obtained in expanded-beds of activated carbon in which biological growth was allowed to develop fully. Because expanded beds require little maintenance, extended periods of undisturbed operation facilitate the development and continuous growth of bacteria on the carbon surfaces. These bacteria utilize organic matter adsorbed on the carbon as a food source, functioning to provide *in-situ* regeneration by renewing the carbon surface for continued adsorption. *Figure 4* after Weber *et al.*[15] is a schematic representation of this adsorption–biological oxidation process.

To provide a good effluent and to utilize the sorption capacity most effectively, an approach to countercurrent contact is commonly required. This can be achieved by causing the wastewater to flow through a number of contactors or stages in series in one direction while the carbon moves in the opposite direction. In powdered carbon contacting systems this is the procedure used. With granular carbon the procedure is generally modified somewhat to avoid undesirable attrition losses due to excessive handling of the carbon. For most granular carbon contact systems the lead contactor in a series of adsorption columns is removed from service when the carbon it contains is exhausted and, after being refilled with fresh carbon, is placed at the end of the series. Each contactor is thus advanced one position in the series by piping and valving arrangements which permit shifting of the inflow

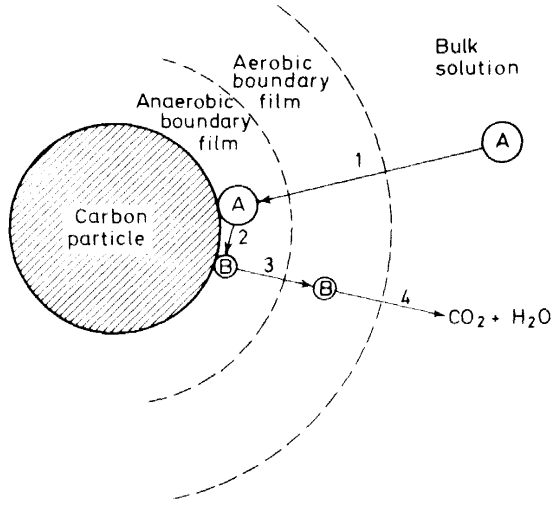

Figure 4. Schematic interpretation of *in-situ* biological regeneration. Event sequence: (1) Diffusion of large adsorbing organic molecule (A), to surface of carbon. (2) Anaerobic degradation of large molecule (A) to small molecule (B). (3) Diffusion of small non-adsorbing organic molecule (B) away from surface of carbon. (4) Aerobic degradation of small molecule (B) to CO_2 and H_2O.

and outflow points of the series accordingly. As the number of stages increases, the piping and valving arrangement becomes more complex and costly. A compromise between the advantage of employing multiple stages to utilize carbon capacity more effectively and the cost of each additional stage must be achieved.

Principal factors which must be considered in the design of a carbon adsorption system may be summarized as: (1) type of carbon, granular or powdered; (2) contact times; (3) flowrate; (4) configuration, series or parallel; (5) number of stages; (6) mode of operation, packed-bed or expanded-bed, pumped or gravity flow; and, (7) adsorption capacity.

Table 1 gives carbon capacities obtained in field operations at several physicochemical pilot plants. In that the wastes, effluent criteria, number of contact stages, etc., varied from plant to plant, it is not surprising that some spread in the results is observed. For general planning purposes a COD capacity of 50 wt % is reasonable if no biological extension of carbon capacity is taken into account. This is approximately equivalent to a requirement of

Table 1. Carbon capacities obtained in physicochemical pilot plants

Plant	Capacities, TOC	Wt %, COD
Blue Plains (Washington)	15	41
Ewing Lawrence (New Jersey)*	50	150
New Rochelle (New York)	20–24	60
Lebanon (Ohio)	22	50

* Biologically-extended expanded-bed operation (Weber *et al.*[15])

500 lb of activated carbon per million gallons (60 g/m^3) of sewage treated. However, the results obtained by Weber *et al.*[15] with biologically-extended adsorption systems suggest that it may be possible to achieve higher effective capacities, reducing the carbon exhaustion rate to less than 200–250 lb per million gallons (24–30 g/m^3).

