CHAPTER 66

WATER POLLUTION CONTROL TECHNOLOGY

Carl A. Brunner, Ph.D.
Retired from U.S. Environmental Protection Agency

66.1 INTRODUCTION

Various degrees of pollution management have been carried out for centuries. Roman sewers are well known. For much of this time, emphasis was on reducing esthetic problems in cities. When a connection was made between disease and microorganisms harbored in human wastes, the urgency to remove these wastes from human contact increased. Although this connection was suspected earlier, it was not proved until the 19th century. The early pollution-management methods did not include treatment and did not have a significant beneficial impact on the environment. Concerns about the impacts of wastes created by mankind upon the environment are relatively recent. In the 19th century, people began to notice that waterways were showing serious signs of pollution and a few states began to consider remedial measures.[1] Widespread use of treatment of wastewater did not occur prior to the early 20th century. The most commonly employed method of solid waste disposal well into the 20th century was simply dumping on the land or sometimes in local water bodies. Municipal incinerators began to be used by the end of the 19th century. The more acceptable sanitary landfill did not become a common substitute for the open dump until after World War II. Similarly, significant efforts to curb air pollution were not initiated until after World War II. Strong concern for pollution control, not only for health reasons, but also to improve the environment, originated in the 1960's with the development of very active environmental organizations. The federal government and some state governments responded by passing much stronger legislation than had been in force up to that time. The result of this legislation and strong public interest in the environment has been a greatly increased level of treatment of solid, liquid, and gaseous discharges.

This chapter will familiarize the reader with the most important treatment methods for treating waste materials, primarily liquid wastes. To understand why these methods are used, it is useful to know something about the regulatory framework that has developed, primarily as a result of federal legislation. Wastewater discharges have been regulated under a long series of legislative acts, but the key legislation that made very great changes to the degree of control required was the Federal Water Pollution Control Act Amendments of 1972. This act has been amended a number of times since and the overall legislation is commonly called the *Clean Water Act.* Under this legislation, specific requirements have been made for the direct discharges of both municipal and industrial wastewaters to a receiving water body and for the discharge of industrial wastewater to the public sewer system, or indirect discharge. For municipal wastewater, the minimum requirement is either for a reduction of biochemical oxygen demand (BOD) and suspended solids (SS) of at least 85% or effluent values

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of both BOD and SS not exceeding 30 mg/l, whichever is more stringent. For discharges to streams where the minimum requirement is viewed as having too great an impact, more stringent standards can be required, including parameters in addition to BOD and SS. Industries have been grouped into categories, of which there are 55 at this time. For each category, there are both discharge standards for direct discharge and pretreatment guidelines for indirect discharge.

For specific information in a community, the first point of contact should be local wastewater officials. Above the local level would be the state environmental agency and finally the U.S. Environmental Protection Agency (EPA), which maintains ten Regional Offices across the country. Changes in clean water legislation will continue to be made, possibly with significant impact on discharges.

Another law that has had a very great impact on control of wastes is the Resource Conservation and Recovery Act (RCRA). RCRA had its origin in 1976 as amendments to the Solid Waste Act. Regulations arising from RCRA and amendments are the primary method of control for hazardous wastes. For a waste to be hazardous, it must exhibit one or more of the following characteristics: ignitability, reactivity, corrosivity, or failure to pass a defined extraction procedure. The regulations are quite complex. One part deals with the land-disposal ban for listed substances. Hundreds of materials are included along with the best demonstrated available technology (BDAT) for controlling each. Questions regarding whether wastes are hazardous and their control should be referred to the state environmental agency.

A third law that has had a great impact on environmental control is the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA). Unlike most environmental laws, CERCLA deals with problems that are the result of past practice. Of the various aspects of CERCLA, the best known is the Superfund Program, which provides for remediation of wastes on the ground and involves a number of approaches for remediating contaminated soil and groundwater. Funds are provided by the federal government unless a party or parties responsible for the pollution can be found. Future legislation may modify this program significantly.

Although this chapter deals with waste treatment, it is important to point out that a widespread attitude has emerged that favors prevention of pollution over pollution control. There are many facets to a pollution-prevention program, including changes in raw materials to less hazardous materials and changes in manufacturing methods. From the standpoint of waste treatment, there should eventually be a measurable reduction in discharges or at least a reduction in the strengths of wastes being discharged. To some degree, treatment methods such as wastewater treatment should change to in-plant reuse and recovery systems with polluting materials and clean water being returned to the manufacturing operation.

66.2 MUNICIPAL WASTEWATER TREATMENT

Every day, billions of gallons of municipal wastewaters are discharged from plants ranging in size from those that handle the discharge from a few houses to more than one billion gallons per day. There are differences in the composition of municipal wastewater from city to city because of differences in the industrial and commercial contributions, and differences in overall contaminant concentration because of varying degrees of stormwater or groundwater entrance into the sanitary sewer system. Even with these differences, however, there is enough similarity that a small group of technologies is able to handle the treatment of most of the sources. Municipal wastewater contains an enormous number of chemical compounds including a wide range of metals and organic materials. The exact composition of all contaminants is never known. Two very common chemical elements, phosphorus and nitrogen, must be emphasized because they act as fertilizer in the receiving water body and can lead to excessive growth of nuisance plants such as algae. In addition, the wastewater contains large numbers of microorganisms, including human pathogens. Ideally, wastewater treatment would reduce all of the contaminants to low levels. In reality, the methods that are used have the primary function of reducing the oxygen demand of those materials that would biologically degrade in the receiving water body. When degradation occurs in the receiving water, oxygen is consumed. Because the stream biota require oxygen, its concentration should not be depressed significantly below the ambient level. As already indicated, requirements have been placed on the BOD and SS in the discharge because these parameters give a measure of the potential for decreasing dissolved oxygen. By settling to the bottom of the receiving water body, SS can also have a direct negative effect on sediment quality and bottom-dwelling aquatic life.

