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Treatment of Petroleum Refinery, Petrochemical and Combined Industrial-Municipal Wastewaters With Activated Carbon

Literature Review

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TREATMENT OF PETROLEUM REFINERY, PETROCHEMICAL AND COMBINED INDUSTRIAL-MUNICIPAL WASTEWATERS WITH ACTIVATED CARBON

Literature Review

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in groundwater; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows, (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries, and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American people.

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ABSTRACT

The Environmental Protection Agency, Effluent Guidelines Division, has prominently mentioned activated carbon adsorption as an attractive treatment concept for satisfying wastewater treatment objectives established by P. L. 92-500, which calls for "best available treatment economically achievable" (BATEA) by July 1, 1983. The recent interest in removal of toxic compounds generated by the settlement agreement between EPA and the Natural Resources Defense Council has also led to consideration of activated carbon adsorption as a part of an industrial wastewater treatment scheme.

A review of the literature on activated carbon adsorption as a treatment concept for petroleum refinery, petrochemical plant, and combined industrial-municipal wastewaters is presented in this report. The principal time period reviewed was 1963-1976. A total of 241 references are cited. These references cover the various aspects of carbon adsorption and its application in the treatment of industrial and municipal wastewaters. An additional 65 references are listed in the Bibliography. These include literature from foreign sources, literature not located during the original search, and literature published after the original search was completed.

There is ample evidence in the literature reviewed to suggest that activated carbon adsorption, using either granular or powdered carbon, should be considered when evaluating treatment alternatives for industrial wastewaters. Successful applications of this mode of treatment have been claimed at numerous municipal, industrial, and combined municipal-industrial installations.

It must always be remembered, however, that there is no single wastewater treatment system which can be applied in all cases. There is enough variations in the adsorption behavior of organic compounds so that adsorption may not always provide a suitable removal process. Each industrial operation has its own effluent characteristics and requirements. Availability of land, complexity of operation, cost of treatment facilities, and variations in wastes all combine to make each wastewater treatment system unique. The optimum treatment system for any given operation can be designed only after careful study of the entire problem and preliminary evaluation of several alternate designs.

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SECTION I

INTRODUCTION

Petroleum refineries and petrochemical plants are faced with the problem of disposing of huge volumes of wastewaters from a wide variety of sources (1,2). Characteristics of these wastewaters vary considerably. Both quality and quantity may fluctuate significantly within a plant. Differences may be even greater between different facilities.

As the petroleum industry strives to comply with provisions of the 1972 Federal Water Pollution Control Act (P.L. 92-500), an intensified interest in use of the adsorption process to treat plant effluents or selected wastewater streams within the plant complex has developed (2,3).

In recent years it has become apparent that conventional biological treatment may not be the optimum solution to all waste treatment problems. Although conventional biological processes are designed to remove organic material from wastewater, neither the trickling filter nor the activated sludge process effectively removes the last portion of this organic material (4). This material, soluble or colloidal, resistent to biological degradation, is often termed "refractory." Industrial wastewaters may contain either refractory substances or materials deleterious to the performance of biological systems (5). Furthermore, operating difficulties, sludge handling problems, and large land requirements are intrinsic to biological processes. These factors have led to consideration of alternative treatment processes.

Of all advanced waste treatment processes, activated carbon adsorption is getting the most attention by industry and appears to be applicable in refinery and, to some extent, petrochemical operations (6). It is not expected that any one process will be universally applicable. The varied nature of the problem, the character of the wastes to be treated, the geographical and logistics considerations, the extent of reuse required, etc., make this probability unlikely.

The use of activated carbon for removing dissolved organics from drinking water and wastewater has long been known to be feasible. The increasing need for highly polished effluents, necessary to accommodate stringent requirements for both surface water quality and water reuse, has stimulated great interest in carbon treatment systems. Adsorption makes it possible to remove compounds that are not readily degradable by biological methods and gives excellent removal of taste, color, and odor (7). Cooper and Hager (8) stated that activated carbon is effective in removing refractory compounds. Furthermore, carbon is effective in adsorbing organics below the concentration where biological treatment systems are efficient. Hager and Reilly (9) presented data

showing that the adsorption process can produce a considerably higher removal of organic contaminants than could be expected from the activated sludge process alone. Kwok (10) observed that activated carbon exhibits a strong adsorptive affinity and an appreciable adsorptive capacity for a wide variety of organic compounds.

Adsorption on activated carbon, both granular and powdered, has been investigated extensively in recent years because of the ability of carbon to adsorb organic materials from wastewater (11). Shell et al. (12) reported that soluble organic materials can generally be removed from wastewaters by activated carbon adsorption; however, certain organic materials do not adsorb on activated carbon, or do so slowly.

Coughlin (13) states that activated carbon is one of the most promising solid adsorbents for removing organic compounds owing to its commercial availability, high adsorption capacity, and affinity for a broad spectrum of chemical compounds. Hager and Reilly (9) report that a wide variety of industrial wastewaters are presently being treated by granular activated carbon.

Swindell-Dressler Company in their manual on carbon adsorption prepared for the Environmental Protection Agency Technology Transfer (14) report that the use of activated carbon for removal of dissolved organics from water and wastewater has long since been demonstrated to be feasible. In fact, it is one of the most efficient organic removal processes available. Both the great capability for organic removal and the overall flexibility of the carbon adsorption process have encouraged its application in a variety of situations. The process readily lends itself to integration into large, more comprehensive waste treatment systems.

Loven (15) reported that the carbon process, usually in conjunction with other processes, functions to remove gross oxygen-demanding and refractory organics, color, and specific pollutants such as phenolic compounds and chlorinated hydrocarbons. Loven feels that as the trend continues toward increased limitation on discharges of hazardous substances, the need for carbon treatment grows.

Physicochemical treatment has proved to be a viable method for achieving improved effluent and receiving water quality. The nucleus of most physicochemical treatment plants is an activated carbon system (16). The authors reported that in 1975 more than 20 municipalities in the U.S. were designing, constructing, or operating physicochemical facilities for wastewater treatment; the number of industrial facilities was an order of magnitude higher. According to Weber and Crittenden (16), this number is expected to increase rapidly in the next decade.

Sigsworth (17) has reported the use of active carbon in a number of industrial applications for reclaiming solutions which otherwise might constitute wastes. Burleson et al. (18) reported that activated carbon treatment of some industrial effluents will remove up to 85% of the refractory organic material expressed as total organic carbon (TOC). The concentration of organic

substances measured as COD has been reduced to 5-15 mg/l depending on previous treatment, carbon dosage, and contact time in the adsorber (7). A broad-range study of a number of industrial wastewaters has shown activated carbon adsorption to be applicable as a viable treatment alternative (19, 20).

Granular activated carbon treatment of water and wastewater in large volume systems began in the U.S., England, and Germany in the early 1960's (19). Hager purposed that the development of granular activated carbon capable of reactivation and reuse made adsorption an economic alternative for removal of dissolved organic contamination from wastewater. He also stated that a comprehensive list of all installations since the early 1960's is not readily available, but the technology is being applied worldwide in a number of European countries, Japan, and Africa.

Culp and Culp (21) stated that the use of granular activated carbon for the adsorption of organic materials from wastewater has become firmly established as a practical, reliable, and economical unit process for water pollution control. Although no unit operation represents a universal cure for dissolved organic removal, the adsorption process utilizing granular activated carbon as a domestic tertiary system has been reported as leading all others in acceptance (22, 23) Cover and Wood (24 reported that tertiary wastewater treatment with granular activated carbon has been found to be an efficient and reliable process for organics removal. The authors stated that granular carbon has proved itself capable of removing such organic chemical compounds as phenol, polyols, herbicides, pesticides, detergents, trinitrotoluene, dyes, and a host of pollutants measured as BOD_2, COD, TOC, color, and odor. Joyce et al. (25) have shown that the organic contents of secondary sewage effluent can be reduced significantly by granular activated carbon treatment in a column process under a wide range of conditions. Davies and Kaplan (26) reported that granular activated carbon systems can remove about 70% of the organics from biologically treated effluents.

Davies and Kaplan also noted that powdered carbon systems have faster adsorption rates than granular systems but that utilization had been limited because of difficulties in handling and regeneration. Powdered activated carbon was first reported as an aid to sewage treatment for overloaded activated sludge plants in 1935 (27). Carbon was observed to improve sludge compaction and filtration. Berg et al. (28) reported that adsorption on powdered activated carbon has been proven to be a feasible method for removing the bulk of dissolved organic materials from a municipal secondary effluent; however, the cost of carbon is such that it must be regenerated and reused.

Operating under all the typical quantity and quality variations encountered in a full-scale sewage treatment situation, Burant and Vollstedt (29) demonstrated that powdered activated carbon used in an activated sludge type process is capable of producing an unusually high-quality effluent. Extensive, full-scale field tests involving a variety of industrial and municipal wastewaters have demonstrated that powdered activated carbon improves organics removal, solids settling, color removal, and foam reduction when added to activated sludge treatment processes (3, 30, 31).

Effluent Guidelines development documents published by the Environmental Protection Agency prominently mention carbon adsorption as an attractive treatment concept for satisfying wastewater treatment objectives established by P.L. 92-500, which calls for "best available treatment economically achievable" (BAT) by July 1, 1983.

No one process, however, can be expected to be the ultimate solution for all wastewater treatment problems. Carbon adsorption is no exception. It is only one of several alternative treatment processes which should be considered for use in a given situation. An optimum treatment system can be selected only after careful evaluation of these alternatives.

The purpose of this report is to present a review of the available literature on activated carbon adsorption as it pertains to the treatment of petroleum refinery, petrochemical plant, and combined industrial-municipal wastewaters. A review of the literature pertaining to adsorption kinetics and process design criteria is also presented, since these aspects are crucial for successful application of the adsorption process for treatment of any wastewater.

SECTION II

APPLICATION OF CARBON ADSORPTION IN WASTEWATER TREATMENT

The technical literature includes numerous case histories regarding the viability of adsorption for removal of many potential contaminants from wastewaters. Full-scale granular activated carbon installations are currently removing toxic or biological refractory contaminants from wastewaters, and exhausted carbon is being reactivated for reuse (32).

Cover and Pieroni (33) presented a literature review of tertiary wastewater treatment giving special attention to activated carbon adsorption. Hager and Fulker (34) discussed the use of granular carbon in wastewater treatment. Examples of industrial and municipal application are given. Ford (35) prepared an excellent treatise presenting pertinent and current information on activated carbon treatment of municipal and industrial wastewaters. This comprehensive paper contains 33 references, 24 figures, and 30 tables. Basic concepts are included as well as case histories with which the author is familiar.

The effectiveness of tertiary treatment for domestic and some industrial wastewaters has been demonstrated in many bench and pilot-plant studies and amply confirmed by plant-scale operations (36). However, tertiary treatment is not without limitations. Operation of the secondary stage can be adversely affected by: (a) fluctuations in temperature and pH; (b) surges in flow of incoming wastewater; (c) sudden inflow of toxic substances. These limitations led to investigations of direct applications of advanced waste treatment processes to raw wastewater usually after primary separation of visible solids. The author noted that cumulative data from bench and pilot-plant research have been impressive.

COMBINED INDUSTRIAL-MUNICIPAL WASTES

Municipal wastewater treatment using activated carbon adsorption as both a tertiary and direct physical-chemical application was summarized and discussed by Swindel-Dressler Company for the EPA Technology Transfer (14). Much of the information presented is based on evaluation and operation of pilot, demonstration, and full-scale plants.

Cohen (5) presented a comparison of carbon adsorption and activated sludge treatment processes for removal of organic material from a primary effluent. Results of the 6-week study conducted at Lebanon, Ohio, showed that carbon adsorption was more efficient in the removal of organics than activated

sludge. Cohen and Kugelman (37) described a system of physical-chemical treatment using carbon adsorption, surveyed the performance of some pilot plants, and gave cost estimates for various sized plants. Joyce et al. (25) reported on a study to determine the economic practicality of using granular activated carbon adsorption to treat secondary effluents. Not only was the organic content significantly reduced, but the feasibility of reactivation and reuse of granular carbon in wastewater treatment was demonstrated.

Direct application of adsorption by granular activated carbon to a primary effluent was examined and reported on by Weber et al. (38) and Hopkins et al. (39). This concept was derived partly from observations by Joyce et al. (25) and Parkhurst et al. (40) regarding the apparent difficulty of removing final traces of organic materials from secondary effluents by treatment with activated carbon as well as the relative economics of a two-stage versus a three-stage system. In a 7200-gallon-per-day pilot-scale facility operated for one year, these workers observed overall organic removals from the combined industrial-municipal wastewater of 95-97%. These levels of removal were maintained constantly despite variations in organic loadings and the presence at times of toxic chemicals which would affect normal biological processes adversely. The work described by Weber et al. (38) and Hopkins et al. (39) represents a significant contribution to the literature on granular carbon treatment systems. A substantial amount of well-documented data was presented. The authors most importantly point out the limitations of such systems--in particular, the difficulty in controlling hydrogen sulfide formation in the columns and the presence of non or slowly sorbable organic fractions in the process effluent.

Hatheway (41) summarized results of studies undertaken to determine methods of removing total organic carbon (TOC) from municipal and industrial wastewaters with the discussion focusing on the physical-chemical process of activated carbon adsorption. Granular activated carbon adsorption, when used in conjunction with chemical precipitation and filtration, was found to remove 95% or greater of TOC, BOD, COD, Total Phosphates, and Suspended Solids and 78% of Total Nitrogen. Examples of plant variables, data, and costs are also given.

The concept of applying direct physical-chemical processes utilizing activated carbon adsorption for treatment of municipal wastewaters was pursued by Weber (42). Operating results from several different pilot installations were summarized.

Fuchs (43) reported that the first major full-scale physical-chemical plant for treatment of municipal wastewaters had gone on stream and that many more were nearing completion. The status of four of the plants was reviewed, including the on-line plant in Rocky River, Ohio, which treats almost totally domestic sewage. Construction of the Niagara Falls plant was reported to be completed in late 1976. Influent to the plant will be approximately 75% industrial wastewater high in phenol and chlorine. The toxic nature of this waste eliminated consideration of biological treatment. A unique feature on the final design for a 15.3-mgd plant in West Fitchburg, Massachusetts, is separate primary clarifiers for industrial (two paper mills) and municipal

wastewaters. Effluents from the separate clarifiers will be combined for feed to 12 carbon adsorbers.

Parker and Callahan (44) reported on the proposed construction of two advanced wastewater treatment plants at Fitchburg, Mass. The East Fitchburg plant is a 12.4-mgd two-stage activated sludge facility with phosphate removal and nitrification to treat domestic wastewaters. The West Fitchburg plant is a 15.3-mgd activated carbon plant that will treat primarily industrial (paper mill) wastewaters. Pilot studies showed that the activated carbon process achieved better and more consistent removal of BOD, COD, and color under all industrial loading conditions. Callahan and Pincince (45) reported that the two plants had been constructed and were in operation. They examined the performance based on available operating information.

Flynn and Thompson (46) reported on extensive pilot-plant studies at Niagara Falls which demonstrated that physical-chemical treatment could be used successfully for providing the equivalent of secondary treatment on combined industrial-municipal wastewaters with variable characteristics. Industrial surveys, interviews, and pilot-plant work were supplemented by close liason with the industries. This industrial-municipal cooperation benefited both parties, since technical problems of collection and treatment were mutually solved and the costs were shared.