Even for the highest capacities observed, the initial costs of carbon are such as to make regeneration and reuse of this material highly desirable. Technically and economically feasible regeneration of granular activated carbon can be accomplished by controlled heating in a multiple-hearth or rotary-kiln furnace in the presence of steam. During each regeneration cycle some carbon is lost by burning and attrition, and some by alteration of surface properties. The overall loss expressed as per cent by weight of virgin carbon required to restore the total original capacity of the batch ranges from five to ten per cent. For planning purposes, carbon make-up requirements can be considered to range from 25 to 50 lb per million gallons (3–6 g/m^3) of wastewater treated, again not taking account of *in-situ* biological regeneration.

At present, regeneration systems for powdered carbon are being developed and tested at the pilot stage. A successful process for regeneration of the powdered form would represent a significant step toward making a system utilizing this lower cost material a technical and economic reality. The key factor will be maintaining carbon loss at a sufficiently low level during regeneration.

DESIGN CONFIGURATIONS

A typical flowsheet for physicochemical treatment of wastewaters is given in *Figure 5*, and a corresponding plant layout in *Figure 6*. In this scheme, coagulant is added to the raw sewage, and flocculation takes place

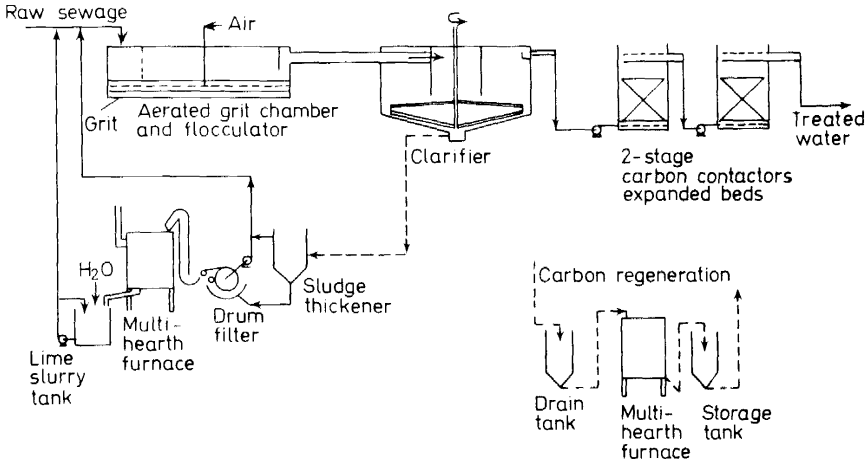

Figure 5. Proposed scheme of treatment of raw sewage by chemical clarification and adsorption on activated carbon.

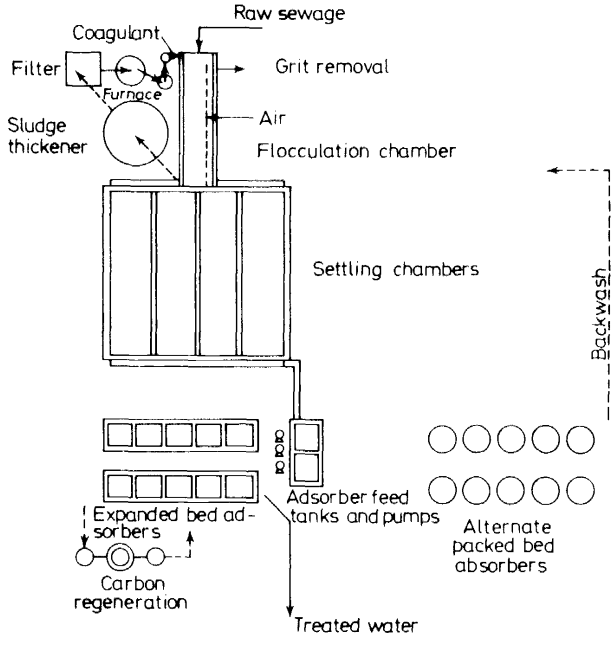

Figure 6. Proposed arrangement of processing units.

in a chamber which provides moderate agitation for an average detention time of 15 minutes. Clarification takes place in a sedimentation basin with an average detention time of two hours. The particular flowsheet presented here is for a single-stage coagulation system.