Nearly all municipal wastewater is treated by biological methods. The more common technologies are well described in the textbook literature.[2] These methods take advantage of the ability of a large group of natural microorganisms to utilize the organic materials in the wastewater for food. These organics include soluble materials and many of the insoluble materials that are solubilized by the complicated biochemical activity taking place. The method used by nearly all large cities and treating the greatest volume of wastewater is the activated sludge process. A second method, the trickling filter, was formerly very common, but has been displaced in many communities by activated sludge. There are a number of variations of these two methods, including combinations. Although these two methods account for a large fraction of total treatment capacity, there are a variety of other, usually less complicated, methods used predominantly by small communities.

Figure 66.1 is a diagram of a sequence of treatment operations and processes that are found in many treatment plants. Incoming wastewater passes through preliminary treatment, which might include screens for removal of very large objects, grinding for reducing the size of large objects and a short-term settling operation for removal of small to moderate but heavy particles (grit). The wastewater is usually pumped to a high enough level that it can flow through the remainder of the plant by gravity. Pumping may precede preliminary treatment or may follow at least some of the preliminary treatment to reduce wear on the pumps.

Following preliminary treatment is primary settling, which is intended to remove large organic particles not removed in preliminary treatment, and results in about 50–60% SS and about 30% BOD removal. This operation is carried out in tanks with circular or rectangular configurations. Residence time is up to two hours. Although the principal action is settling, there is also some biological activity. If the settled sludge is not removed quickly enough, biological activity can result in unpleasant odors and floating sludge. In large plants, there may be many settlers operating in parallel. A sludge-removal mechanism moves the sludge in the bottom of each settler to an opening for discharge to the sludge-processing system. Primary treatment is not required for all plants, but is almost always used in large plants.

The partially treated wastewater or primary effluent flows next to secondary treatment, where the major biological activity occurs. In the commonly used activated sludge process, treatment is carried out in tanks supplied with aeration devices. These may be various kinds of diffusers, mounted in or near the bottom of the tanks, that bubble air through the water or surface-mounted mixers or mechanical aerators. In addition to providing oxygen to the water, the aeration devices keep solids in suspension throughout the volume of the aeration tanks, which may be very large. In the aeration tanks, aerobic degradation of the organic matter in the wastewater takes place. Commonly a level of SS of about 2000 mg/l or higher is maintained. The very large number of microorganisms in these solids, commonly referred to as activated sludge, accomplish the biological degradation. The residence time in the aeration tanks is often about four to six hours, but there can be great variation from high rate treatment to extended aeration. In the latter, the residence time might be 24 hours. Extended aeration plants may not require primary treatment. Water leaving the aeration tanks flows to the secondary or final settling tanks. Although these settling tanks are used with technologies other than activated sludge, they play a unique role with activated sludge. As indicated in Fig. 66.1, part of the sludge removed from these tanks is returned to the aeration tanks. The amount of sludge is adjusted to maintain the desired SS concentration in these tanks.

The frequently used trickling filter form of secondary treatment consists of one or more beds of rock or other packing. The wastewater is dispersed over the upper surface of the filter bed and is collected at the bottom in an underdrain system. Biological slime accumulates on the packing. Oxygen is usually provided by the natural flow of air through the packing, although forced air may be employed. From time to time, some of the biomass sluffs from the filter bed and is carried, along with the water leaving the filter, to the secondary or final settler. Many trickling filters operate with return of some of the water from the underdrain system back to the top of the filter, where it is mixed with incoming feed water. Only very rarely is there any return of material from the final settler.

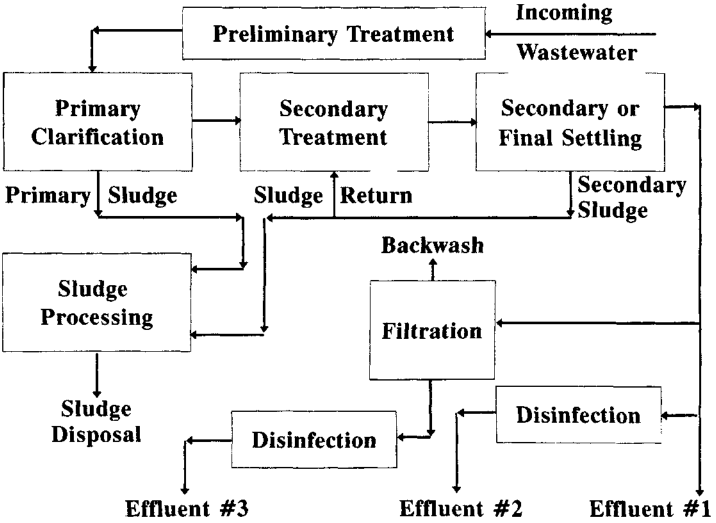

Fig. 66.1 Municipal wastewater treatment.

There are a number of variations and combinations of activated sludge and trickling filter or fixed film devices that are being operated. The rotating biological contractor (RBC) combines the two concepts. RBC systems include basins which contain some biologically active solids, but they also are equipped with banks of partially submerged vertical disks that rotate. Biomass accumulates on the disks. Oxygen is supplied to the system primarily through exposure of the rotating disks to the air. Adequate flocculation of the biomass from a trickling filter to provide effective settling in the final settler can be a problem. Adding a short-residence-time aeration tank following the trickling filter along with returning some sludge from the final settling tank has been found to improve flocculating and settling. These systems are referred to as trickling filter-solids contact.

The primary function of the final settling tanks is the removal of suspended matter from the water to a level that meets discharge requirements. For the standards of 30 mg/l BOD and 30 mg/l SS, this degree of treatment should be adequate, assuming there is no upset in the biological system. The settling tanks are of circular and rectangular configuration and typically have an overflow rate of 400 to 600 gallons/day per square foot. The important function of providing sludge to the aeration tanks in the activated sludge process has already been mentioned.

Figure 66.1 indicates three possible routes for the secondary effluent leaving the final settlers. Direct discharge to a receiving water is allowed in some locations. Disinfection is frequently required. To meet discharge requirements significantly less than the 30 mg/l requirements would necessitate a minimum of additional SS removal. Additional SS removal may also be a practical approach for meeting a phosphorus requirement.