Joyce and Sukenik (47) reported that activated carbon in packed-bed column contactors removed much of the organic matter in secondary effluents from municipal sewage treatment plants. They noted, however, that for the process to be economically attractive, carbon must be reactivated and reused.

Sulick (48) discussed various methods of tertiary treatment of sanitary wastewaters with particular emphasis on activated carbon adsorption. He proposed adsorption with granular activated carbon as the technological tool applicable for removal of nondegradable organics from these wastewaters. Furthermore, adsorption could remove either dissolved or suspended organics and suspended or settleable inorganic solids.

In an additional paper, Sulick (49) reviewed the operation of three municipal tertiary wastewater treatment plants. With a granular carbon exhaustion rate of approximately 250 pounds per million gallons of wastewater treated, the Lake Tahoe plant has consistently produced an effluent with 10 mg/liter of COD and 1 mg/liter of BOD_5. Water produced by the plant in Orange County, California, meets drinking water requirements and is injected into the Orange County ground-water basin. The plant at St. Charles, Missouri, has two interesting features which make it unique. First, the granular carbon process is not preceded by filtration; the secondary effluent is applied directly to the carbon. The second unique design feature is that chlorination takes place prior to carbon filtration for ammonia-nitrogen removal.

The effectiveness of granular activated carbon for continuous treatment of an unfiltered activated sludge effluent was demonstrated in Pomona, California, (50). A 0.3-mgd, four-stage, fixed-bed, granular activated carbon pilot plant was operated for a 4-year period. High-quality product water,

characterized by a COD of 10 mg/liter was produced on a routine basis. Regeneration of the carbon was shown to be a feasible process; and successful backwashing of the first-stage carbon, which serves as a filter and an adsorber, made pretreatment of the effluent unnecessary.

Zanitisch and Morand (51) reported on results of a study at a 120-mgd activated sludge treatment plant receiving combined industrial-municipal wastewater containing organic dyes. Applying the plant effluent to granular activated carbon columns produced a colorless effluent with an average BOD_5 and suspended solids of 3 mg/liter each in the 61-day trial.

Barnes et al. (52) discussed in detail the operation and performance of a pilot-scale waste treatment facility at Owasso, Michigan, which demonstrated the feasibility of using chlorination followed by dechlorination with granular activated carbon for removal of ammonia-nitrogen from a domestic wastewater source. The pilot facility removed an average 85% of the ammonia-nitrogen applied to the system. Barnes stated that complete removals could be obtained if desired.

Bishop et al. (53) reported on the physical-chemical treatment of raw wastewater in a 50,000 to 100,000-gpd pilot plant consisting of two-stage lime precipitation with intermediate recarbonation, filtration, pH control, ion exchange or breakpoint chlorination for nitrogen removal and carbon adsorption. The complete system with breakpoint chlorination removed approximately 98% of phosphates, 94% of COD, and 86% of total nitrogen. Addition of 10 mg/liter of chlorine to influent filter controlled biological growth and produced filter runs of greater than 50 hours. Chlorination oxidized ammonia to nitrogen gas leaving a residual ammonia-nitrogen concentration of less than 0.4 mg/liter. Without chlorine addition, heavy biological activity in the columns resulted in hydrogen sulfide production with 2-3 mg/liter in the effluent.

A carbon adsorption plant to recover p-cresol from a wastewater process effluent stream by adsorption on granular activated carbon followed by chemical regeneration was piloted, designed, and constructed to meet air pollution standards (54). Additionally, it was noted that the unit had been in satisfactory operation for more than a year, not only reducing emissions to acceptable levels but also returning a valuable product to the process, eliminating odor problems, and reducing the discharge of pollutants in wastewaters being discharged to the Metropolitan Sanitary District of Greater Chicago. Design and installation of the system was based on laboratory and pilot-plant work cited plus an economic evaluation indicating an after-tax return which would pay back the installation cost in less than two years.

The Chipman Division of Rodia, Inc., has succeeded in stripping dangerous levels of toxic phenolic compounds from wastewaters flowing from its herbicide plant by installing an adsorption-filtration process using activated carbon (53). The system was installed to pretreat wastewaters prior to introduction into the municipal sewage treatment facility. The carbon system reduced the phenolics concentration below the required limit of 1.0 mg/liter. Cost and performance of the system outmatched several alternatives including a conventional biological system, alterations to the then-existing chlorination system,

substitution of bromine for chlorine, ion exchange, and oxidation using ozone, peroxide, and permanganate. Total expenditures were $300,000 for a plant that treats 150,000 gallons of wastewater per day. The 1971 operating costs were estimated to be 35.6 cents per 1,000 gallons of treated water.

Shuckrow et al. (56) developed and pilot-tested a powdered activated carbon treatment system for raw and combined sewage. Shuckrow and his co-workers (57) successfully demonstrated this physical-chemical process utilizing powdered activated carbon on a 100,000-gpd scale at Albany, New York. This project established the technical and economic feasibility of this process for sewage treatment while removals in excess of 90% COD, 94% BOD_5, and 99% suspended solids were consistently achieved. The workers noted that the carbon dosage could be adjusted to effect the degree of organics removal required. Additionally, a residual, nonsorbable fraction ranging from 10-20 mg/liter BOD_5 and 20-50 mg/liter COD existed at times which could not be removed at carbon dosages as high as 1,000 mg/liter.

Burns and Shell (58) discussed treatment of a municipal wastewater by chemical coagulation-precipitation, powdered activated carbon adsorption, and granular media filtration. The Powdered Activated Carbon-Physical Chemical Treatment (PAC-PCT) system as depicted in a nominal 100-gpm pilot plant produced a treated effluent similar to that expected for biological treatment followed by tertiary treatment for phosphate removal. Solids contact units were used for chemical treatment and carbon contacting. Spent carbon was gravity thickened, vacuum filter dewatered, and thermally regenerated in a fluidized-bed furnace. The process produced a highly clarified effluent with COD values of 8-36 mg/liter for carbon dosages of 350-75 mg/liter.

Additional pilot-plant work with the above process was reported by Burns et al. (59) and Wallace and Burns (60). During the 16-month study period, a high-quality effluent was consistently produced. Soluble organic materials were found to be removed by a combination of chemical coagulation, anaerobic biological activity, and adsorption on powdered carbon. Using alum or ferric chloride pretreatment and two-stage countercurrent carbon contacting (100 mg/liter), the PAC-PCT process consistently produced an effluent of 5 mg/liter COD and suspended solids and 0.3 mg/liter phosphate. Powdered carbon regeneration using a fluidized-bed furnace resulted in fixed carbon recoveries on the average in excess of 90%. Thermally regenerated carbon did not exhibit full recovery of adsorption capacity; but when reused in the PAC-PCT process, no significant loss of treatment effectiveness was found.

Burant and Vollstadt (29) reported on a full-scale demonstration of sewage treatment with powdered activated carbon and carbon regeneration with wet air oxidation at Rothschild, Wisconsin. This study successfully demonstrated that powdered activated carbon could be used in the conventional activated sludge process to provide highly efficient wastewater treatment and that spent carbon could be effectively regenerated for reuse by a partial wet air oxidation process. The authors reported that powdered carbon acts as a treating and weighting agent compacting a large number of organisms into a small volume. Data generated reflected improved removals of BOD_5 and suspended solids. It was observed that an unusually high-quality product water

could be produced at a cost only slightly higher than that of conventional activated sludge treatment.

Powdered activated carbon was added to the aerator of the activated sludge process of the Norfolk, Nebraska, water pollution control plant to help solve operational problems (61). The plant had a 2.1-mgd average flow containing 35-50% meat packing wastes. Despite the fact that flows were less than 60% of design capacity, the plant effluent was characterized by high and variable solids content. After the powdered carbon concentration reached 200 mg/liter, average effluent solids concentration decreased 67%, sludge volume index decreased 33%, secondary sludge solids decreased 28%, and sludge bulking was essentially eliminated. Furthermore, despite a 10% higher organic load, effluent BOD_5 concentrations were maintained at about 4 mg/liter. Other noticeable improvements were reduction in effluent color, plant odors, and aerator foam.

Adams (62, 63) discussed laboratory and full-scale tests using powdered carbon in upgrading the performance of anaerobic digesters. In both laboratory reactors lignite carbon increased methane production fivefold. At a 2-mgd activated sludge plant, a carbon dosage of 100 pounds per day significantly reduced sludge volume by providing sites for anaerobic reactions to occur, thus breaking down more volatile solids. Adams proposed that long-term use of powdered carbon could reduce sludge handling costs by 60-70%. He also noted that powdered carbon would adsorb toxic materials such as pesticides or heavy metals that inhibit the anaerobic system.

Adding powdered activated carbon to anaerobic digesters at the Norristown, Pennsylvania, sewage treatment plant markedly improved operation of that plant (64). In addition to adsorbing organics and reducing odors, powdered carbon reduced solids settling and increased gas production.

INDUSTRIAL WASTEWATER TREATMENT

Activated carbon adsorption systems, widely used in the chemical process industries for several decades, are now assuming an important role in cleaning up plant effluents (36, 65). Sigworth (17) reviewed the uses of active carbon in treatment of trade wastewaters, particularly for the reclamation of valuable products. Myrick et al. (66) discussed the theory of adsorption, with particular emphasis on the use of active carbon as an adsorbent for polluting materials in trade wastewaters. Cohen (5) briefly reviewed the use of physical-chemical processes to remove polycyclic hydrocarbons (carcinogens), metals, pesticides, and viruses from wastewaters.

Adsorption studies have indicated that most of the EPA proposed dissolved toxic organic chemicals may be removed from wastewaters by activated carbon (32). Furthermore, other similar chemical contaminants, aromatic, nonpolar, high-molecular-weight compounds, such as OSHA-defined carcinogens and other chemicals under examination by EPA for inclusion on the toxic chemicals list, are also predicted to be adsorbable from wastewater by activated carbon. Hager (20) reported that data from adsorption isotherms on water samples containing aldrin, dieldrin, endrin, toxaphene, DDD, DDT, DDE, and PCB (toxic

chemicals defined by EPA) revealed that the toxic chemicals in all samples were reduced by more than 99%.

Rizzo (67, 68) discussed case histories of the successful use of activated carbon adsorption in treating industrial wastewaters. He proposed that these case histories depict the versatility of granular carbons in respect to removal of many different kinds of organic compounds.

Activated carbon adsorption has been demonstrated as an effective method for improving the effluent quality of textile dying wastes (69). Porter (70) conducted a pilot-plant study on a textile waste stream using chemical coagulation carbon adsorption as the treatment system. Results indicated that color and organic contaminants could be removed by both. Carbon adsorption was also found to be suitable for regenerating the raw wastewaters for reuse without chemical clarification. MacCrum and VanStone (23) discussed the successful use of granular activated carbon in the treatment of wastewaters from two textile mills. In both instances treated wastewaters are reused in normal plant operations.

Phipps (71) described the wastewater reclamation system at the Hollytex Carpet Mills plant in Southampton, Pennsylvania. The key element in the reclamation system is an adsorber containing 50,000 pounds of granular activated carbon. The adsorber reclaims 80% of the wastewater discharged from the plant's carpet dying operation. The remaining 20% is discharged intermittently to the municipal sewer system.

Full-scale field tests have shown that powdered activated carbon added to activated sludge systems can resolve unique operating problems and upgrade the quality of biological treatment (72). Several case histories are presented which show that powdered carbon addition to activated sludge plants has improved removals of organic pollutants, aided solids settling, improved aeration efficiency by reducing foam, adsorbed color bodies, and protected biological systems from shock or toxic loadings. The carbon has also been found to level effluent quality at plants subject to periodic organic or hydraulic overloads.

Georgia-Pacific developed a temporary treatment system for investigation of the feasibility of using granular activated carbon to decontaminate impounded resin plant wastewaters before discharge to a natural stream (73). Operation of the temporary system, as well as bench-scale laboratory and field trials upon which the system was developed, is discussed.

Lang et al. (74) conducted a 4-year pilot-plant program to investigate the technical and economic feasibility of treating unbleached Kraft pulp and paper mill effluent for reuse. It was concluded that water of reusable quality could be provided by several combinations of treatment utilizing activated carbon. Reusable water quality was defined in this study as 100 color units and 100 mg/liters TOC. A microlime-carbon process that uses low dosages of lime and clarification followed by carbon adsorption in down-flow granular carbon beds was the most economical treatment scheme indicated by estimated capital and operating costs. A novel continuous countercurrent process (FACET) for carbon adsorption using stirred tanks of carbon slurries (75, 76)

was shown to have considerable promise for reducing capital and operating costs, and its development is being continued.

Kraft mill evaporator condensates have a relatively small volume with a high polluting load. Treatment of these wastes by activated carbon before they are mixed with other mill effluents was investigated by Hansen and Burgess (77). In batch and continuous-flow tests using two types of carbon, it was found that activated carbon could remove 75% of the organic material from the Kraft mill condensates; this could not be greatly improved by varying load and contact periods. Extended contact periods in batch tests reduced toxicity to the mussel, Mytilus edulis, by factors up to 17; but in column tests, with shorter contact periods, toxicity was reduced only by factors of 2-5.

Kroop (78) concluded from laboratory tests that granular activated carbon adsorption with thermal regeneration was the best treatment process to use for treating large volumes of phenolic wastewaters generated by aircraft paint stripping. Carbon adsorption would provide better reduction of phenolics and COD and would be less expensive to construct and operate than other methods. The phenolic concentration was reduced to less than 10 mg/liter in the first 5 minutes of contact time, after which removal proceeded at a slower rate. A contact time of 75-100 minutes was required to reduce phenolics to 3.1 mg/liter or less and a residual COD of less than 200 mg/liter. Kroop also noted that the total chromium concentration was substantially reduced by "plating out" on the activated carbon.

Based on information from actual field studies conducted at a steel producing plant, VanStone (79) reported that the phenol content of coke plant wastewaters could be reduced to less than 0.1 mg/liter by a treatment system consisting of clarification, adsorption with granular activated carbon, and catalytic oxidation. Additionally, it was noted that the process could handle toxic materials such as phenolics and cyanides and would not be affected by fluctuations in the concentration of dissolved organics. The economics were reported to be favorable in most cases.

El-Dib et al. (80) investigated the efficiency of granular carbon columns in removals of two carbamate pesticides, Sevin and Baygon, from polluted waters. Adsorption was found to conform with Freundlich and Langmuir isotherms. The workers concluded that adsorption of total carbamates was dependent on their chemical structure and branching of side chains.

Results of various stages of a demonstration pilot-plant study applying the activated carbon process to treat actual rinse waters from a hard chrome plating operation indicated that activated carbon adsorption for chromium removal may have practical application in many small plating plants (81). A demonstration pilot-plant study was conducted by Batelle-Columbus employing actual rinse waters from a zinc cyanide plating operation (82). The pilot system operated at 99% efficiency of cyanide removal. Cost estimates for the process were given.

Hager (19, 20) reported on a broad-range adsorption study on industrial wastewater purification. A series of adsorption isotherms tests was run on 327 samples of wastewater representing 104 manufacturing operations to determine the effectiveness in reducing TOC concentrations. Selected removals of color and phenol were also evaluated. Results of the tests were tabulated by Standard Industrial Classification (SIC) for convenient reference. Hager noted that results revealed only the degree of purification that might be achieved and the approximate amount of carbon required to reach the treatment objective. Examination of the survey data from the six major water-consuming industries shows subtle differences in the degree of purification achievable by carbon adsorption.