The clarified effluent is then passed through activated carbon adsorption units for removal of dissolved organics. The preferred mode of operation is an expanded bed, which permits the use of simple open-top concrete contacting basins and relatively trouble-free operation. The use of open tanks with overflow weirs at the surface of the contacting basin provides a means for additional aeration of the wastewater during treatment, thus helping to control anaerobic conditions in subsequent reactors. Two-stage contacting of the activated carbon is outlined in the treatment sequence given in *Figure 5*. However, a larger number of stages can be utilized if desirable for a particular application. The plant layout given in *Figure 6* is based on five parallel adsorption units of two stages each for a design capacity of 10 million gallons (37 850 m^3) per day. When the granular carbon in the first stage of one unit is spent, that unit is taken off stream while the spent carbon is removed and regenerated in the furnace provided for this purpose. During the time this unit is off-stream for regeneration, the other four units can run at 25 per cent higher feedrate each. Upon completion of the regeneration, the carbon is returned to the adsorber, which then becomes the second stage of that unit: the former second stage with partially spent carbon becoming the first stage. Feed is then evenly divided to the five units until another carbon bed is spent.

The water resulting from the clarification and activated carbon treatment will enhance the quality of surface waters, and with disinfection is suitable for many reuse applications. A final filtration may be desirable to ensure a crystal clear effluent for some uses. This post-filtration would remove any suspended matter passing through or generated biologically in the carbon columns.

CAPITAL AND OPERATING COSTS

A detailed analysis of capital and operating costs has been carried out for the physicochemical treatment sequence outlined in *Figures* 5 and 6, for a nominal design capacity of 10 million gallons (37 850 m^3) per day. The capital cost for a complete treatment system was determined to be approximately 3.4 million dollars, and the operating cost, including amortization at six per cent for 24 years, is 19.7 cents per thousand gallons. These costs are based on a carbon utilization of 500 lb per million gallons (60 g/m^3). However, as already noted, biological extension should significantly reduce the carbon exhaustion rate. If the exhaustion rate were reduced to 250 lb per million gallons (30 g/m^3) as seems feasible from the Ewing Lawrence pilot studies (Weber *et al.*[15]) the cost of carbon treatment alone would drop from 8.2 cents per thousand gallons (2.1 cents/m^3) to 6.8 cents per thousand gallons (1.8 cents/m^3), and the combined physicochemical treatment operating costs would be less than 19 cents per thousand gallons (5 cents/m^3). This assumes no reduction in capital investment, which by use of a smaller regeneration facility to reactivate the smaller volume of spent carbon produced, would result in additional savings in total operating costs as well.

SUMMARY

Physicochemical wastewater treatment consisting of coagulation and adsorption holds significant promise as a means for economically meeting today's higher effluent standards and water reuse requirements.

The system consistently produces high levels of treatment and has a high degree of stability and reliability. Unlike biological waste treatment systems, it is highly resistant to shock loads and toxic waste constituents. Biological systems are notoriously sensitive to changes in environmental conditions. If a toxic material gains even temporary entrance to a biological plant, or a hydraulic peak occurs, not only will the efficiency of the plant drop off, but recovery may take from several days to several weeks. In a physicochemical plant serious upsets are unlikely. Further, it can be expected that an immediate recovery of the plant will take place once the source of the upset is eliminated. This inherent stability of performance is also reflected in greater design and operational flexibility. Entire sections of a physicochemical plant can be cut in or out of the process stream as required, and a temporary overload can be absorbed with little effect. The major advantages of a physicochemical system over a biological system are summarized below:

(1) less land area required ($\frac{1}{2}$ to $\frac{1}{3}$ that for a biological system):
(2) lower sensitivity to diurnal variations:
(3) not affected by toxic substances:

(4) potential for significant heavy metal removal:
(5) superior removal of phosphates:
(6) greater flexibility in design and operation: and
(7) superior removal of organic waste constituents.

The effective design and application of the adsorption operation in physicochemical treatment requires performance prediction, which in turn requires thorough knowledge of the process itself and of the interplay of control and response variables. Once the process is defined thermodynamically and kinetically, and conditions of specific operation are delineated, mathematical modeling techniques can be employed for forward prediction of performance and adsorber design.

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