Disinfection is frequently carried out using either elemental chlorine or a chlorine source, such as sodium hypochlorite. The chlorine is mixed with the water in a chlorine contact chamber, which often has a residence time of about 30 minutes. Because the addition of chlorine to waters containing organic materials has the potential for producing toxic chlorinated species, there is increasing concern about the health and ecological impacts of chlorination. Possible chemical substitutes are chlorine dioxide, which does not result in significant formation of chlorinated organics, and ozone. Use of these chemicals is more costly and at this time is rare. A non-chemical method, ultraviolet radiation (UV), is being used increasingly as a substitute for the traditional chlorination. This is a rapidly evolving technology with further improvements in the radiation sources being likely. In a typical installation, the water is passed through a chamber containing banks of tubular lamps. The lower the SS concentration, the more effective is the disinfection, which is dependent upon sufficient radiation reaching all of the water. There is also the obvious question of the ability of UV (and to a lesser degree with chemical methods) to disinfect within particles constituting the suspended matter. Parker and Darby reviewed the literature on this question[3] and carried out tests using rapid stirring to break up solids particles in secondary effluent that had been UV disinfected with low pressure UV lamps. They found some shielding of coliforms as measured by increases in these organisms in the water phase after stirring and stated the need for greater emphasis on pretreatment of the wastewater before disinfection, including particulate removal. Higher pressure UV sources are being developed which may largely overcome the problem.

The usual method in large plants for removal of SS below the concentration in secondary effluent is in-depth filtration. An in-depth filter contains two feet or more of sand, or a combination of sand covered with larger-particle-size-coal (dual media), or sand and coal over a fine, high-density material such as garnet (multimedia). Water is introduced at the top of the filter bed. These filters strain much of the remaining SS from the water by several mechanisms, including incorporation in biological slime. Eventually the solids deposits increase the pressure drop across the filters to the point that they must be backwashed. Backwashing suspends the filter media particles and removes most of the deposited solids. After backwashing, the media particles in the dual-media and multimedia filters naturally grade themselves with larger particles (coal) at the top. The reason for considering a combination of media such as sand and coal of a larger particle size is the increased solids holding capacity and increased run length between backwashes. The multimedia system should result in the highest degree of solids removal. To avoid the need for disposal, the backwash stream must be returned to an appropriate point in the treatment sequence, possibly before secondary treatment or the final settler.

In Fig. 66.1, the concentrated solids streams are referred to as sludge and are shown leading to sludge processing. To improve public acceptance of the treated sludge for use as a soil amendment, there is a tendency in the profession to refer to adequately stabilized sludge as biosolids. Although the volume of sludge produced is only a few percent of the volume of water treated, its processing constitutes a significant fraction of the overall treatment activity. A variety of methods exist that vary somewhat with plant size and possible modes of disposal for the treated sludge or biosolids. Metcalf and Eddy mention eight categories of sludge-processing operations or processes, under which are included 34 specific methods (Ref. 2, p. 767). In the liquid handling sequence of a sewage treatment plant, much of the capital cost is in concrete. In the sludge treatment sequence, there is greater opportunity for companies to manufacture major parts of the system. Both U.S. and foreign manufacturers are responding. Unless the sludge contains unusually high concentrations of hazardous materials, such as certain metals, it is very useful as a soil amendment. EPA and many environmental groups favor this beneficial use of sludge. Where application to the soil is not practical, incineration or landfilling are alternatives. For any of these methods, substantial processing of the primary and secondary sludge streams is necessary. Because their solids concentrations are only a few percent or less, these streams are usually first thickened. The simplest method is gravity thickening. If the sludge is to be incinerated, to reduce the fuel requirement to the incinerator, it must be further dewatered by mechanical means, such as filtration using belt filters or plate and frame filters, or centrifugation. Solids concentrations of up to 30% are desirable. For other than incineration, a very common method of sludge treatment is digestion. The objective of this biological process is to stabilize or further reduce the biodegradable content of the sludge and to reduce the concentration of pathogens. Digestion is commonly carried out under anaerobic conditions in large plants, but is also frequently conducted aerobically. Usually, the temperature is elevated, if possible, by using the heat generated by biological activity or, in the case of anaerobic digestion, by burning of methane produced by the digestion process. Another method to stabilize sludge is by adding chemicals which raise the pH and form a cement-like residue. In small plants, it is common to stabilize sludge by long-term storage in lagoons. Recent sludge disposal regulations determine to a considerable extent the condition of the sludge for landfilling, beneficial use on land and production of marketable products. For large-scale spreading on agricultural land, digestion may be sufficient. Composting has become common for producing a marketable product. The process has encountered odor problems that necessitate careful control of the operation.

Although very large plants will consist of a system included in Fig. 66.1, occasionally plants of 10–20 million gallons per day and many smaller plants may have somewhat simpler systems such as treatment ponds, or lagoons, wetland systems, and land application systems. Most of these systems will include some form of preliminary treatment. They may or may not include primary sedimentation. Biological degradation occurs in the ponds, on the surface of the land, or underground. Final settlers would not ordinarily be required. In some cases, such as land application with percolation, there is no surface discharge. These methods are land-intensive and are most appropriate in locations where large expanses of inexpensive land are available.

Although removal of organic materials is the usual objective of wastewater treatment, there is also a need in some locations to remove phosphorus and to control nitrogen. Phosphorus contributes to nuisance plant growths, such as algae blooms. Nitrogen exists in raw wastewater largely either as ammonia or in organic compounds that result in ammonia as they are degraded. Because ammonia exerts an oxygen demand from bacteria that convert it to nitrate, nitrification, there is sometimes a need to carry out this oxidation before discharge. In a few locations even the nitrate is undesirable because it, usually along with phosphorus, contributes to nuisance plant growths. In these cases, there is a need to remove the nitrogen entirely. Both phosphorus and nitrogen control can be attained biologically through manipulation of the dissolved oxygen, through recycle within the system, and sometimes by adding treatment stages to the system. Total nitrogen removal or denitrification is the most difficult, requiring oxidation followed by reduction to elemental nitrogen. For a very high degree of nitrogen removal, an organic supplement such as methanol is added to the last biological stage. Phosphorus can also be removed chemically by precipitating with iron or aluminum salts.