Subsequent to tests conducted on the initial 220 samples (19), several plants elected to conduct pilot studies to determine system design data. Following these pilot studies, adsorption systems for treatment of a wide variety of contaminants were installed at 15 plants. Hager (20) presented design parameters covering prominent features of the 15 systems. He noted that in every case some form of pretreatment has to be used prior to carbon adsorption. Flows for the 15 systems range from 6,000 to more than 1 million gpd with carbon contact times ranging from 8 minutes to approximately 23 hours. In some instances carbon adsorption has been installed to remove toxic chemicals prior to biological treatment. These chemicals, toxic in nature, would have a tendency to retard biological activity of the system. In two cases, adsorption has been added after a biological system because the biological system could not meet stated objectives. In both cases, the TOC has been reduced to 1.0 mg/liter or less. All systems rely on off-site reactivation where both rotary kilns and multiple-hearth furnaces are employed. Hager observed that treatment objectives have been met at all 15 installations.

PETROLEUM REFINING

Numerous comparative pilot granular studies and several full-scale in-plant powdered carbon evaluations have been conducted by ICI United States, Inc., to determine the effectiveness of carbon in solving refinery wastewater treatment problems (3). Results of these studies have shown that refinery wastewaters can be successfully treated with granular carbon in columns or powdered carbon added to activated sludge systems.

Ford and Buerklin (83) reported on extensive pilot-plant evaluations using activated carbon as both a total treatment process and as an effluent polishing unit for treating petroleum refinery and petrochemical wastewaters. The authors stated that, generally speaking, the total carbon system is not satisfactory because of "excessive" leakage of organics. Limitations of using carbon adsorption as a total treatment process are underscored. Synergism of biological-carbon treatment was demonstrated. Practical realities and economics of system operation were also discussed.

Carbon treatment has been proposed by Hale and Myers (84) as a relatively efficient method for removing organics from refinery wastewaters. Data are presented illustrating that an activated sludge treatment system reduced saturates and aromatic organic materials to low levels in the final clarifier effluent but was relatively ineffective in removing some of the polar type

compounds. Carbon treatment removed polar type compounds as well as saturates and aromatics. The authors note that none of the wastewater treatment systems now in use at petroleum refineries will remove all of the organics from the water.

Hale et al. (85) used adsorption isotherms to indicate the effectiveness of activated carbon for treatment of specific petroleum refinery wastewaters under controlled conditions. Eleven commercially available virgin carbons were evaluated. Adsorption varied with the carbon being evaluated and the wastewater sample. Since refinery wastewaters are composed of a rather complex mixture of materials, some of which are resistent to biological degradation, these workers also conducted pilot-scale studies to determine if carbon adsorption might be employed to further reduce the organic material in refinery effluents. Two complete pilot plants were installed and operated simultaneously, one treating API separator effluent and the other treating final clarifier effluent.

In addition to Hale et al., Hale and Myers (84), Short and Myers (86), and Short et al. (87) have reported and discussed results of these pilot-scale studies. Data presented and discussed by these workers are based on a specific activated carbon for one refinery. Comparable results might not be achieved using a different carbon or the same carbon at another refinery. Dual-media filtration pretreatment was used for oil and suspended solids removals to prevent premature plugging of the columns. Both biological treatment and carbon treatment were found to produce a significant reduction in all organic parameters; e.g., BOD, COD, TOC, phenols, and oil. Biological treatment provided better BOD reduction than activated carbon treatment. COD reductions were equivalent for the two systems, while TOC removals were greater for carbon treatment. Best results of reduction of all parameters were obtained with biological treatment followed by carbon adsorption. Concentrations of the metals, chromium, copper, iron, and zinc were significantly reduced by carbon treatment. Sulfide buildups, apparently a byproduct of anaerobic activity, were observed to be a problem in the carbon columns.

Short et al. (87) noted that although both biological and activated carbon treatment systems exhibited a high capacity for removal of phenols, biological systems appear to become easily "upset" with changes in phenol concentrations. Furthermore, activated carbon systems can provide excellent treatment capability for phenol removal if the hydrogen ion concentration of the waste stream is controlled. It is particularly important to avoid caustic conditions in the carbon columns. Other workers have reported that activated carbon treatment of phenolic wastewaters seems to be competitive with biological treatment (51, 88).

Results of laboratory tests conducted on primary and secondary wastewaters from 10 refineries selected by the API committee on chemical wastes indicated that activated carbon could be an economically attractive means for improving the quality of refinery effluents (89, 90, 91). Paulson reported that granular carbon treatment could produce an effluent containing less than 20 mg/liter BOD and less than 10 units of Recognition Odor Number (RON) from either primary or secondary effluents. Those organic compounds contributing

to odor were found to be preferentially adsorbed relative to the total mixture of organic contaminants. Pretreatment would be required for the majority of primary effluents and some secondary effluents to effect suspended solids reduction below 60 mg/liter and oil below 20 mg/liter. Paulson concluded that granular activated carbon treatment could be used in lieu of biological treatment or following biological treatment to improve the quality of refinery effluent wastes. Capital cost estimates and direct operating costs based on BOD removal are presented for 1-, 5-, and 10-mgd plants. Essentially, capital costs estimates will vary directly with the total wastewater volume to be treated.

Burleson et al. (18) presented isotherm data for two refinery wastes using four different carbons and one petrochemical waste using two different carbons. The data indicated that up to 85% of the refractory organic materials expressed as TOC could be removed from secondary effluents of refineries and petrochemical plants by activated carbon treatment.

Carbon adsorption capacities in terms of pounds of COD removed per pound of carbon have been found to range from less than 0.1 to 0.55 in the petroleum refining industry and from 0.2 to 0.4 in the petrochemical industry (35). These are lower than reported carbon capacities for municipal wastewaters, emphasizing the inaccuracies which can occur by extrapolating results from the treatment of one wastewater and using them as the basis for predicting another.

Examination of the data presented by Hager (19, 20) reveals that 15 of 18 samples in the petroleum SIC category showed greater than 90% TOC reduction. In the chemical SIC category, 103 of 177 samples showed greater than 90% TOC reduction, but 51 samples showed less than 85% reduction.

Stensel et al. (92) described results of a pilot-plant study at the Atlantic Richfield (ARCO) refinery in Carson, California, to determine the most feasible method of treating combined storm-water runoff and refinery process water to achieve imposed COD limitations. It was concluded that a biological system alone could not produce the low effluent COD concentration required. Activated carbon treatment, either after biological treatment or alone, would produce the desired effluent quality.

Mehta (93) presented a chronological description of the evaluation of the wastewater treatment system installed at the ARCO refinery in Carson, California. Actual plant cost data are shown. Mehta reports that carbon adsorption is an effective means of treating refinery effluents to achieve high purity levels relative to color, odor, and COD. He also noted, however, that economics would vary greatly with each refinery, depending on specific requirements and feed quality.

Prosche et al. (94) described and discussed the design and operation of the carbon adsorption process for treatment of intermittent wastewater from the ARCO refinery in Carson, California. The process proved easy to maintain, easy and quick to start up, simple to shut down and leave in the standby stage, and very reliable in its performance. For the unique intermittent type of operation required at this refinery, the authors believe that the carbon adsorption process proved successful; however, they do not believe that this

conclusion would necessarily be the same for continuous operation requirements or some other unique situation. Problems with varying feed COD and algal growth were experienced. It was noted that these are real problems that exist when treating refinery wastewaters.

A thorough and complete discussion of the ARCO project is presented in the final EPA report prepared by Loop (1). This report describes the carbon treatment system and its first two years of operation. During the project period, the plant processed 172 million gallons of water, removed 408,000 pounds of COD, and regenerated 1,644,000 pounds of carbon. Carbon was exhausted at the rate of 9.5 pounds per 1,000 gallons of water processed. At an average feed COD concentration of 250 mg/liter and an average effluent concentration of 50 mg/liter, the carbon was loaded to an average of 0.26 pound per pound of carbon. Following solution of initial start-up problems, the system was operated at a cost of 40 cents per 1,000 gallons of water treated, or 18 cents per pound of COD removed. The plant demonstrated excellent reliability and the ability to start up or shut down without delay or difficulty. This gives the process a distinct advantage over biological systems for use in handling intermittent runoff. Operation of this system has now been discontinued because of the change of treatment requirements imposed by the Los Angeles Regional Water Quality Control Board.

Although the ARCO project demonstrated that activated carbon can be used on a commercial scale to reduce COD concentrations of some petroleum refinery wastewaters, Loop recommended several areas which need further investigation:

1. Further determination of quantities and types of COD materials that do and do not adsorb an activated carbon.

2. Feasibility of pretreatment to reduce the load on carbon.

3. Optimum number of stages in an adsorption process with controlled feed concentrations.

Peoples et al. (88) reported on a pilot investigation to determine the most suitable method of treating process wastewater from an oil refinery. The workers felt that results clearly demonstrated the applicability of activated carbon treatment, even with widely varying effluent concentrations. In addition, Krishman et al. (95) reported that this pilot investigation demonstrated that high-rate, deep-bed sand filtration could remove significant amounts of oil and suspended solids from the API separator effluent and produce an effluent suitable for direct application to activated carbon. Activated carbon could reduce the remaining organics to a very low level; thus, a combination sand filter-activated carbon treatment system could provide a high degree of treatment for refinery wastewaters. The system also would require low land area and costs when compared to the conventional activated sludge system.

McCrodden (96) reported on operation of a 2.2-mgd filtration-carbon adsorption wastewater treatment plant placed on line at the 105,000 BPD Marcus Hook refinery of BP Oil Corporation in March 1973. Data from bench-scale single-media filtration tests, adsorption isotherm tests, and operation of a sand

filtration pilot plant followed in line by a dynamic carbon column test were used as the basis for process design. Final design consisted of three parallel dual-media filters for oil and suspended solids removal, an intermediate basin to control flow surges and equalize influent loads, three parallel activated carbon adsorbers, and a regeneration system with a multiple-hearth furnace for thermally reactivating spent carbon. The plant demonstrated varying performance over the first 12-month period as a function of individual operating characteristics. During the first year of operation, the plant demonstrated 76, 89, 42, 38, and 39% reduction for suspended solids, oil, first-stage ultimate oxygen demand, COD, and phenol, respectively. An increase in sulfide concentration was indicative of anaerobic digestion in the carbon columns. Carbon losses were 10% per regeneration cycle.

McCrodden (96) and DeJohn and Adams (3) reported that after 18 months of plant operation, the adsorptive performance of regenerated virgin carbon had fallen off by about 37% for phenol removal and 82% for COD removal. In an effort to maintain purification levels obtained with virgin carbon, the carbon regeneration rate was increased from the design figure of 125 to 250 pounds per hour; the carbon dosage was increased from the design figure of 0.86 to 2.7 pounds of carbon per 1,000 gallons throughput. The regeneration rate was 5,000 pounds per day, reflecting a carbon dosage of 2.3 pounds per 1,000 gallons throughput and representing an approximate 14% increase in carbon makeup alone. The major reason for decreased performance of the system and increased operating costs was that the system design and operating costs were estimated from data developed in studies using virgin bituminous coal carbon. This particular wastewater stream contains predominately small molecules. Since micropores are lost as carbon is reactivated, the carbon exhaustion rate was much faster than anticipated. Therefore, carbon had to be regenerated more often, causing an increase in the carbon usage rate which simultaneously increased operating costs. Subsequently, the company has reviewed operational data and process performance and decided to install a biological oxidation secondary treatment system (97). The new system is planned to be placed in operation in 1981.

DeJohn (98) and DeJohn and Adams (3) reported on the comparative adsorption performance of lignite and bituminous coal carbons using oil refinery wastewaters. Studies were conducted on the total refinery effluent at two East Coast refineries and at a selected sulfonate waste stream at a West Coast refinery. Although effluent COD concentrations from columns containing both types of carbon were equal, carbon dosage (pounds carbon per 1,000 gallons wastewater) was greater for bituminous coal; conversely, the loading on carbon (pounds COD remover per pound carbon) was greater for lignite coal.

Results of these studies indicate that when treating a total refinery effluent or an effluent from a selected refinery wastewater stream where the pollutants are relatively large molecules, breakthrough is due to transitional pores becoming exhausted. Lignite carbon, having a higher transitional pore surface area and pore volume, should be expected to perform better. For treatment of a selected refinery wastewater stream or total refinery effluent which contains predominantly small molecules, virgin bituminous carbon should perform better because of its higher surface area in the small pore range. However, after a number of regenerations, properties of the two carbons would

tend to converge, and both should perform equally in removing small molecules. On a long service basis, however, economics may still favor use of lignite carbon.

Huang and Hardie (99) conducted a research program to test the applicability of using physical-chemical processes employing activated carbon adsorption for treatment of refinery wastewaters. The study was conducted on wastewaters from the American Oil Company, Wood River, Illinois, refinery. Effluents produced from both fixed-bed and expanded-bed adsorbers were consistently of high water quality. Combined use of chemical clarification-coagulation and carbon adsorption was able to reclaim the water successfully since the effluent had a TOC of less than 3 mg/liter. Since physical-chemical treatment of wastewater does not encounter any of the complexities often associated with biological processes, use of this approach for future water reclamation seems promising. The potential value of physical-chemical treatment employing activated carbon adsorption must be considered greatest when applied to nondegradable and/or nutrient deficient wastewaters for which biological treatment often cannot be successfully or economically used. It must be understood, however, that all complex wastewaters contain some organic materials which cannot be adsorbed effectively.

Huang et al. (100) summarized results from a research study designed to investigate effectiveness of carbon adsorption for treatment of three selected industrial wastewaters: a refinery waste, a high-strength acid waste, and a pharmaceutical waste. The extent of organic removal not only varied from one industrial waste to another but also from one carbon to another for the same kind of waste.

In the treatment of the refinery waste, the carbon bed was very effective in adsorbing organic pollutants. Neither ammonia nor organic nitrogen was removed by the carbon adsorber. Huang and his coworkers noted that, although a very high percentage of organic removal can be achieved by carbon treatment, there are always certain amounts of residual organic materials which resist carbon adsorption. This was evidenced by the fact that some variable amounts of COD or TOC were invariably present in the produced effluent. The nature of these leaked organics was not examined.

Refinery and petrochemical wastes can be treated biologically by the activated sludge process; however, conventional systems often experience many effluent quality and operating problems: (1) Oil that is not removed in the API separators can pass through the aerator and clarifier and will be measured as TOC or COD. (2) Oil can also entrap solids, prevent them from settling, and lead to high effluent suspended solids. (3) Surface active agents often cause foaming in the aerator and on the receiving stream. (4) Shock toxic loads can kill the active biomass. (5) Oil characteristics of waste sludges can make them difficult to dewater and handle. DeJohn and Adams (3) noted that addition of powdered activated carbon to activated sludge systems has proved to be a satisfactory method for solving such problems. In addition to improved operation of the activated sludge system, the use of powdered activated carbon also may result in real operating cost savings. It was reported that four refinery and/or chemical plants have evaluated the use of powdered activated carbons in full-scale activated sludge systems. In

all systems, addition of powdered carbon improved organic removals, aided solids settling and sludge handling, provided protection from toxic or shock loadings, and monitored nearly colorless effluents with a more consistent effluent quality.