In the 1960s, there was much enthusiasm for advanced-waste-treatment systems that would produce very-high-quality water from municipal wastewater. To justify the cost of these systems, the water had to be reused for a high-quality purpose, including potable water. Although a pilot system operated at Denver, Colorado, indicated that, by all practical measures, water of potable quality could be produced, no full-scale plant has been constructed in the United States for the direct reuse of treated wastewater. There have been a small number of full-scale plants constructed, however, that do produce very-high-quality water. The systems include, among other technologies, chemical clarification, activated carbon treatment, and in at least one case reverse osmosis. These technologies are discussed in section 66.3.

Table 66.1 summarizes the municipal wastewater treatment technologies included above.

Capital and operating costs have not been included because of the wide variability, depending on site-specific conditions. As expected, there is an economy of scale for both capital and operating costs. At the time of writing, federal funds are available through each state to aid in payment for construction of municipal sewage-treatment plants.

66.3 INDUSTRIAL WASTEWATER AND HAZARDOUS WASTE TREATMENT

Although nonhazardous industrial wastewater and hazardous wastes are regulated under different legislation, methods for their control may be similar or even identical. In contrast to municipal wastewater, there is a very great diversity in the types of waste to be treated and an equally great variety in the kinds of treatment that might be used. Because it is impossible to include discussion of all of these methods, a few commonly used methods have been selected. It must be emphasized that biological treatment is used for treatment of many organic industrial wastewaters. Systems described for municipal wastewater treatment are applicable for this purpose.

Table 66.1 Municipal Wastewater Treatment Technologies

Technology	Usual Function
Preliminary treatment	Removal of large objects or reduction in size Removal of grit
Primary settling	Removal of large organic particles not removed in preliminary treatment Results in about 30% BOD reduction
Secondary treatment	Most common use is for further BOD and SS reduction to levels of 30 mg/l or less Can be designed to remove phoshorous, nitrify ammonia and denitrify nitrate
Disinfection	Reduction in levels of pathogenic microorganisms
Filtration (sand, dual media, multimedia)	Reduction of SS and BOD where effluent requirements are less than 30 mg/l Can be used to improve effectiveness of disinfection
Sludge processing	Preparation of sludge for beneficial use or disposal Can involve a wide variety of technologies for thickening, dewatering, biologically or chemically stabilizing and thermally treating, including drying and incineration

66.3.1 Chemical Precipitation and Clarification

Chemical clarification can be very effective for removal of contaminants from aqueous streams where the contaminants are particulate in nature. Figure 66.2 is a diagram of a typical chemical clarification system. To obtain a high degree of solids removal requires the formation of flocculent particles that will trap other particles and that will settle well. Flocculating chemicals such as aluminum sulfate (usually referred to as *alum*) or various iron salts are rapidly mixed with the feed under pH conditions that will cause the insoluble hydroxides of these metals to form. The water then flows to the flocculator, where it is slowly agitated. Under these conditions, large gelatinous particles form that settle to the bottom of the settler and are removed as sludge. The overflow from the settler may be of satisfactory clarity. If solids removal to very low levels is needed, a filter can be added to the system. In large installations, a commonly used type of filter would be a sand, a dual-media, or a multimedia filter. Similarly to the situation with municipal wastewater treatment, a large clarification system would consist largely of concrete tanks. For small systems, a number of manufacturers provide package systems which may have unique flocculator–settler combinations and filters.

As already indicated, clarification may be the only treatment needed for some industrial wastewaters where the intent is to reduce BOD and SS—for example, discharge to a public sewer. By carrying out precipitation of soluble materials, it may be possible to extend use of clarification to removing some hazardous materials, such as toxic metals. Lime can be used for this purpose where the hydroxide form of the metal is insoluble. In some situations, the precipitate that forms from lime addition settles well without adding other chemicals. If not, inorganic flocculants or a wide range of organic flocculants called polyelectrolytes can be added. Other materials that can be used for metals precipitation are compounds containing sulfide and carbonate, most likely sodium sulfide and sodium carbonate. Sulfides of many metals are very insoluble; some carbonates are insoluble. Because very toxic hydrogen sulfide can be formed from sulfides at low pH, care must be taken to prevent pH

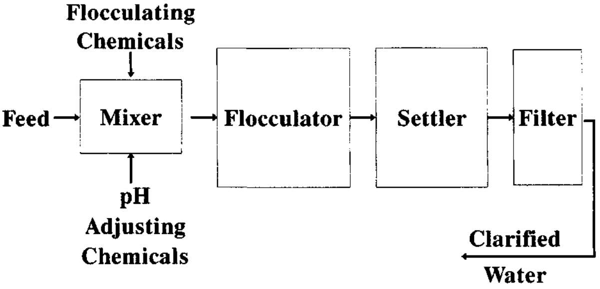

Fig. 66.2 Chemical clarification system.

reduction after precipitation has occurred. Sulfide dose must be controlled closely to prevent excess sulfide in the water leaving the system, which is a potential source of hydrogen sulfide. Also, sulfide is a reducing agent that exerts an oxygen demand until it is converted to sulfate.

Clarification and chemical precipitation may function as pretreatment prior to discharge to a public sewer system or prior to other treatment technologies where particulate matter causes problems. Two examples would be granular activated carbon treatment and most membrane processes.