In an effort to expand the performance of the existing biological treatment facilities, full-scale trials utilizing powdered activated carbon were conducted at the Sun Oil Company, Corpus Christi, Texas, refinery (101). The main objective of adding the powdered carbon was to reduce the effluent suspended solids loading for compliance with 1977 NPDES and State permit conditions. Although powdered carbon addition could not guarantee compliance with 1977 suspended solids criteria, improvements in performance of the existing system were significant for BOD and COD removals as well as suspended solids. Treatment costs ranged from 1.7-4.3 cents per 1,000 gallons, depending on influent flow and quality. Compiled data showed reduction in final effluent loadings of up to 56% for suspended solids, 76% for BOD, and 36% for COD. Other improvements noted were more uniform effluent quality, a clearer effluent, elimination of foam in the aeration system, more consistent sludge wasting at two-thirds the volume, and reduced chances of biological upsets. The system was maintained at the carbon operating level by batch addition of about 100 pounds per day of carbon. The carbon used in these trials had a bulk density of 44 pounds per cubic foot, which is an important factor when improved settleability is the primary objective of carbon addition to the system.

Stenstrom and Grieves (102) and Grieves et al. (103) reported on the evaluation of an alternate process to granular activated carbon treatment of refinery activated sludge effluent. The proposed process would be used by refineries to meet their BAT effluent quality goals in 1983. The new treatment alternative involves using powdered activated carbon to enhance the performance of the activated sludge section of the BPT treatment sequence. The degree of enhancement was found to be considerably affected by the physical characteristics--in particular, surface area--of the activated carbon used. In addition to commercially available carbons, an experimental carbon with an exceptionally high surface area was tested. The experimental carbon was found to be several times more effective than the best commercial grade--that is, an equivalent effluent quality can be attained at a lower carbon addition rate using the new carbon. The advantage of the high surface area carbon was more more pronounced at high sludge ages or mixed-liquor suspended solids (MLSS) concentrations.

These workers concluded that the powdered activated carbon-activated sludge process is a promising technique for meeting BAT effluent requirements for oil refineries. Data collected during this study generally met or exceeded the target effluent quality. The process was reported to offer significant cost incentives over add-on granular activated carbon columns while being much easier to operate. It was also found that the use of high sludge age is a viable method of maintaining process performance while lowering carbon addition requirements. The increased sludge age, resulting in higher MLSS concentrations, reduces carbon make-up requirements and size of regeneration facilities. Process technology covered in these papers formed the basis for a number of U.S. and foreign patent applications.

ORGANIC CHEMICAL

To investigate the possibility of using activated carbon technology on effluents from biological treatment plants treating organic chemical wastewaters, a series of carbon isotherm tests was run at standard conditions using a contact time of 30 minutes (104). Results of these tests are presented. Inspection of the specific data shows that carbon adsorption has varying degrees of amenability with regard to cost effective wastewater treatment; however, the data do indicate that specific wastewaters are readily treatable using activated carbon. Results of a plant survey program of six activated carbon plants treating raw wastewaters are also presented. The most interesting fact about the data generated is that, while domestic wastewater treatment experience indicates that efficient treatment is provided with contact times between 10 and 50 minutes, the design contact times at the six plants surveyed varied between 22 and 660 minutes (calculated on an empty column basis). These higher contact times are required because of the much higher raw waste loads generated by industry.

The technical literature describes numerous laboratory studies regarding the viability of adsorption for the removal of organic compounds from wastewater. A list of organics amenable to carbon adsorption has been presented by Rizzo (22). Rizzo noted that carbon adsorption is favored by higher molecular weight, nonpolarity, and limited solubility of the contaminants.

Union Carbide has studied the application of activated carbon adsorption as tertiary treatment to follow biological (secondary) treatment of wastewaters from their integrated, multiproduct petrochemical facilities for several years. Several of these studies, along with studies on the amenability to adsorption of specific petrochemicals, have been reported in the open literature (105, 106, 107, 108).

These studies have revealed that, in contrast to experience with domestic secondary effluents, activated carbon treatment of petrochemical wastewaters may <u>not</u> produce an effluent essentially free of organics. Even assuming high-quality biological effluents (BPT) and a long contact time in the adsorbers, activated carbon removes only 50-70% of the COD remaining in effluents from typical petrochemical plants. As the quality of the activated sludge effluent improved, the percent of additional organic removal in a tertiary adsorber increased. Increasing contact time increased the percent of organic removal and the adsorber effluent quality. <u>In all cases, however, there appeared to be a limiting percentage organic removal above which no additional removal could be achieved, even at truly massive carbon dosages.</u>

Giusti et al. (105) screened 93 compounds from 10 functional groups commonly found in petrochemical waste streams. Single dosage tests were used to evaluate their relative amenability to activated carbon adsorption. In addition to the single dosage tests, isotherm studies with four commercially available carbons were conducted on representative compounds from five of the functional groups. Carbon loadings for each compound studied were determined on the basis of grams of sorbate removed per gram of carbon. A discussion of results for each of the functional groups is presented.

Some conclusions drawn by Giusti and his co-workers were:

1. As molecular weight increases and polarity, solubility, and branching decrease, the degree at which pure components are adsorbed by activated carbon increases somewhat predictably.

2. Of the classes of compounds studied, aromatics exhibited the greatest amenability to activated carbon adsorption because of their relatively low solubilities in aqueous solution and bonding to the aromatic surface of the activated carbon.

3. Functionality was seen to have a substantial effect which was interrelated with solubility and polarity. For the straight chain compounds, relative amenabilities to carbon adsorption for compounds of less than four carbons were: undissociated organic acids>aldehydes>esters>ketones>alcohols>glycols. For compounds above four carbons, alcohols moved ahead of esters.

Data were presented by Lawson (106) on the relative amenability to adsorption of 23 typical petrochemical wastewater constituents. Under the test conditions (5 grams/liter powdered carbon dosage), benzene and nitrobenzene were the most amenable compounds to adsorption (95-96%) while ethylene glycol and monethanolamine were the least amenable (7%).

The problem in applying adsorption to petrochemical wastewaters lies in the limited amenability of many common low molecular weight oxygenated petrochemicals to adsorption on activated carbon (107). These difficult-to-adsorb compounds are produced in high volume in the industry. They often persist in effluents from biological treatment processes because of their high initial concentration and the seemingly inherent problems in efficiently treating petrochemical wastes in biological systems. Activated carbon adsorption can be an excellent upgrading technique for dilute wastewaters contaminated with large, nonpolar organics. It is not a panacea, however. Upgrading multicomponent petrochemical effluents to reuse quality likely would require a multifaceted attack:

1. Reduction of organic pollutants discharged at the production unit source through process changes.

2. Application of best practical biological treatment techniques to the combined wastewaters.

3. Application of activated carbon adsorption to waste streams containing organics which have a high adsorptive capacity or where small wastewater volume can help offset a limited adsorptive capacity.

4. Application of yet-undeveloped techniques for final polishing to a low residual organic level.

5. Application of techniques such as ion exchange or reverse osmosis to remove dissolved inorganic salts.

Giusti et al. (105) reported that, in a typical flow scheme for a facility treating petrochemical wastewaters, carbon treatment could be applied at two positions. A tertiary treatment stage for removing refractory organics following conventional secondary biological treatment is usually visualized. However, because of the high concentration of impurities found in various individual waste streams contributing to the discharge, some of the streams might be treated more effectively at their sources. This latter approach could be beneficial, particularly in handling process unit wastes that produce shock loads to a treatment plant, produce materials that inhibit biological activity, or produce economically recoverable materials.

Lawson and Hovious (108) presented an excellent summation of the studies conducted by Union Carbide. Some noteworthy conclusions were:

1. In pure component studies, specific organic chemicals were shown to differ widely in their amenability to adsorption, depending on molecular weight, structure, polarity, and solubility.

2. The relative ease of adsorption of different functional groups can vary strongly with pH, depending on the chemical nature of the adsorbates. An optimum pH cannot be predicted for a multicomponent wastewater of unknown or varying composition.

3. While pure component data could be used to predict binary adsorption capacity in isotherms fairly closely, a four-component mixture isotherm showed only about 60 percent of the adsorptive capacity predicted.

4. While isotherm capacities were somewhat extrapolatible to continuous column behavior in pure component adsorption and simple mixture studies, such extrapolations have not proved to be possible with complex mixtures, particularly biotreated effluents.

5. The key parameters of interest in real wastewater treatment situations, percentage organic removal achievable, and water volume treated per pound of carbon before breakthrough cannot be predicted from isotherm tests.

6. The physical differences between an equilibrium adsorption situation in a powdered carbon isotherm and the dynamic, multicomponent interactions in a continuous granular carbon bed are too great to permit prediction of column performance from isotherms or pure component data.

Examples of refractory materials which are difficult or impossible to remove by conventional biological processes but are removable by adsorption techniques include benzene sulfonate and heterocyclic organic compounds (109). Phenols, nitriles, and substituted organics can also be adsorbed from wastewaters when they are present in low concentrations.

Geibler (110) reported that benzene hexachloride and other chlorinated aromatics had been successfully removed from pesticide manufacturing plant effluents by using carbon.

Treatment of a high-strength industrial chemical wastewater which had a COD of approximately 3,000 mg/l and a pH of 3.0 was attempted by activated carbon adsorption to evaluate feasibility of yielding effluents of reusable qualities (111). Experimental methods included both batch and column studies. The COD of the test solutions was reduced to approximately 300 mg/l, which indicated that activated carbon adsorption was very efficient in removing COD from the chemical waste. Initial pH adjustments to 7.0 did not improve COD removal efficiency. Removal of COD from the test solutions was generally accompanied by a corresponding degree of color removal from the wastewater.

Hardwicke Chemical Company, Elgin, South Carolina, manufacturer of a variety of specialty organic chemicals, conducted an evaluation of different wastewater treatment processes that might reduce their average BOD_5 of 3,000 mg/liter to less than 62 pounds per day to meet discharge requirements imposed by the South Carolina Pollution Control Authority (112). Laboratory and pilot-plant studies demonstrated both the technical and economical feasibility of removal of organics by activated carbon adsorption. Following the favorable pilot studies, an adsorption system was installed consisting of two upflow carbon adsorbers, each containing 20,000 pounds of granular carbon. The author reports that the system has consistently met the 62-pound BOD_5 objective since going on stream. The entire system is owned and maintained by a supplier who also performs analyses of weekly samples and provides monthly reports. Hardwicke pays a monthly service charge for the entire system.

Data presented by Schimmel and Griffen (113) indicate that the adsorption process is capable of significantly upgrading the quality of liquid industrial wastes. Results of an investigation of alternate treatment systems for a complex industrial wastewater containing phenols is discussed. The waste effluent resulting from operation of the Rechhold Chemicals, Inc. (RCI), plant at Tuscaloosa, Alabama, may be considered as typical of that from multiproduct chemical plants. The aqueous waste results from both batch and continuous operations contain both organic and inorganic wastes and vary in both composition and concentration. The report describes selection of carbon adsorption as the most dependable process for secondary treatment of this waste and details the evaluation of a full-scale installation treating some 500,000 gpd of wastewater.

A biological oxidation process applied to the RCI wastes resulted in a significant reduction in BOD_5 loading, substantially complete removal of phenols, and an adequate reduction in COD loading. However, lack of reliability ascribed to the biological process led to development of an activated carbon process that, when placed in commercial operation, resulted in average removals of 90, 75, and 99% of the COD, BOD_5, and phenol loads from the RCI process wastewaters. The authors concluded that, although biological oxidation should not be overlooked for treating industrial wastewaters, its usefulness is limited with respect to bacterial poisons such as phenol and by ambient temperature changes that result in variable biological activity. Also, biological oxidation is more easily adapted to wastewaters from continuous type, as opposed to batchwise, chemical processes. The carbon adsorption process should be considered if the wastewater to be treated is variable in composition or concentration. The process will handle many refractory organic compounds that contribute to the COD load but are not susceptible to biologi-

cal oxidation. Adsorption should not be considered if a substantial portion of the pollutional load consists of low-molecular-weight organics. Organic compounds having a molecular weight below about 50 are poorly adsorbed, if at all, by activated carbon.

Neville Chemical Company, Neville Island, Pa., manufacturer of a variety of organic chemicals and synthetic resins, had to upgrade wastewater treatment to meet Ohio River discharge requirements. After considering economic and technical aspects of various alternatives, a treatment system was selected consisting of API separators followed by flow equalization, pH adjustment, multimedia filtration, and granular carbon adsorption (114). The waste treatment system was placed in operation on March 1, 1974. During the first year of operation, the effluent from the system contained less than 0.1 mg/liter of phenol, less than 250 mg/liter of BOD_5, and was free of oil and suspended solids. The complete system, including installation, operation, and maintenance, is contracted from a supplier for a monthly service fee.

Brunotts et al. (115, 116) described techniques used to develop a physical-chemical treatment system capable of treating a complex chemical plant wastewater. Operating data compiled from operation of the full-scale treatment system at the Stepan Chemical Company plant located in Fieldsboro, New Jersey, are compared to data predicted by laboratory and pilot-plant studies. After 10 months of operation, the plant achieved the goals that were set when the plant was designed. This illustrates that, given the proper design criteria and a clearly defined set of objectives, a physical-chemical system employing granular carbon adsorption can be constructed to meet the desired goals.

Wiseman and Bawden (117) described an industrial wastewater treatment plant using activated carbon adsorption to process wastewater from a synthesized terpene plant that uses isoprene as the raw material. Overall performance of the total system is indicated by a final discharge representing over 90% removal of BOD, TOC, and COD.

Dawson et al. (118) conducted a study designed to determine the effectiveness of activated carbon for removing fishery chemicals from water and to evaluate some physical and chemical influences on the adsorptive capacity. The study demonstrated that activated carbon was effective in removing fish toxicants and anesthetics from water solutions. All seven chemicals tested were adsorbed by carbon to some extent, with their absorptive capacities ranging from 0.1-64.0 milligrams per gram of carbon. While each chemical probably has a different rate of adsorption and some may not be adsorbed at all, factors such as the concentration of other organic constituents in the water and variations in activated carbons also affect adsorption. For these reasons, the investigator should evaluate the efficiency of adsorption of a particular system in situ to accurately establish the adsorptive capacities.

Zeitoun and McIlhenny (119) studied several alternative processes for the treatment of the saline wastewater resulting from the production of polyhydric organic compounds by the chlorohydrin process. Carbon adsorption was found not to be feasible because of the low capacity of the activated carbons for the glycols. The capacity is further reduced by the competitive adsorption of the chlorinated organics present in the wastewaters.

Zeitoun et al. (120) concluded that carbon adsorption of relatively high concentrations of organics from petrochemical wastewaters is technically achievable but economically feasible only if the organics can be recovered and recycled to the production facility. In addition, it was concluded that low concentrations of organics that are highly adsorbable on activated carbon cannot be removed from petrochemical wastewaters at a reasonable cost because of the cost of regenerating the carbon thermally. These workers recommended that in-place regeneration of activated carbon be investigated for each particular wastewater in order to reduce the cost of carbon adsorption treatment.

A 100-gpm pilot plant was constructed and operated for 1 year to demonstrate the feasibility to remove and recover phenol and acetic acid from an 18% sodium chloride brine by adsorption on fixed beds of activated carbon (121). Regeneration of the carbon was accomplished by desorption with dilute sodium hydroxide. The phenol desorbed was recycled to the phenol manufacturing plant, while the acetate regenerant was processed to underground disposal wells. More than 23 million gallons of brine were purified. Fourteen cycles of phenol adsorption and regeneration and 105 cycles of acetic acid adsorption and regeneration were completed with no significant deterioration of carbon performance. Process results are discussed in detail along with costs.

The B. F. Goodrich Chemical Company performed extensive laboratory and pilotplant investigations in order to competently design an industrial wastewater treatment system for a proposed polyvinyl chloride manufacturing facility in Salem County, New Jersey (122). Activated carbon adsorption was determined to be impractical for this waste. Poor adsorption capacities were attributed to the presence of water soluble long-chain organic soaps contained in the waste stream.

Frohlich et al. (123) reported on results of a side-by-side pilot-scale comparison of a conventional activated sludge system and a biophysical system (activated sludge and powdered activated carbon) on a high-strength industrial wastewater from a pharmaceuticals organics chemicals producer. Both systems appeared to have acceptable stability; however, performance of the biophysical system was superior in terms of removing BOD, COD, color, odor, and nitrogen. There was no observable long-term degradation of the biophysical system after over 120 days of operation. Frohlich and his coworkers claimed the following advantages for the biophysical system:

1. The weighting effect of the carbon makes possible the ability to carry the active biomass at levels two to three times higher than activated sludge and thus reduce the aeration basin size and hydraulic detention time.

2. The massive amounts of carbon present in the aeration basin tend to serve as an "organic sink" for shock loads of toxic and refractory materials.

3. Oxygen transfer is improved--probably as a result of adsorption--desorption from the activated carbon.

4. A larger portion of marginally degradable organics can be biologically assimilated due to the long sludge residence time, enabling the carbon to carry a higher load of truly refractory material.

5. Nitrification is easily achieved with the long residence time.

6. Odor, color, and foaming problems are reduced.

Pilot-plant studies conducted at the DuPont Chambers Works Multi-product Organic Chemical Plant revealed that addition of powdered activated carbon to the aerator of an activated sludge system (76) would result in a significant increase in performance over an activated sludge system alone (124, 125, 126, 127, 128). Some additional improvement in performance also was obtained by combined systems consisting of carbon columns either preceding or following biological treatment. All three combined systems achieved desired effluent quality for this particular waste stream during the 15-month test period, while the other two systems, biological treatment alone or carbon column treatment alone, were found to be inadequate. The DuPont workers determined the PACT system to be the least expensive system meeting Chambers Works effluent criteria for BOD_5, COD, TOC, color, and fish toxicity.

Toxicity values, expressed as 96-hour median tolerance limit (TL_m), for the raw effluent, primary effluent, and activated sludge effluent were 5, 16, and 35%, respectively; there was no fish mortality at 100% for the PACT effluent (125).

The effluent quality obtained by the PACT system is reported to be a function of aeration basin temperature, sludge age, and powdered carbon dosage. An inherent limitation of the PACT system is that for a given biological system, the powdered carbon dosage which can be added is physically limited by the solids-handling ability of the solids separation devices.

Flynn et al. (127) listed the following advantages of adding powdered carbon to aerators of existing activated sludge plants:

1. Improved effluent water quality in a cost effective manner.

2. Enhanced treatability of wastewaters inhibitory or toxic to biological treatment.

3. Expanded hydraulic capacity of existing plants without expansion of unit processes.

4. Uniform plant operation and effluent quality.

5. Minimized operating problems; e.g., foaming, sludge bulking.

6. Eliminate ultimate disposal of secondary solids.

7. Compatible with existing plant operations.

DuPont has subsequently installed a 40-mgd secondary/tertiary treatment system incorporating the PACT process at the Chambers Works plant. The initial start-up phase of operation of the system was begun in November 1976 (129). Operational data for the system will be published in a forthcoming EPA report.

SECTION III

DESIGN CONSIDERATIONS

There are a rather limited number of treatment processes which are capable of removing refractory organic materials from wastewater. Adsorption on powdered and granular activated carbon is included in these (21). Upon contact with a wastewater containing soluble organic materials, activated carbon selectively removes these materials by adsorption.

Although it has been claimed that the carbon adsorption process as a secondary treatment step has some potential advantages over biological processes, Rizzo (130) reported that the activated carbon process, unfortunately, cannot accomplish everything that a biological process can. Smith (131) reported that unit costs for removal of biodegradable compounds from wastewater by carbon adsorption are generally more expensive than by biological treatment. At the same time, however, adsorption is capable of removing nonbiodegradable materials.

BASIC PRINCIPLES AND CONCEPTS OF THE CARBON ADSORPTION PROCESS

Adsorption is primarily a surface phenomenon whereby organic materials are attracted and held to the surface of a solid material with which they come into contact, because of forces of attraction at the surface. Activated carbon is a particularly good adsorbent because it has an extremely large surface area per unit volume. It has been noted that the carbon adsorption process may be physical, chemical, electrical, or a combination of all three (42, 98).

The concept of carbon adsorption and the basic principles involved have been discussed by numerous workers. Some noteworthy publications that will provide information on the nature, preparation, and properties of activated carbon and the principles involved in its application as a method for removing organic materials from wastewater are those by Ford (35), Hassler (36), Weber (42, 132), Davies et al. (133), Rinehart et al. (134), and Westvaco Corporation (135).

While each manufacturer has his own specific techniques for producing activated carbon, the preparation involves two basic techniques--carbonization and activation. Specific properties of activated carbons depend on the material source and the mode of activation.

Appropriate consideration must be given to each of two different aspects of adsorption when evaluating the suitability of adsorption as a unit of opera-

tion for wastewater treatment or when designing a treatment system incorporating the adsorption process (136). The first of these two aspects is kinetics, and the second is the ultimate capacity for adsorption or adsorption equilibria. Weber and Morris (136) stated that efficient use of adsorbents can be obtained only if the equilibria of adsorption are clearly understood and if the factors that control capacities for adsorption are well defined.

The primary property for which one uses an activated carbon is its adsorption capacity (134). While various tests, e.g., iodine number, have been developed to give relative removal capacities of activated carbon under specific conditions, the best measure of adsorptive capacity is the effectiveness of the carbon in removing the critical constituent from the actual wastewater in which it is to be found (35).

Al-Bahrani and Martin (137) observed that, although adsorption on activated carbon has been the only advanced process used to any significant extent for removal of dissolved organics from wastewater streams, more research is needed to study the various factors that influence their adsorption.

Ford (138) stated that the overall adsorption rate represents the combined effects of diffusion through a laminar layer of fluid surrounding the constituent, surface diffusion, and adsorption on the internal pore surfaces. Essentially, there are three consecutive steps in adsorption of materials from solution by porous sorbents such as activated carbon:

1. Transport of adsorbate through surface film of exterior of adsorbent (film diffusion).

2. Diffusion of sorbate within pores of sorbent and/or along pore wall surfaces (intraparticle diffusion).

3. Adsorption of solute on interior surfaces bounding pore and capillary spaces of sorbent.

Forces that govern uptake kinetics of organic solutes from dilute solution by activated carbon are frequently quite different from those which control the ultimate capacity of carbon for adsorption (136). The rate-limiting mechanism generally is either film diffusion or intraparticle transport, depending largely on the hydrodynamic character of the system in which activated carbon is used. In contrast, the final portion of adsorptive equilibrium is governed by the forces of adsorption, either chemical or physical in nature. As a result of possible differences in the nature of kinetic and equilibrium forces, factors that enhance rates of uptake may well decrease the capability of activated carbon for certain adsorbates--the converse may also be true. It is necessary, then, that these factors and their relative significance to both rates and capacities of adsorption be clearly defined.

Braus et al. (139) found that experimental adsorption data for granular sorbents such as activated carbon could be explained by assuming that the adsorption rate is controlled by rate of diffusion of the solute within the

adsorbent particles. Morris and Weber (140), experimenting with activated carbon adsorption of alkylbenzene sulfonate (ABS), also attributed control of the adsorption rate to diffusion of the solute in the adsorbent pores.

Weber and Morris (141) carried out studies on factors affecting adsorption with a view to using this method for the treatment of wastewaters. They reported that the overall rate of adsorption appears to be controlled by the rate of diffusion of the solute within the micropore structure of the granular carbon. Relative reaction rates were found to vary reciprocally as the square of the diameter of the individual carbon particles for a given weight of carbon.

The carbon particle is extremely porous--the pores being classified as macropores and micropores. Macropores are generally regarded as playing little part in adsorption, merely serving as an avenue into the micropores (133). Therefore, for any adsorbate molecule the effective surface area for adsorption can exist only in the pores which the molecule can enter. Thus, the equilibrium capacity for a given adsorbate will depend on the total internal surface area and the pore size distribution. The pore structure and size distribution of the pores of activated carbon are extremely important in determining its adsorptive properties since adsorbate molecules are physically prohibited from entering pores smaller than those molecules (135).

Recognizing the potential value of activated carbons for removal of water pollutants, West (142) initiated a study for the general purpose of obtaining information on the effect of porous structure of a carbon on that carbon's activation. He found that the adsorptive capacity of an activated carbon is determined by the inherent properties of the carbon and by its degree of activation. The amount of surface area per unit mass of carbon, the accessibility of that surface to the adsorbate molecules, and the concentration on the surface of sites capable of attracting and holding specific adsorbates are the keys to the adsorptive capacity of the carbon. The rate of uptake of adsorbates is a distinct function of the porous structure of the adsorbent and the character of the adsorbate.

Properties of carbon that are of prime importance in an adsorption operation include total surface area and pore size distribution (11). It is the total area which determines the capacity of a carbon for adsorption, and it is the pore size distribution which determines the accessibility of the surface area to specific sorbate molecules. Carbon particle size primarily affects rate of adsorption and not total adsorptive capacity of the carbon (21). The most important effect of particle size reduction is a decrease in time necessary to reach adsorption equilibrium--that is, an increase in the rate of adsorption (11). The most significant parameter in determining a powdered carbon's performance for oil refinery wastewater treatment has been reported to be surface area (102, 103). The pore size had no apparent effect on the experimental results.

Since adsorption is an equilibrium phenomenon, capacity will also be strongly dependent on concentration of the sorbate in solution around the carbon particles (133). The rate of adsorption will be governed by particle size, as it is dependent on diffusion of adsorbate molecules through macropores so that in a smaller particle the center of the particle will reach

equilibrium with the solution more rapidly than in a larger particle. It is an advantage in liquid-phase applications to have a well-developed macropore structure throughout the particle.

Because adsorption is a surface phenomenon, the extent and properties of the surface will control adsorptive effects (134). For a particular type of adsorbent, the greater the surface available the greater the amount adsorbed. However, surface properties and conditions can affect the course and type of adsorption. Because of its high porosity, activated carbon is one of the few solids that can provide extremely high surface area per unit weight or unit volume at relatively low cost. Activated carbons are prepared so as to exhibit a high degree of porosity and an extensive surface area (132).

The surface properties of different carbons can have profound effects on both the reate and capacity for adsorption (42). Chemical properties of the surface are important in determining activity, or capacity for a specific sorbate. Chemical properties of the surface depend on the starting material, activation process, and conditions employed in activation (143). It is not possible to determine activity or capacity from basic carbon properties, such as surface area, or to relate activity for a reference sorbate, such as iodine or methylene blue (42, 134). Activity or capacity must be determined directly on the system of interest.

Information on the structure and function of activated carbon used in water and wastewater treatment systems was reviewed by Snoeyink and Weber (144) and correlated to provide a simple model to explain the properties of activated carbon. The basic structural unit was examined, and raw materials, method of preparation, activation additives, and noncarbonaceous impurities--all factors affecting its sorptive properties--were discussed. Snoeyink and Weber described the surface of activated carbon as a collection of functional groups containing oxygen, occurring primarily at the edge of broken graphite planes and basal planes, consisting of large, fused aromatic ring systems in a graphite-like structure.

Anderson (145) discussed two classes of adsorption--physical adsorption and chemisorption. In physical adsorption, impurities are held on the surface of carbon by weak van der Waals' forces; whereas chemisorption bonding results from relatively strong bonding between the impurity and active sites on the carbon surface. Thus, the efficiency of a carbon depends upon the accessible surface area and the presence of active sites upon the surface. It should be noted that physically similar sites on the carbon surface need not be chemically similar. Highly adsorbent forms of carbon often contain substantial amounts of hydrogen bonded to the surface carbon atoms. Some surface sites may readily adsorb a molecule for which a nearby site shows little, if any, affinity.

Snoeyink et al. (146) studied the sorption of phenol and p-nitrophenol (PNP) from aqueous solution on particulate active carbon of two types. Equilibrium measurements suggested a heterogeneity of active surface sites with respect to the energy of adsorption, while desorption studies revealed significant hysteresis effects when long equilibrium periods were involved. Although

the two carbons tested had similar total surface areas, the coal-base carbon sorbed phenol at low concentrations more extensively. Sorption on the coconut-shell carbon was affected by strong acids.

Mattson et al. (147) investigated characteristics of the uptake of phenol and nitrophenol by active carbon. The measurements of solution equilibrium parameters as well as surface structural characteristics determined by infrared internal reflection spectroscopy are presented. A charge-transfer interaction is postulated which explains the observed adsorption and spectroscopic characteristics on the basis of the electron densities in the sorbate molecule as well as the types and concentrations of surface functional groups present on the carbon. All of the data support the mechanism of a donor-acceptor complex with surface carbonyl oxygen groups with adsorption continuing after these sites are exhausted by complexion with the rings of the basal planes. Interaction of the aromatic ring with the surface of the active carbon must be considered the major influence in these processes interacting through the pi-electron system of the ring. There is considerable evidence in the literature for the formation of donor-acceptor complexes between phenol and several kinds of electron donors (148).

Coughlin and Ezra (148) observed that a change in the adsorptive capacity for phenol and nitrobenzene took place upon oxidation or reduction, or both, of the carbon surfaces. They observed that upon oxidation of the surface, capacities for both decreased and with reduction, capacities for both increased. The oxidation of the carbon surface increases the amount of strongly acidic oxygen containing functional groups through the oxidation of carbonyl groups.

Mattson et al. (147) reported that many adsorption processes involving organic molecules result from specific interactions between identifiable structural elements of the sorbate and the sorbent. Different substitute groups, even though of similar size, differ greatly in their influence on adsorbability (36). The specificity so often encountered in adsorption often depends on mutal relations between the lattice structure of the sorbent and the configuration of the adsorbate molecule.

Every adsorptive power does not exist on all portions of the surface (36). Specific affinities can reside in separate areas (active centers) of the surface. Selective adsorption can be caused by qualitative characteristics of the surface. Although each active center exhibits selectivity as to the kinds of substances that can be adsorbed, the selectivity may not be limited to the adsorption of only one molecular species.

DiGiano and Weber (150) illustrated PNP isotherms obtained for four different activated carbons. Adsorption capacities indicated by these isotherms were significantly different. The adsorption capacity is a function of the total surface area available to the PNP molecules but is also a function of the type of activation treatment to which the carbon has been subjected. Many activated carbons have comparable surface areas and pore size distributions, yet do not exhibit similar PNP adsorption capacities.