66.3.2 Activated Carbon Adsorption

A very commonly used method for removing many organic materials from both gas and liquid streams is activated carbon adsorption. This discussion will involve only liquid (water) treatment, although much of what is said pertains also to treatment of gas streams. Activated carbon is made either from coal or organic materials that are carbonized and activated, usually by a thermal treatment that creates a pore structure within each carbon particle. This pore structure creates a large internal surface area that allows, under some circumstances, percentage amounts of contaminants, based on the mass of carbon, to be adsorbed from solution. The amount adsorbed varies from solute to solute, depending on the attraction between the carbon surface and the adsorbed material. The amount of adsorption for any solute is a function of the concentration of that solute in the aqueous phase. For a simple system with a single solute, adsorption capacity data can be obtained as a function of liquid concentration to produce a relationship called an isotherm. Very often the Freundlich isotherm is used to correlate the data. The form of this equation is as follows:

$$q = K_1 C^{1/n}$$

where q = amount of solute adsorbed, mass/mass carbon
K_1 = a constant for the specific solute.
C = the solute concentration in solution, mass/volume solution
n = a constant for the specific solute

For low concentrations, it can often be assumed that there is a linear relationship between q and C, as follows:

$$q = K_2 C$$

where K_2 = a constant for the specific solute.

Observing either equation, it can be seen that the amount adsorbed decreases with decrease in solution concentration, approaching zero as the solution concentration approaches zero. For multicomponent systems, the isotherm for one component depends upon the overall composition. It is important to remember, however, that in general the amount of adsorption, q, increases or decreases with increase or decrease of that component in solution. To devise contactor systems that will make efficient use of the carbon, this principle must be kept in mind.

Activated carbon is available as a very fine powder or in a granular form with an average particle size of about one millimeter. Aqueous wastes are usually contacted with powdered carbon in a mixing and settling operation, conducted batchwise or as a continuous operation. A single tank can be used for batch operation by first mixing and then settling. Often a flocculating chemical must be added to attain adequate separation of the carbon. Continuous operation requires a mixer and a settler. Filtration of the effluent might be necessary for good removal of the carbon. Ultimately, in batch operation, and clearly in continuous operation, carbon is in contact with water of effluent concentration. Recalling the isotherm discussion, the loading of organic on the carbon will be low. More effective use of the carbon could be made using a multistage operation, but the cost of the system would be substantially increased. Use of powdered carbon does not lend itself easily to carbon reactivation.

Treatment with granular activated carbon is usually carried out by passing water through columns of the adsorbent. Figure 66.3 is a diagram of a two-column system using downflow operation. Operation can also be carried out in an upflow mode, either at a rate that allows carbon particles to remain as a packed bed or at a high enough rate to fluidize the bed. Conducting carbon treatment as shown in Fig. 66.3 results in much higher loading of organics on the carbon than is usually possible with powdered carbon treatment. In this case, carbon initially is in contact with water of feed concentration and, in terms of an isotherm, can adsorb an amount equivalent to that concentration. As the water passes downward, the concentration of contaminants in the water decreases, producing an S-shaped concentration curve (solution concentration versus column length) designated as the adsorption zone. Assuming the length of the carbon bed is somewhat longer than the adsorption zone, effluent concentrations of adsorbable materials can approach zero. As the carbon becomes loaded, the adsorption zone moves down the column and eventually breakthrough of contaminants occurs. At that point, it becomes necessary to replace the carbon with new or reactivated carbon. If the adsorption zone is very short, a single column may be sufficient. If the adsorption zone is long,

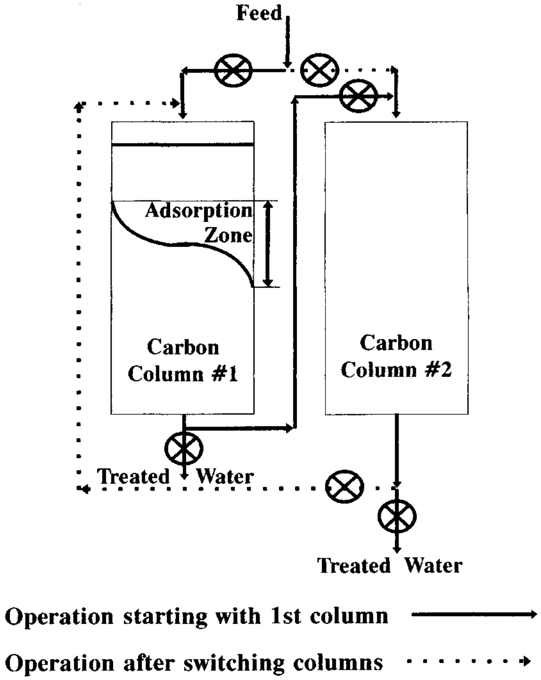

Fig. 66.3 Granular activated carbon treatment.

multiple columns in series can be used to increase the effectiveness of carbon utilization. With multiple columns, breakthrough is delayed until the lower end of the adsorption zone reaches the bottom of the last column. At that point, only the carbon in the first column needs to be replaced and the flow needs to be changed, as shown by the dotted lines in Fig. 66.3. With this mode of operation, high loading of most of the carbon in the system can be attained. If treatment cannot be interrupted, a standby column or multiple systems in parallel must be provided. Granular carbon is frequently reactivated because of the high cost of replacement carbon. Also, reactivation eliminates the need for and the cost of disposal of the contaminated carbon. Reactivation is a thermal process that is similar in function to the original activation. Reactivation can be done on-site if the size of the operation is large. Some companies provide a reactivation service if on-site reactivation is not practical. When dealing with carbon loaded with hazardous materials, careful attention must be given during reactivation to assure that the hazardous materials are either destroyed during reactivation or are controlled by an adequate air pollution-control system. Carbon loss during reactivation may be about 10%.

Operation of granular activated carbon systems has a number of problems, two of which can occur in essentially all cases. Activated carbon and ordinary steel form an electrolytic cell that corrodes the steel. To protect the metal, carbon columns are lined with rubber or coated with a nonporous organic coating. If the coating sustains damage, rapid corrosion of the tank wall can occur. Biological activity usually occurs in carbon systems when they have operated for a period of time. Surprisingly, this activity can be found even in systems treating toxic materials. If the activity remains at a low enough level that serious clogging does not occur, the result can be beneficial because biological degradation substitutes for loading of the carbon. If biological activity does cause clogging, backwash of the carbon columns is necessary. Not only does backwashing create an added operating cost, but it results in a biomass residual that must be further handled. Mixing of heavily loaded and lightly loaded carbon during backwashing reduces the overall time to breakthrough. Biological activity can create anaerobic conditions resulting in odor problems.