Jain and Snoeyink (151) found that p-nitrophenol (PNP) and p-bromophenol (PBP) compete for the same kinds of sites on the carbon surface. Both the

nitro group and the bromo group are electron-withdrawing, and it is likely that the mechanism of adsorption for both PNP and PBP on the carbon surface is similar. These workers reported a very pronounced effect of PNP on the adsorption rate of PBP. The magnitude of this effect is consistent with strong competitive interaction. Further studies with PNP and benzenesulfonate (BS) revealed that PNB and BS adsorb primarily at two different types of surface sites without significant competition.

Coughlin (13) has shown by experiment that acidic surface oxides on active carbon can profoundly influence the sorption of various organic molecules from aqueous solution. Not only is the equilibrium sorption capacity of the carbon affected, but the rate of sorption is also changed. However, these changes are reversible, for removal of the acidic surface oxides can restore the carbon to its original sorption capacity or beyond. In the cases of sorption of phenol, nitrobenzene, sodium benzenesulfonate, and dextrose, surface oxides reduced the sorption capacity of the carbon as well as the speed of sorption. In the case of urea sorption, the sorption capacity of the carbon was increased by the presence of acidic surface oxides. It appears that the influence of these surface oxides depends on the relative strength of their interactions with both the water solvent and the solute to be adsorbed.

As a general rule, organic compounds are adsorbable, but there are many exceptions, and there are all degrees of adsorption (134). Two broad generalizations which may be helpful are:

1. The larger the molecule, usually the better the adsorption, provided the pores in the activated carbon are of suitable size.

2. The greater the solubility of the adsorbate, usually the poorer the adsorption.

Mass (152) presented some generalities relating to the types of materials adsorbed by carbon:

1. Weak electrolytes are adsorbed better than strong electrolytes.

2. The more ionic a material is, the more difficult it is to adsorb.

3. Sparingly soluble materials usually are adsorbed better than highly soluble materials.

4. High-molecular-weight materials may be adsorbed better than those of low molecular weight.

Zuckerman and Molof (153) stated that the adsorbability of organic material in a wastewater will be determined by molecular size or weight distribution of the soluble organic material. Davies et al. (133) observed that each molecule will, for a given adsorbate, have an "adsorption potential." This potential is a measure of the free energy of adsorption released when the adsorbate molecule moves from solution to the adsorbed state on the carbon

surface. The adsorption potential can be linked with molecular weight and molecular structure. Generally speaking, the higher the molecular weight, the more strongly a given material is adsorbed.

Weber and Morris (141) proposed that activated carbon adsorption of soluble organic material in wastewater is controlled by intraparticle diffusion. If this extrapolation is valid, then the molecular size and configuration of individual soluble organic compounds will be factors of great significance in determining the aggregate adsorption capacity of organic material in wastewater.

There have been a number of published reports of evidence that molecular weight is only one of many factors affecting adsorption of organic matter from aqueous solution. Joyce and Sukenik (47) reported that adsorption decreases with a decrease in concentration of organic material. Eskuty and Admundson (154) postulated that rate of adsorption is controlled by rate of diffusion of solute in the capillary pores of the carbon. Weber and Morris (141) found that the rate of uptake was affected by the initial concentration of the solute and by the molecular size and configuration of the adsorbate. Thus, the rate of uptake decreases with increasing size of the molecule and with molecules of highly branched structure.

According to Weber (132), molecular size is significant if the adsorption rate is controlled by intraparticle transport, in which case the reaction generally proceeds more rapidly the smaller the adsorbate molecule. He emphasized, however, that the rate depends on the class or series of molecules. Large molecules of one chemical class may sorb more rapidly than smaller ones of another if high energies (driving forces) are involved. Lang et al. (74) found that a large portion of TOC remaining after carbon adsorption was made up of low molecular weight organic compounds which are not readily adsorbed by activated carbon (ethanol, acetaldehyde, acetone, formic acid, acetic acid).

The rate of adsorption of a solute at a solid surface may be expected to vary with the surface area and, thus, for a constant weight of adsorbent, with the particle size (155). In water, activated carbon has a preference for large organic molecules and for substances which are nonpolar in nature (21). Forces of attraction between the carbon and the adsorbed molecules are greater the closer the molecules are in size to the pores. Best adsorption takes place when pores are just large enough to admit the molecules.

In addition to size, studies by Morris and Weber (155) showed that molecular configuration has an effect on the rate of adsorption--extensive branching tends to reduce the rate of adsorption. Al-Bahrani and Martin (137) reported that structure of the adsorbate molecule has a significant effect on its adsorption.

Al-Bahrani and Martin observed the effect of molecular structure on 26 low molecular weight aromatic pollutants from aqueous solution. Batch-type experiments were used to investigate adsorption equilibria of each compound. Equilibria data for adsorption of the individual compounds studied were found to

correlate with both the Langmuir and Freundlich equations for adsorption isotherms in the range of concentrations studied; however, two-step isotherms were observed. They observed H bonding and steric hindrance to be significant factors in the adsorption process.

Reimers et al. (156) reported that the principal factors influencing the adsorption of organic solutes are the general molecular structure of the organics, solubility of the organics, and degree of the organics ionization. Some observations by these workers were:

1. Aromatics generally adsorb better than aliphatics.

2. Increased branching generally improves adsorption.

3. Both the position and type of group can influence adsorption of compounds with substituted rings.

4. Increased solubility generally decreases the organics affinity to adsorption on carbon.

5. With decreasing pH, organic acids, on a whole, will ionize less and adsorb better, while the exact opposite phenomenon is usually observed with organic bases.

Bartell and Miller (157) found that introduction of OH and NH_2 groups to organics acids had an adverse effect on their adsorption. Linner and Gortner (158) found that a branched chain had little effect on the maximum adsorption of an organic acid, while the introduction of hydroxyl and keto groups increased, the adsorption markedly decreased.

Cheldrin and Williams (159) showed that the adsorption of 33 amino acids, vitamins, and related substances fit the Freundlich adsorption isotherm. The presence and position of polar groups and absence of aromatic nuclei were noted as important factors in aqueous adsorption of organics by activated carbon.

Ford (35) presented a summation of the influence of molecular structure and other factors on adsorbability:

1. An increasing solubility of the solute in the liquid carrier decreases its adsorbability.

2. Branched chains are usually more adsorbable than straight chains. An increasing length of the chain decreases solubility.

3. Substituent groups affect adsorbability:

Substituent Group	Nature of Influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic are more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double Bonds	Variable effect as with carbonyl.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.

4. Generally, strong ionized solutions are not as adsorbable as weakly ionized ones; i.e., undissociated molecules are in general preferentially adsorbed.

5. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.

6. Unless the screening action of the carbon pores intervenes, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute carbon chemical bonds being formed, making desorption more difficult.

7. Molecules with low polarity are more sorbable than highly polar ones.

Giusti et al. (105) conducted an extensive investigation to quantify some aspects of adsorbability of specific organics. The effects of functionality, molecular weight and structure, aqueous phase, pH, solubility, polarity, carbon surface structure, and adsorbate interactions were investigated. These workers concluded that adsorbability, as reflected in constant dosage tests, is favored by increasing molecular weight, aromaticity, and degree of unsaturation. Increasing polarity, solubility, branching, and degree of dissociation tends to severely limit the extent of adsorption. Typical graphs of adsorbate loading versus molecular weight showed the favorable effect of unsaturation. Aromatics, even those containing polar groups (OH^-, NH_2^-, Cl^-), proved quite amenable to adsorption, while the polyfunctional oxygenated compounds (glycols, glycol ethers) proved especially difficult to adsorb.

Hassler (36) presented a long list of factors influencing adsorption at the carbon/liquid interface. The algebraic sum of all these forces is measured

by the quantity of substance adsorbed by a given weight of carbon. The published data on adsorption of organic compounds from solution provide ample evidence that the architecture of a molecule is an important factor in adsorption phenomena. Some generalities presented by Hassler are:

1. Aromatic compounds are in general more adsorbable than aliphatic compounds of similar molecular size.

2. Branched chains are usually more adsorbable than straight chains.

3. The influence of substitute groups is modified by the position occupied; e.g., ortho, meta, para.

4. Stereoisomers show an inconsistent pattern of adsorption; fumaric acid (trans) is more adsorbable than maleic (cis), but the trans form of hydrobenzoin is less adsorbable than the cis form.

5. Optical isomers (dextra and levo) appear to be equally adsorbed.

Hassler also presents a good discussion of the influence of separate factors on adsorption. Some of his most interesting observations are:

1. Although any change that causes in increase in solubility may be accompanied by a decrease in adsorption, even great solubility does not prevent adsorption of a substance that is strongly attracted to the carbon surface; e.g., the very soluble chloracetic acid is well adsorbed. Conversely, a slightly soluble substance will be adsorbed only if and when an attraction exists to the carbon surface.

2. Ionization is usually adverse to adsorption by carbon. Undissociated molecules of organic compounds are more adsorbable than ions of dissociated molecules; therefore, the acidity or basicity of the solution may be an important factor. The optimum pH is specific for each solute; low pH promotes adsorption of organic acids, while high pH is favorable for adsorption of organic bases.

3. While an increase in temperature may cause a decrease in adsorption, the increase accelerated the velocity of adsorption by stepping up the diffusion of solute molecules.

The extent to which the full surface area of an activated carbon can be used for adsorption depends on the concentration of solute in the solution with which the carbon is mixed (136). Temperature effects on adsorption equilibria generally are not felt to be significant, particularly over the range of temperature encountered in water and wastewaters.

As adsorption reactions are generally exothermic and high temperatures usually slow or retard the adsorption process, lower temperatures have been reported to favor adsorption (36, 132). Very little information has been presented, however, which documents significant shifts in adsorbability within the temperature range 65-90°F.

Snoeyink et al. (146) reported that because phenol sorption is apparently exothermic, an increase in temperature would result in a decrease in sorption of phenol. Lower temperatures should increase adsorption, but the effect in aqueous solutions is very small (138). However, the rate of adsorption is strongly temperature dependent, and generally higher temperature promotes better adsorption.

The hydrogen ion concentration of a solution from which adsorption occurs, for one or more of a number of reasons, may influence the extent of adsorption on activated carbon (145). In general, adsorption of typical organic pollutants from water increases with decreasing pH; thus, there is an increasing adsorption of sulphonated alkyl benzenes on active carbon as the pH of the solution is reduced.

Ward and Getzen (160) reported on studies of the adsorption of three herbicides over a wide pH range. Equilibrium adsorption data on these and seven other structurally related compounds fit Langmuir isotherms in the range of concentrations studied at all pH levels. There was a marked increase in removal of all solutes from aqueous solutions on lowering the pH below 7.0. Adsorption in the acid region was greater than expected from the molecular-ionic ratio of the bulk solution. The effect was explained in terms of an enhanced specific ion adsorption resulting from increasing the proton concentration as the pH was lowered and a subsequent alteration in surface properties of the carbon. Maximum adsorption was attained near the point where the pH = pK_a.

Freundlich adsorption isotherms were obtained on 1,000-mg/liter solutions of five different organic compounds using four different carbons at different aqueous phase pH levels (105). The pH had a marked effect on the isotherm adsorptive capacity of all carbons tested for butylaldehyde and ethyl acetate. A detailed discussion of differences between the carbons tested and the effects of carbon surface properties is presented.

Ford (138) reported that a change in ionization can drastically affect adsorption. A low pH, for example, promotes adsorption of organic acids, whereas a high pH would favor adsorption of organic bases. Phenol adsorbs strongly at neutral or low pH, while adsorption of the phenolate salt at a high pH is poor.

Wang et al. (161) reviewed and investigated the effect of the initial hydrogen ion concentration on activated carbon adsorption mechanisms in single and multicomponent organic aqueous systems. The adsorption mechanisms discussed adequately describe carbon adsorption of single organic compounds from aqueous solution. The effect of pH upon activated carbon treatment of a heterogeneous organic wastewater is complicated. Adjustment of the pH may increase adsorption of one species while suppressing removal of another at the same time. The optimum pH for activated carbon treatment of a specific industrial waste must be determined experimentally because many competing adsorption mechanisms are involved.

Zogorski and Faust (162) evaluated the chemical and physical parameters involved in the adsorption of aromatic hydroxyl (phenolic) compounds by

granular activated carbon. The rate of movement of the mass transfer zone was independent of pH values between 2.5 and 6.4; on the other hand, pH values greater than the pK_a value of the adsorbate significantly influenced the rate at which the adsorbent was utilized. Snoeyink et al. (146) studied adsorption of phenol at various pH values and found maximum adsorption occurred at the pH value of 7.5.

Giusti and his coworkers (105) indicated that a potential problem exists in applying activated carbon to multicomponent wastewaters. It is not possible to select a pH level that assures maximal adsorption of all wastewater constituents. The optimum pH is solute specific and must be determined for each wastewater (138).

Decreasing temperature and pH act to increase both the capacity of the carbon and the rate of adsorption. It seems evident, however, that the cost of controlling either pH or temperature far exceeds any benefit that could be obtained by this action (163).

Most wastewaters contain a myriad of compounds which may mutually enhance, interfere, or act independently in the adsorption process (35, 132). Factors which affect the overall adsorption of multiple adsorbates include the relative molecular size and configuration, relative adsorption affinities, and the relative concentrations of the solutes (132). Factors affecting the rate and magnitude of adsorption include molecular structure, solubility, ionization and mixture of solutes (35).

Jain and Snoeyink (151) reported on a study of competitive adsorption from bisolute aqueous systems on active carbon in batch systems. Adsorption of the two organic species without competition was consistent with adsorption of each species on different sites. A model based on some amount of adsorption without competition is proposed.

This study of competitive adsorption was performed to give insight into some of the factors affecting selective uptake of organic compounds on active carbon from bisolute aqueous solutions. Results of the study are consistent with a number of phenomena which include: (a) adsorption with equal competition for adsorption sites, (b) adsorption of each of the two species on different kinds of sites to an extent that only minor competitive effects were observed, and (c) competitive adsorption of organic anions with electrostatic repulsive forces between adsorbed species. Weber (164) has shown the significant effect of competitive adsorption on the breakthrough curve, thus demonstrating the importance of competitive effects in column design and operation.

The effects that can result from the presence of multiple organic solutes can be quite specific, depending on relations existing among the various ingredients (36). Some components diminish the adsorption of others; others may cause a mutual increase; still others show no measurable change. Compounds that show great adsorbability from pure solutions are often preferentially adsorbed from a mixture, but there are many exceptions; the quantity adsorbed does not always reflect the strength of the attachment to the surface. Consequently, amounts adsorbed from the pure state should not be used to predict the proportions in which ingredients will be adsorbed from a mixture. 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 (42). 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.

Lang et al. (74) stated that the adsorption of organic substances from a mixed solution is a complex phenomenon, possibly owing to the effect of one substance on another. This can manifest itself in preferential adsorption of one substance over others, nonadsorption if a substance is only weakly adsorbed at best, or the displacement of a weakly adsorbed by a strongly adsorbed substance. This selective or preferential adsorption must be kept in mind in the evaluation of equilibrium adsorption data.