66.3.3 Air Stripping

Air stripping is useful for removal of volatile organic materials from a variety of aqueous streams, including industrial wastewaters, drinking water sources, contaminated groundwater, and contaminated soil itself. The treatment method is practical for dilute solutions with concentrations less than about 100 mg/l[4] and for hydrophobic compounds, such as chlorinated solvents, that exhibit large

Henry's law constants. Where the solutes being stripped are hazardous materials, air stripping may result in an exhaust air stream that is in violation of air pollution requirements, necessitating some form of air pollution control.

For an aqueous system with one contaminant at low concentrations, the equilibrium concentration of contaminant in air contacting the aqueous phase bears a linear relationship to the liquid concentration. This line passes through the origin. The slope of this curve is given by the Henry's law constant. For multicomponent systems, the Henry's law constant of any one component will almost certainly be affected by the presence of the other components, but generally, for each component, the concentration in the gas phase in equilibrium with the liquid will increase as aqueous phase concentration increases.

Air stripping can be carried out by simply bubbling air through water in a tank. In a batch operation, assuming one contaminant, the effect on a plot of gas concentration versus liquid concentration would be to move down that curve toward the origin. In a single-tank continuous operation, concentration of the liquid in the air stripping vessel is essentially that of the treated water and, therefore, the maximum concentration in the air must be very low. In either batch or continuous operation with this simple system, the amount of air required can be very large. This mode of operation may be acceptable if the air can be discharged without a need for pollutant removal. Much more efficient operation results from using a countercurrent contacting device. A commonly used example is a packed tower with downflow of the contaminated water countercurrent to the upward flow of air. The packing can be wood slats, rings of ceramic or other materials, or plastic packing of various geometries. The packing provides a large surface for mass transfer of contaminants from the aqueous phase to the air to take place. In a countercurrent contactor, treated water leaving from the bottom contacts clean air just as it would in a simple single-stage device. As the air travels upward, however, it contacts water of increasing contaminant concentrations. The result is a continuing transfer of the contaminant to the air. If the contactor were very long, representing a large number of equilibrium contacting stages, the air concentration would approach the value predicted by Henry's law for the feed, resulting in a greatly reduced air volume compared to the equivalent situation with a single-stage device. In an actual case, a compromise would be made that resulted in minimizing the cost of the overall operation, including air pollution control.

Although the packing in air strippers would ordinarily be substantially larger than particles of granular activated carbon, there is still the opportunity for clogging by suspended matter in the feed, biological growth, and possibly precipitation of inorganic material as a result of chemical oxidation. Chemical clarification or other methods of solids removal might be necessary.[4] If a significant precipitating oxidation reaction is expected, preoxidation with removal of the precipitate would be necessary.

66.3.4 Steam Stripping

Steam stripping can be used to remove volatile organic materials from aqueous streams at higher concentrations than is practical for air stripping. In addition, the method can remove lower-volatility materials than can reasonably be removed by air stripping. The process is more complicated, however, than air stripping and has higher capital and operating costs.

In its simplest form, steam stripping can be carried out by sparging steam into a vessel of water, either batchwise or as a continuous process, resulting in heating the water to boiling followed by conversion of some of the water to water vapor. The resulting vapor is condensed, producing a more concentrated aqueous solution of the volatile materials. Operating in this manner requires a large amount of energy and produces a condensate that is still quite dilute. The treatment method can be made much more energy efficient by utilizing a countercurrent stripping tower, as described for air stripping. The tower might be packed, but it might also contain multiple trays, typical of distillation columns. Steam stripping is actually a distillation operation. The water to be treated would be fed continuously to the top of the stripping tower typically after heat exchange with the hot treated water leaving the bottom of the tower. Steam would be injected at the bottom of the tower and would flow upward countercurrent to the downward flowing water. Just as in the case of air stripping, the water vapor rising through the tower would contact increasingly concentrated liquid water until it exited at the top of the tower approaching equilibrium with the feed water. The contaminated water vapor would then be condensed. This system not only makes efficient use of energy, but produces the highest possible concentration of contaminants in the condensate. Depending on solubility of the contaminants, it is possible for a separate contaminant phase to be formed that might be reusable in the manufacturing operation. Unlike air stripping, this process produces only a small amount of uncondensable gas to be discharged to the atmosphere.

66.3.5 Membrane Technologies

Natural membranes of various types have been used for centuries to remove solid materials from liquids. With the advent of synthetic polymers, mostly developed since World War II, the usefulness of membranes has been greatly expanded. It is now possible to produce membranes with removal capabilities ranging from what is usually considered ordinary filtration or removal of solid particles through ultrafiltration and hyperfiltration, which can remove large molecules, to reverse osmosis (some authors do not differentiate this from hyperfiltration), which can effectively remove even inorganic ions such as sodium and chloride to very low levels. A very extensive discussion of membrane technologies is given by Kirk and Othmer.[5] Much of the early development of these membranes was done for the purpose of producing potable water from mineralized sources such as brackish water and seawater. Potable water production continues to provide a significant market. Reverse osmosis, because it has such good rejection, has widespread potential in industrial wastewater treatment and in industrial processing for separating contaminated water into reusable water and a concentrate stream that also may be reusable. An example of the latter is in treatment of plating rinsewaters.

In addition to membrane systems such as reverse osmosis, where water passes through the membrane, leaving contaminants behind, there are systems in which the contaminants pass through the membrane. One of these that has been in use for many years is electrodialysis and a much newer method is pervaporation. In the latter method, volatile contaminants are vaporized through a membrane for which a vacuum or a stream of a carrier gas is maintained on the downstream side.

Reverse Osmosis

Ultrafiltration, hyperfiltration, and reverse osmosis have similar system configurations. Reverse osmosis will be described, but much of what is stated applies also to the other two operations. Reverse osmosis utilizes membranes that can exclude a large fraction of almost all solutes. The earliest membranes were made of cellulose acetate formulated in such a way that a very thin rejecting layer formed on the surface, with a much more porous layer beneath. Other materials are now available including thin-film composites. During operation, water under pressure is forced through the membrane. This water is called the permeate. To treat at practical flow rates, a large membrane area is needed. This need has been accommodated by development of several high area-to-volume configurations. One of these is the spiral wound module, which contains sandwiches of membrane and spacer material that are wrapped around an inner permeate collection tube and placed in a cylindrical pressure vessel. The permeate-carrying compartment is sealed around the edges. Feed entering one end of the cylinder is forced through the appropriate spaces in the membrane roll. Concentrate not passing through the membrane exits at the opposite end of the pressure vessel. Another high-surface configuration is the hollow fiber module. These modules contain bundles of reverse osmosis membrane in the form of fine hollow fibers. The ends of the fibers are mounted in a material such as epoxy. There are a number of specific configurations. These modules operate by having the water pass from the outside of the fibers into the hollow center, where it flows to one or both ends of the bundle. Two other configurations include tubular modules and plate-and-frame modules. Tubular modules contain much larger-diameter tubes with the reverse osmosis membrane in the interior of the tubes. Plate-and-frame modules contain stacks of circular membranes on supports with spacers between the membranes. The stacks are connected so that feed water flows upward through them and permeate is collected from each support. Neither the tubular nor plate-and-frame configurations have the surface-to-volume ratio that is possible with the other two configurations. The tubular modules have the advantage of being the easiest to clean.

To operate reverse osmosis, the feed water is forced under pressures of up to several hundred pounds per square inch through the modules. The minimum theoretical pressure to force water through the membrane is that which just exceeds the difference in osmotic pressure of the water on the upstream and downstream sides of the membrane. The osmotic pressure increases throughout the system as the contaminants in that stream are concentrated. In actuality, the operating pressure is usually well above the osmotic pressure. The water flows through the system until it emerges as a residual concentrate. The volume of this residual is an important consideration if it contains hazardous materials that interfere with simple methods of disposal. There are limits to which the water can reasonably be concentrated. Usually there is a minimum rate at which the water should flow along the membrane surface to minimize fouling and concentration gradients which can lead to unexpected precipitation of scaling materials on the membrane surface. As the feed stream is concentrated and reduced in volume by water passing through the membranes, the flow rate will decrease. In practice, a combination of staging of the membrane modules with decreasing membrane area in each stage, and some degree of recycling of the residual flow from a module back to that module to be mixed with new feed, could be used to maintain proper hydraulic conditions. As concentration on the upstream side increases, the concentration in the permeate also increases and may exceed either a discharge requirement or a reuse quality requirement. Finally, however, the concentrated stream reaches the point at which solubility limits are exceeded and precipitates begin to form. High turbulence can minimize precipitation or scaling on the membrane, but cannot totally prevent it. Calcium carbonate is a scale that commonly forms from treatment of natural waters because these waters contain calcium and a pH-dependent mixture of carbonate and bicarbonate alkalinity. To prevent this scale, feed water is acidified to convert the alkalinity to CO_2.

Fouling of the membranes is almost always found during operation of reverse osmosis and is also a problem with other membrane processes. Fouling is sometimes considered the same as scaling, but it differs from scale formation in not being the result of precipitation. The two can be found to occur together. Fouling results primarily from deposition on the membrane of suspended matter from the water. There is also the possibility of slimes forming from biological activity. One way to minimize fouling is to pretreat the feed water for removal of suspended matter. There are enzyme and chemical rinses that have been used to reduce fouling.

Electrodialysis

This treatment method is used to remove part of the ionic materials from water. It has been used for many years to partially demineralize heavily mineralized groundwater for production of potable water. The equipment consists of one or more stacks of membranes that have the ability to transmit either cations or anions, but not a significant amount of water. In each stack, the cation and anion membranes alternate and are separated by spacers that form a path for water passage. When a direct electric current is imposed on the stack of membranes, cations will tend to move toward the negative electrode and anions to the positive electrode. The ions can only pass through one membrane, however, before being blocked. The result is that the alternating spacer compartments become diluting compartments and concentrating compartments. All of the diluting streams are connected and produce the treated water. All of the concentrating streams are connected and produce a concentrate that must be disposed or possibly reused in the manufacturing operation.

Use of electrodialysis for pollution control is less flexible than reverse osmosis and some other treatment methods because it is not able to reduce the ionic content of the treated water to very low levels that might be required for discharge. Uses for industrial wastewater treatment would most likely occur where useful materials can be recovered from the concentrate stream and where the product water is acceptable for in-plant uses. Electrodialysis is subject to fouling and scale formation and operates most effectively on feed waters with very low concentration of suspended matter.

Pervaporation

As already indicated, this treatment method functions by the passage of volatile materials from an aqueous solution through a membrane to a gas phase consisting of a carrier gas or produced by a vacuum. Without considering the details of what occurs in the membrane, this method can be looked upon as a membrane-assisted evaporation that increases significantly the ratio of volatile materials to water in the gas phase compared to ordinary evaporation without a membrane. The treatment method accomplishes results similar to air stripping. It has the advantage over air stripping when using vacuum operation of capturing the volatiles in a highly concentrated form that may in some situations allow recovery and reuse. This technology is just beginning to reach the stage of commercial use, but could see rapid expansion in its application to process and waste streams.

66.3.6 Ion Exchange

Ion exchange has been used for many years for the softening of water and for production of deionized water. The technology is also being used for recovery of useful materials from in-plant streams and for treatment of some industrial wastewaters. With increased regulation of metals in wastewaters, increase in use can be expected. Traditionally, ion exchange has been used to remove only inorganic ionic materials by direct exchange with other ions on a solid matrix. Resins are now being produced by ion exchange resin manufacturers that remove some organic materials and selectively remove inorganic materials by more complicated mechanisms than simple ion exchange.