Davies et al. (133) stated that when considering adsorption from multicomponent adsorbate solutions, the solid-liquid system becomes more complex but will tend to equilibriate at the lowest possible energy state. Hence, a heavy molecular weight adsorbate will tend to replace a previously adsorbed adsorbate of lower molecular weight. In the case of activated carbon, the exact mechanism of adsorption on the surface is of less significance in practical terms than the sheer magnitude of available surface area.

Masse (152) stated that in general, however, the net effect of mixed materials is not detrimental, and there may be an enhancement of the total weight of materials adsorbed from mixtures.

ADSORPTION MODELS

There are several theoretical models which have been used to describe the adsorption phenomenon, none of which have been shown to be universally applicable to wastewater-activated carbon systems (58). This is not surprising considering the extremely heterogenous nature of soluble organics in wastewaters (molecular size, concentration, functionality, etc.) and of activated carbon (pore size and distribution and functionality).

The analysis of steady state adsorption data may take several forms (18). The most common form is the adsorption isotherm. Among the equations applied to equilibrium adsorption data are the Langmuir equation and the Brunauer, Emmet, Teller (B.E.T.) Model. These equations may be deduced from either kinetic considerations or the thermodynamics of adsorption. The Langmuir equation is valid for single-layer molecule adsorption, while the B.E.T. Model reflects apparent multilayer adsorption. The familiar Freundlich isotherm is of empirical origin but has since been derived by assuming a logrithmic distribution of adsorption sites, a treatment valid only when there is no appreciable interaction between adsorbed molecules. Burleson et al. (18) stated that a mathematical representation of the adsorption characteristics for unknown mixed solutes present in biologically treated industrial wastewaters is difficult, if not impossible.

Adsorption results in removal of solutes from a solution and their concentration at a surface until such time as the amount of solute remaining in

solution is in equilibrium with that at the surface (42). This equilibrium is described by expressing the amount of solute adsorbed per unit weight of sorbent as a function of the concentration of solute remaining in solution. An expression of this type is termed an adsorption isotherm. Weber (42) stated that the adsorption isotherm is useful for representing the capacity of an activated carbon for adsorbing organics from a wastewater and in providing a description of the functional dependence of capacity on the concentration of pollutants. Theoretically, the sharper the rise of the isotherm to a given ultimate capacity as the concentration increases, the more effective will be the activated carbon in adsorbing organics from the wastewater. Experimental determination of the isotherm is routine practice in evaluating the feasibility of adsorption for treatment in selecting an activated carbon and in estimating carbon dosage requirements.

Fornwalt and Hutchins (165) have outlined the isotherm procedure in detail. They also discussed interpretation of the Freundlich isotherm. Qualitatively, very steep isotherms, while indicating high ultimate adsorptive capacities, also indicate the possibility that very low effluent concentrations cannot be achieved without massive dosages of carbon.

The Freundlich isotherm is valid within the context of a batch test for pure substances and some dilute wastewaters (35). Its application is limited in certain cases when a significant portion of the organic impurities are not amenable to sorption, resulting in a constant residual regardless of the carbon dosage.

The empirical Freundlich model has been widely used for wastewater-activated carbon adsorption systems (47, 133, 135, 166). However, its complete adequacy has not been fully established (58). Two major shortcomings are that a maximum adsorption capacity (loading) or any unadsorbable soluble organic fraction are not accounted for. When evaluating relative effects of carbon type, pretreatment, and method of contacting, these shortcomings do not limit utility of the Freundlich model.

Hutchins (65) stated that, since granular activated carbon is not suitable for treating all types of wastewater, preliminary feasibility testing should be conducted. He proposed the adsorption isotherm as a useful first step in determining the feasibility of granular carbon for treating a given wastewater. The isotherm provides a good idea of the effectiveness of the carbon in adsorbing the impurities present in the wastewater and an indication of the maximum amount of impurities that will be adsorbed by the carbon. The main limitations of an adsorption isotherm are:

1. It provides no indication of the biological removal that may occur.

2. Lack of precision in measuring the parameters, e.g., BOD, COD, may result in considerable scatter in the data points.

3. Adsorption isotherms are equilibrium tests, and they do not indicate the actual performance of the carbon.

4. Granular carbon is not always completely exhausted in the adsorber.

5. Powdered carbon has a significantly greater adsorption rate than granular material.

Mathematical description of adsorption isotherms for a particular system is also required for development of predictive models for design application (16, 132). Details of conventional Langmuir and Freundlich isotherm expressions are readily available in the literature (132). Laboratory techniques and procedures for carbon adsorption isotherm studies and related analyses are outlined by Eckenfelder and Ford (167).

Lawson and Fisher (107) reported that the use of "adsorptive capacity" calculated from Freundlich adsorption isotherm in the design of continuous systems is highly unreliable. Isotherm capacities are consistently higher, often several times higher, than capacities achieved in columns. This indicates the necessity for actual column tests to define the anticipated performance. Batch isotherm tests are useful, however, in determining the trend of organic removal with increasing carbon dosages. Data are presented comparing adsorptive capacities calculated from Freundlich isotherms with those observed in continuous column studies when the breakthrough curve was taken to exhaustion.

Hager and Reilly (9) ran carbon isotherm studies on 11 different municipal wastewaters. They concluded that standard isotherm testing is definitely inadequate to determine the dosage and feasibility of the adsorption process in treating wastewaters. One phenomenon that has often manifested itself in activated carbon studies has been the inability to match ultimate carbon loadings found from isotherm tests with those experienced in continuous systems (105).

Lawson and Hovious (108) stated that isotherm tests provide a relative indication of the amount of organic removal achievable by adsorption and the ultimate adsorptive capacity of the carbon. Unfortunately, these data are useful only in a relative sense--for comparing the relative merits of two different carbons or for comparing the relative amenability of different wastewaters to adsorption. Isotherm data are not suitable for designing continuous granular carbon adsorption columns, since the dynamic effects and interactions in a continuous bed differ too greatly from the batch equilibrium situation in an isotherm.

Lawson and Hovious also reported that while pure component adsorption data are useful in determining which waste streams are potential candidates for activated carbon treatment, the data cannot be used to quantitatively predict adsorption from multicomponent systems. Ford (138) maintains that adsorption theory is rigorous for single solutes but becomes much less definitive when applied to wastewaters containing multiple components with varying molecular weights and chemical characteristics. He adds that batch isotherm studies are not necessarily indicative of continuous flow carbon treatment systems. Results of comprehensive carbon pilot testing of refinery wastewaters depict an average organics removal significantly less optimistic than that indicated in isotherm tests.

Giusti et al. (105) examined interactions in multicomponent systems by running adsorption isotherm tests on binary and four-component mixtures. The total adsorptive capacity, as depicted by the isotherm results, was significantly less than the sum of the pure component capacities. Thus, while pure component data may be useful in determing which waste streams are potential candidates for activated carbon treatment, the data cannot be used to quantitatively predict adsorption from multicomponent systems. An additional phase of the study consisted of operating continuous column granular carbon adsorbers to exhaustion for comparison of ultimate capacities with isotherm capacities. In all cases, the ultimate capacity (at exhaustion) was less than that predicted by isotherms.

Ford (35, 138) observed that there are many factors which influence both the rate and magnitude of adsorption, underscoring the difficulty in developing predictive models which would apply to all complex wastewaters. He reported that predictive models obviously require validation for complex wastewaters, as extrapolation from investigations using synthesized wastes containing controlled concentrations of selected adsorbates may not reflect all of the interactions occurring in the waste. A summary of the more important factors which potentially influence adsorbability is presented. Culp and Culp (21) stated that for liquid adsorption systems, there is no precise method for predicting the performance of carbons founded on their basic properties or those of the adsorbing materials.

Limitations of theoretical adsorption concepts relative to the practicalities of treatment requirements for refinery and petrochemical wastewaters necessitate that comprehensive process simulation studies precede the finalizing of design decisions (83). There is a tendency for investigators and equipment developers to oversimplify the adsorption process adaptability for industrial wastewater applications. The technical and economic justification for applying carbon adsorption for the treatment of refinery and petrochemical wastewaters at any point in a process sequence can be determined only after a thorough investigation using continuous-flow pilot systems. Proper interpretation of the results is then necessary to consummate the process evaluation, determine the economics, and select the most appropriate treatment sequence.

A completely developed system of adsorption column design has been presented by Hiester and Vernuelen (168). They solved graphically the equation for second-order reversible adsorption. Based on the Hiester and Vernuelen reaction-kinetics solution for packed beds, Keinath and Weber (169) developed a mathematical model for description of mass-transfer processes in columns of fluidized activated carbon. According to the described tests, this model predicts adequately the concentration-time profiles for systems in which flow rate, particle size of the adsorbent, solute concentration, and depth of bed varied.

Work was done by Weber and Morris (170) to define and evaluate the characteristics of adsorption from aqueous solution in columns of fluidized media. The kinetics of adsorption were investigated in terms of uptake profiles relative to the velocity dimensions, time and length, for selected values

of these variables and for different sized particles of adsorbent. Thirteen fluidized-bed studies were conducted. Postulated models show the kinetics of the systems studied.

Bell and Molof (171) described a conceptual model of batch adsorption kinetics. Intraparticle transport was proposed to occur in a series of distinct adsorption-desorption steps, each linear with respect to time.

Allen et al. (172) discussed some of the process engineering aspects of adsorption columns for the purification of liquid wastes. These workers reported that laboratory data on a liquid-phase adsorption system can be fitted to an empirical equation which then can be used to study a wide range of plant design and operation variables. A computer program for determining the rate constant that gives the closest fit between experimental and calculated effluent concentrations has been developed by these workers and is summarized in this paper.

Neretnieks (173) proposed a simple method whereby the film transfer coefficient and coefficient of diffusion in the particles may be determined from finite bath adsorption experiments. The method also makes it possible to separate pore and surface diffusion. Under certain conditions, it is also possible to determine the influence of the particle phase concentration on surface diffusivity. The method is based on models describing the interstitial diffusion in the solids. Data from six different adsorption systems were analyzed using this method. It was found that in all systems surface diffusion was the determining transport mechanism in the particles.

Westermark (7) presented an adsorption model which incorporates a linear adsorption isotherm and accounts for both film and pore diffusion in the carbon bed. Design of different modes of carbon contact were presented with the optimization of contact time. Equilibrium constants and pore diffusivities were evaluated for four different carbons. The theoretical model was used for the development of design criteria and optimization criteria for continuous and periodic adsorption plants.

Work by Andrews and Tien (174) represents the first attempt to separate contributions of adsorption particle deposition and bacterial activity to overall removal of TOC. By making several assumptions about mechanisms that are described and their interactions, a mathematical model capable of predicting TOC breakthrough curves was developed. Experimental work proved the model basically sound. The authors are hopeful that it will be possible to develop the model into a useful tool for the designer of wastewater treatment plants.

Hsieh et al. (175) concluded from their batch adsorption kinetic experiments on multicomponent systems that the adsorption isotherm for the wastewater activated carbon system is of the Freundlich type. Furthermore, the internal diffusion model appears to be a more suitable one than the pore diffusion model in describing the adsorption process, mainly because diffusion coefficients based on this model exhibit relatively smaller variations. The internal diffusion model, in addition, leads to simpler mathematical formulations.

Hutchins (176) presented a new calculation method called Bed Depth/ Service-Time (BDST) analysis that could speed up the design process by reducing the amount of preliminary testing. Basically, it is a means of predicting effects of different feed concentrations, flow rates, or effluent compositions. BDST analysis applies only to granular carbon systems which are not in equilibrium. Hutchins cautioned, however, that even with good BDST data, design should be tempered with experience and judgement.

Vanier and Tien (177) devised a mathematical model to simulate the adsorption and filtration of wastewater in an isothermal column packed with granular activated carbon. The adsorption process is considered to be controlled by a combination of liquid-phase diffusion and interparticle diffusion. In addition to adsorption and filtration, effects of backwashing and regeneration are included in the model. A computer program has been prepared and coded in Fortran IV. A unique feature of this program is the clear separation of calculation framework and model for the column behavior.

Weber and Crittenden (16) have developed a general modeling scheme termed MADAM I (Michigan Adsorption Design and Application Model I). Based on numeric solution techniques, MADAM I is not restricted to simplified rate and equilibrium expressions to facilitate analytical solutions. Rather, it can accommodate the dynamic aspects of fluid dispersion, solids mixing, multisolute interactions, and biological growth on activated carbon surfaces--aspects which must be excluded because of mathematical complexity from models which are based on analytical solution techniques. Mathews and Weber (178) have recently described the use of a general, widely applicable, 3-parameter isotherm model for multicomponent waste streams.

Straightforward mathematical procedures for predicting breakthrough curves of continuous flow columns, as described by Westermark (7) and Weber (132) may be used for process design in certain cases when time or budget constraints prohibit the conduct of column tests (179). These methods require prior knowledge of such fundamental data as the equilibrium adsorption capacity, kinetic parameters of the adsorption process, and the hydrodynamics of flow within the columns. Various assumptions are necessary in order to facilitate the mathematical solutions, and these further restrict their applicability to a limited number of ideal systems.

Lukchis (180) discussed the mass-transfer-zone (MTZ) concept for use in designing a fixed-bed adsorption system. Both rate and capacity considerations confront the engineer designing a fixed-bed system. Mass-transfer coefficients provide insight into the mechanism by which adsorption occurs but can be difficult to determine and tedious to use in designing problems. The MTZ concept provides a simple, effective method for considering rate phenomena in fixed-bed adsorption systems. The concept is particularly amenable to rapid determination and correlation of rate data and simple design procedures. Thus, a simpler calculation of column height and diameter is possible.

An appraisal of the suitability of activated carbon for an untried operation involves two basic considerations (36):

1. Will activated carbon accomplish the desired objective?

2. If so, does efficiency compare with that provided by other means?

MacCrum and Van-Stone (23) have suggested a method by which an industrial plant can determine the feasibility of using a carbon process. The method involves four initial fact-find steps: wastewater survey, pretreatment requirements, laboratory adsorption isotherms, and pilot studies.

PROPERTIES OF ACTIVATED CARBON

In addition to loading capacity, other properties must be considered when choosing a carbon for a given application (74). These properties include whether powdered or granular carbon is best, the rates of adsorption, the friability of the (granular) carbon, handling problems, and cost. If a carbon is to be used in a column contactor, it should be evaluated in continuous column tests with the particle size most likely to be used in the future plant scale of operation. The choice between powdered or granular carbon is usually decided on grounds of economy and/or convenience (145). Both powdered and granular forms of activated carbon are manufactured in a wide variety of grades and sizes to accommodate the various liquid- and gas-phase applications (181). Kelso and Lapp (181) have compiled information on various aspects of the manufacture and use of this material. Specific areas of interest were the raw materials and methods of production, manufacturers, production capacities and actual production, and consumption patterns of activated carbon.

Commercially available carbons vary widely in their characteristics and more particularly in their effectiveness in removing dissolved TOC or color from different effluent streams (74). By using a wide variety of commercially available activated carbons in the laboratory program, it is possible to select suitable commercial carbons for pilot-plant operation as well as for potential full-scale application.

Activated carbons have specific properties, depending on the material source and mode of activation. As a rule, granular carbons made from calcined petroleum coke have the smallest pore size, largest surface area, and highest bulk density (182). Lignite carbons have the largest pore size, least surface area, and lowest bulk density. Carbons from bituminous coal have an average pore size and surface area somewhere between that of petroleum coke and lignite carbons and a bulk density equal to that of petroleum coke.