Ion exchange is carried out using granular, usually resinous, materials. The traditional ion exchange resins are cation or acid resins and anion or base resins. Furthermore, there are strong and weak acid resins and strong and weak base resins. The following equations describe two typical ion exchange reactions:

$$R_1\mathrm{H} + M^+ \rightarrow R_1M + \mathrm{H}^+$$

$$R_2\mathrm{OH} + A^- \rightarrow R_2A + \mathrm{OH}^-$$

where R_1 = a cation or acid resin
R_2 = an anion or base resin
M^+ = a metal ion
A^- = an anion

Both of these reactions are easily reversible. If the resin in the form R_1M were treated with acid, M^+ would be liberated and the resin would revert to the acid form $R_1\mathrm{H}$. If the base resin were treated with a base, A^- would be liberated and the resin would revert to the base form $R_2\mathrm{OH}$. If water containing the neutral compound MA were passed through a column of $R_1\mathrm{H}$ and then a column of $R_2\mathrm{OH}$, the water could be demineralized. $R_1\mathrm{H}$ could be a strong acid or a weak acid cation resin. The difference is that the strong acid resin will function over a wide range of pH. Weak acid resins have a stronger affinity for H^+ than the strong acid resins and do not function well at low pH (high

H^+ concentration). If there were a large amount of M^+ in solution, the large amount of H^+ potentially entering the water phase might result in only partial M^+ removal. A strong acid resin would be a safer choice. Weak base resins, on the other hand, function well under acid conditions. A weak base resin could be used to complete the demineralization. If the weak base resin were placed before the cation exchange resin, it would not remove A^- significantly from a solution of a neutral salt.

As the ion exchange materials are exposed to more and more water, their ion exchange capacity is finally exhausted. The active sites in this case would have either M or A attached. At this point, the resin columns must be regenerated, the cation exchange resin with an acid such as sulfuric acid and the anion exchange resin with a base such as sodium hydroxide. The primary reason for using the weak acid and weak base resins whenever possible is their greater ease of regeneration. The most effective regeneration, utilizing only a slight excess of regenerant, would be accomplished by passing the regenerant solutions countercurrent to the direction of flow of the water being treated. In many systems, however, the resins are first backwashed before regeneration. Backwashing mixes the resin particles and eliminates the advantage of countercurrent regeneration. In these systems, both treatment and regeneration would most likely be downflow. Backwashing is done to flush from the beds particulate matter that might cause fouling and loss of ion exchange capacity. For most effective operation, the feed to an ion exchange system should have a very low concentration of particulate matter. Both the backwash and the used regenerant streams represent a waste. The volume of this waste would usually be only a small percentage of the volume of water treated. The objective of ion exchange is to concentrate the contaminants in a small volume. For industrial wastes containing hazardous materials, disposal becomes a problem. In these cases, recovery for reuse of the hazardous material has obvious advantages. There is also an obvious advantage to reusing the clean product water.

The above discussion was aimed at giving a general understanding of ion exchange. For industrial waste treatment, deionization would not be a likely objective. Possibly only a cation exchanger would be involved, or, as in the case of one chromium recovery system,[6] a cation exchanger for removing metallic ion impurities followed by an anion exchanger for removal of chromate. In addition, there are some organic removing resins that may use an acid or base for regenerant or may use a solvent.

Table 66.2 summarizes the industrial wastewater treatment technologies included above.

Table 66.2 Industrial Wastewater and Hazardous Waste Treatment Technologies

Technology	Contaminants Removed	Typical Applications
Chemical precipitation and clarification	Particulates BOD associated with particulates Trace metals when appropriate precipitants are used	Treatment prior to discharge to a public sewer Treatment prior to particulate sensitive technologies such as granular activated carbon and membrane processes
Activated carbon adsorption	A very broad range of soluble organic materials	Many industrial wastes containing soluble organic materials
Air stripping	Highly volatile materials	Dilute solutions of volatile materials, including industrial wastewaters, drinking water sources, contaminated groundwater and contaminated soil
Steam stripping	Volatile materials of lower volatility than appropriate for air stripping and at higher concentrations	Dilute to moderately concentrated solutions of a wide range of volatile materials
Reverse osmosis	A high proportion of organic and inorganic contaminants	To produce very-high-quality water
Electrodialysis	Inorganic ions	To remove a significant fraction of minerals from water
Pervaporation	Highly volatile materials	Not yet widely used Uses similar to air stripping
Ion exchange	Primarily inorganic ions	Deionization For recovery of ionic materials from industrial aqueous streams and industrial wastewaters

Capital and operating costs have not been included because of wide variability likely for different applications. Demineralization technologies can be expected to be somewhat more expensive than the other technologies.

66.3.7 Other Methods

There are a great many other technologies that could be included. In some cases, the methods are more closely associated with chemical processing than pollution control. In some cases, they have very limited or very specific uses. Some technologies might show promise, but are not far enough along in their stage of development to be considered for full-scale use. Treatment of contaminated soils and groundwaters has become increasingly important as the public has been informed by EPA and other environmental groups of the large number of contaminated sites that exist. Incinerators of various kinds have been used to destroy both concentrated hazardous organic wastes and soils contaminated with hazardous organic materials. At the time of this writing, incinerators are receiving a large amount of criticism because of the air pollution they can create if not properly operated. Thermal desorption, which vaporizes organic materials from contaminated soils, has been used at a number of sites. The air pollution risk from this process is substantially less than from incineration. Solvent extraction is usually thought of in the chemical industry as a method for concentrating solutes from a liquid processing stream into another liquid stream. The technology has been applied to contaminated soils for extraction of contaminants into a liquid stream. Solidification has been used to greatly reduce the pollution threat from contaminated soils. This technology utilizes addition of chemicals to the soil to create a solid mass with a very low rate of contaminants leaching. It is generally more effective with inorganic contaminants than organic. One form of solidification involves electrical heating of the soil to form a vitreous mass.

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