A comparison of activated carbons produced from lignite and bituminous coal was presented by DeJohn (183). Lignite carbon gave higher organic loadings and during regeneration lost surface area at a slower rate. Also, larger pore structure and ash content of lignite permitted lower temperature regeneration. Comparative properties of these two carbon types are presented by Swindel-Dressler (14).

DeJohn (184) reported that the best design data can be obtained by using a long-service activated carbon which has been regenerated five or six times. Since such carbon is not readily available and a virgin carbon must generally be used, a lignite carbon will generally be the best alternative because it is less susceptible to changes in properties and performance upon successive regeneration than bituminous coal carbons.

There is no adequate explanation of the selective action of different carbons for different materials (145). This selectivity is best established by means of experiments using the same waste material, the same conditions, and the same carbons as proposed for the full-scale treatment systems.

Chaney et al. (143) summarized the general problem of the physical nature and interrelationships of various forms of activated carbon. The type of carbon to be selected for a given purpose cannot be considered apart from the development of the appropriate engineering methods for its employment. All types of carbon do not respond similarly to changes in operating conditions; consequently, the carbon that shows the most promise in the initial test may not prove to be the best under operating conditions finally adopted (36).

Ford (35) reported that the selected carbon should:

1. Have the adsorption capacity to meet the effluent requirements.

2. Incur minimum losses during carbon transport and regeneration.

3. Have good hydraulic characteristics with respect to head loss or pressure drop.

4. Represent the most cost-effective media to accomplish the prescribed task.

These general areas of consideration should be augmented by test data and process requirements developed from bench- or pilot-scale evaluations using representative wastewater samples and selected carbons.

It is well known that carbons differ in their adsorptive capacity for a given substance (36). Furthermore, carbons show highly specific interactions with various substances. Thus, a carbon that has a high capacity for decolorizing molasses may have a relatively low capacity for removing phenol.

Large differences have been found between carbons, but no useful correlation has been found between efficiency and either surface area or the ability of the carbon to adsorb specific model substances (185). Therefore, index numbers can be misleading, although they have merit for initial screening. Bishop et al. (185) studied 12 carbons and sought to correlate adsorption efficiency with other parameters that might be used as purchasing specifications. He stated that the superior performance of some carbons seems to be related to their ability to remove a portion of the organic matter in suspension.

When an adsorbable solute molecule makes contact with a suitable unoccupied space on the carbon surface, the molecule will adhere instantly; therefore, time required for the adsorption process depends on the rate at which solute molecules can diffuse to the carbon surface plus time to find the unoccupied space (36). In carbon columns, initially many sites are available on the exterior portions of the surface. Molecules arriving later must find sites in the interior, which requires a longer time. After a brief, rapid initial adsorption rate, the subsequent rate becomes much slower, especially for larger molecules. Granular carbons may require many hours to utilize an appreciable

portion of the total potential adsorptive capacity. With powdered carbon, if the mixing is adequate, a major portion of adsorption is accomplished within an hour, although adsorption may continue at a diminishing rate for days or longer.

In comparing adsorption data of different investigations, one should be aware that quantitative data (i.e., precise quantities of substance adsorbed) are reproducible only when the studies are conducted under identical operating conditions (36). A different temperature or concentration or use of a different carbon can alter the amount adsorbed. Masse (11) reported that with a given carbon and a specific wastewater, the product quality is a function of the contact time and the amount of wastewater that has been passed through the column.

The two most popular sizes of granular carbon for wastewater treatment are 8 x 30 mesh and 12 x 20 mesh (21). Suggested specifications for granular activated carbons to be used in wastewater treatment are also presented. It is proposed that the best methods for evaluating and characterizing carbons are: (a) quantifying the adsorption characteristics, (b) describing the physical properties, and (c) conducting and interpreting pilot carbon column studies.

The decision on the choice of carbon is not always easy since so many factors must be considered (186). All granular carbons are not alike; and differences exist among carbons from different manufacturers and, very likely, for different batches from any single manufacturer. Before final selection of a carbon, it behooves the consulting engineer to do some preliminary testing, including some pilot work.

As a general rule, suppliers of activated carbon provide a table of quality parameters for their products. Mattson and Kennedy (150) have reported that most of this information is of little or no value to the individual whose responsibilities include evaluating the economics of several competing activated carbons. They suggested that potential users undertake an evaluation of each carbon in their own system and ignore the data provided by the suppliers.

Brunauer et al. (187) presented suggested specifications for granular activated carbon for use in wastewater treatment. Hassler (36) stated that two different grades of carbon should be employed when a single grade does not have all the properties needed for purification.

GRANULAR CARBON SYSTEMS

In the general area of treatment by granular activated carbon adsorption, the economics are such that the carbon columns are utilized best by driving them to their equilibrium adsorption capacity and then regenerating and reusing the carbon as many times as possible (150). An increase in the adsorption capacity for any carbon can be economically offset by a corresponding decrease in its ability to resist attrition. The ability of a granular carbon particle to resist mechanical and hydraulic attrition plays the most important economic role in selecting the carbon that will result in the lowest operating costs. Carbon must be regenerable for these systems to work, and the regeneration losses must be kept to a minimum.

With the high first costs of carbon, it is essential in most applications that the carbon be regenerated and removed after exhaustion of the initial adsorption capacity to be economically feasible (188). The economic basis for the use of granular activated carbon for removal of dissolved organics lies in: (a) having a high capacity to remove residual organics and (b) the regeneration of the carbon capacity for reuse in the treatment facility.

The most economical way to minimize operating costs in an established granular carbon system is to use the carbon that gives the best performance as a long-service carbon, provides the lowest loss, and has the lowest delivery cost (189). Minimizing the dosage is the most effective method of minimizing the effect of carbon-related factors on operating costs. Carbon loss or price has a minor effect.

Whether bituminous coal or lignite carbons are used does not greatly affect the operating costs of the system (189). Generally, the most economical granular carbon system is the least expensive, properly designed system that contains the least expensive, suitable granular activated carbon.

The technology required to employ granular activated carbon for adsorption has been developed and available for several years. The commercial availability of high-activity, hard, dense granular activated carbons made from coal, plus the development of multiple-hearth furnaces for on-site regeneration of this type of carbon, led to the early establishment of granular activated carbon as an economically attractive unit process for wastewater treatment (21).

Joyce and Sukenik (47) and Joyce et al. (25) successfully demonstrated that granular carbon can be reactivated thermally for reuse and a practical operating capacity maintained. Thermal regeneration refers to the process of drying, thermal desorption, and high-temperature heat treatment in the presence of limited quantities of oxidizing gases (15). Thermal regeneration using a multiple-hearth furnace has been the most widely applied method in wastewater treatment (35).

Reactivation of granular carbon by thermal reactivation has been discussed in detail by Juhola and Tepper (190). The relative merits of directly and indirectly fired furnaces for regeneration were presented. They concluded that indirectly fired furnaces were capable of reducing regenerating losses to less than 3%. Regeneration losses experienced in field tests have been found to be from 5-20%, including mechanical attrition, for 8 x 30 and 12 x 40 mesh carbons (150). Additional discussions of thermal reactivation of granular carbon have also been presented by Culp and Culp (21), Schuliger and VanCrum (191), and Juhola (192).

Himmelstein et al. (193) explored the technical and economic advantages of in-situ regeneration of activated carbon. Operating experience from the use of reactive regeneration and solvent regeneration is presented. Reactive, solvent, and thermal regeneration are compared over a large range of concentrations. In-situ regeneration has the advantages of minimizing losses--first, due to transport to and from the regeneration site and, secondly, due to the avoidance of losses associated with thermal regeneration. An added attraction is the opportunity to recycle products from the waste streams. As the concen-

tration of the adsorbate increases, solvent and reactive regeneration systems become more attractive than thermal regeneration. Several systems which have been developed by the authors are presented as technological alternatives to thermal regeneration.

Offline batch biological regeneration of spent activated carbon has been shown to effectively maintain the carbon capacity near that of virgin carbon (194). Recirculating aerated water through the contactor at incipient fluidization velocities proved to be a simple means of regeneration.

Carbon usage for treating industrial wastes may overshadow the municipal use (186). It is in the industrial use of carbon where regeneration other than thermal may be used. The recovery of product value from the adsorbed material, in many cases, favors these approaches over thermal regeneration.

Johnson et al. (195) investigated the chemical regeneration of exhausted carbon by the use of nine inorganic oxidizing agents. They concluded that the economic feasibility of chemical regeneration was not promising. Friedman et al. (196) reported that none of the chemical regenerants used restored the original activity of the lightly loaded activated carbon upon which the tests were performed. Generally, regeneration methods other than thermal will not be effective enough if a complex mixture of organics have been adsorbed (197).

Loven (15) prepared a state-of-the-art report on carbon regeneration in liquid-phase applications including historical development, recently developed and experimental processes, and thoughts for further development. Attention is directed to regeneration processes for spent carbons from wastewater treatment systems utilizing both powdered and granular carbon processes. Loven proposed increased research and development into the mechanisms of thermal, chemical, and biological regeneration in order that better understanding of these processes might be developed. He sees a clear need for continued growth and improvement of carbon regeneration.

Extensive cost information on thermal carbon regeneration in a multiple-hearth furnace has been presented by Hutchins (176). To determine if spent carbon should be regenerated on site for reuse, custom regenerated, or discarded, operating costs must be compared. Carbon should be discarded at usage rates lower than 350-400 pounds per day and thermally regenerated at higher usage rates. If less than 580 pounds per day is used, it is generally more economical to have the carbon custom regenerated than to regenerate it yourself or to discard it. At higher rates, on-site regeneration will be more economical. Cohen and English (186) reported that the minimum size physical-chemical plant for which it is economical to provide on-site facilities for carbon regeneration has not yet been established. In the future, small plants for which on-site regeneration is not now economical may use jointly owned facilities or may be able to use excess furnace capacity in some larger plant.

Lang et al. (74) reported that it is possible for the recovery of by-products by adsorption-desorption cycles with activated carbon. The return of such by-products could be credited against effluent treatment costs.

Because small pore surface area will decrease substantially as a result

of thermal regeneration, column studies using carbon regenerated five or six times should be conducted before a carbon system is designed (3). This is extremely important if the wastewater contains predominantly small molecules.

Joyce and Sukenik (198) reported that granular activated carbon in packed-bed column contactors 20 feet deep and operated at a flow rate of 4 gpm/ft^2 reduced the COD to an average of 18.5 mg/liter. The removal was not significantly different from the removal obtained when operating the same columns at 10 gpm/ft^2. The cyclic saturation and regeneration of activated carbon through 16 cycles had an average carbon loss of 4.6%.

Design of carbon beds for removing organic colloids has also been discussed by Cookson (199). He illustrated how kinetic and equilibria data could be used to predict the behavior of activated carbon beds. The variables of flow rate, bed depth, void fraction, particle and bed characteristics, and removal efficiency were evaluated by mass transfer theories. Mathematical descriptions were used to predict the efficiency and bed capacity.

Culp and Culp (21) devote considerable attention to granular carbon adsorption from selection of the carbon to design of full-scale treatment facilities. The authors listed three controlling factors as most important in determining effluent quality and carbon dosage: (a) contact time, (b) pretreatment, and (c) extent of the use of countercurrent principles. Bernadin (200) listed the major design parameters as: (a) contact time, (b) carbon usage rate, and (c) pretreatment requirements. He also discussed how to determine whether activated carbon treatment is feasible and how to go about collecting preliminary process design parameters.

Argaman and Eckenfelder (179) discussed design of activated carbon treatment systems for industrial wastewaters, conduct of laboratory and pilot experiments for specific applications, and application of experimental results for process design. Industrial wastewater is extremely variable in nature and concentration and should be considered on a case-by-case basis. The most reliable approach to design of a carbon adsorption system is to conduct pilot column tests under conditions similar to those expected in the prototype.

Carbon column tests are often run in ways that give unreliable results, e.g., testing at unrealistic flow rates or residence times, columns less than 1 inch in diameter, short runs, or unrepresentative feed (65). Obviously, column tests should be based on the same conditions as those expected in the actual plant system.

Anderson (145) highlighted the most important process engineering design parameters for an activated carbon waste treatment system. The prime operating cost is the expense of makeup carbon. The volume of makeup carbon can be reduced to a minimum by careful attention being paid both to the chemistry of the adsorption process, specifically to the treatment problem being considered, and to the engineering design of the treatment system.

Cooper and Hager (8) reviewed the technical and economical feasibility of waste treatment systems utilizing regenerable granular activated carbon. Diagrams of the granular carbon reactivation cycle and the three basic adsorber

design configurations (fixed beds in series, moving beds, and fixed beds in parallel) are included. Design parameters are discussed; however, the infinite variety of wastewaters from municipal and industrial sources makes any generalization of design parameters difficult at best. Cooper and Hager stated that operating costs of granular carbon systems reflect two major items of expense--carbon makeup and equipment amortization. System optimization requires an analysis of all factors as they vary with the treatment design.

Cover and Pieroni (33) summarized findings of the work on tertiary wastewater treatment with activated carbon. The first phase consisted of a thorough literature review of the data on tertiary wastewater treatment with a view to generating sufficient basic data for process design of various schemes for carbon adsorption. The data extracted from the various sources should provide sufficient information to make empirical designs of the type that have already been demonstrated. The second phase consisted of preliminary economic evaluations of several contacting schemes with a view toward finding which variables have economic significance. Adsorbent cost and regeneration loss were found to have a significant effect on total operating costs. Additional variables of importance are velocity, contact time, particle size, adsorber configuration, and number of contacting stages.

Cover and Wood (201) presented the engineering design and cost estimates of a 10-mgd plant for tertiary treatment of wastewater with granular activated carbon. This report contains the process description, design bases, plant operation, control rationale, equipment list, equipment specifications, and cost estimate. The design incorporated reliability, economy, and then state-of-the-art technology. The design was based upon the application of mature engineering judgement to available data.

Cover and Wood (24, 202) presented detailed designs and cost estimates for treating by carbon adsorption 1, 10, and 100 mgd of municipal wastewater from biological treatment. These papers deal with the economic importance of several design variables. Variables considered are plant size, velocity, contact time, carbon loss, capacity, cost, type of contactor, number of contacting stages, and certain combinations of these variables.

A process design manual for carbon adsorption was prepared for the EPA Technology transfer by Swindell-Dressler Company (14). The manual includes sections on general process considerations, process configurations, process design parameters, equipment design, evaluation and selection of carbons, and personnel requirements. Some of the more interesting observations presented are:

1. The carbon adsorption process readily lends itself to integration into larger, more comprehensive waste treatment systems.

2. The greatest cost within the carbon treatment process is the cost of carbon itself. Thermal regeneration of the spent carbon makes the process economically feasible; the cost of the regenerating equipment, however, represents only a small fraction of the total capital cost.

3. The most important design parameter is contact time. Hydraulic loading within the ranges used has little effect on adsorption.

4. Data from laboratory and pilot tests, as well as experience from existing full-scale plants, must be carefully interpreted prior to the design of a new plant.

Fornwalt and Hutchins (165) presented a method of evaluation that enables the engineer to select the activated carbon that will economically yield the product purity desired. It also describes how to get the data from which the plant system can be designed. Fornwalt and Hutchins (203) also presented a rationale for scaling up single-column breakthrough data to a full-scale, multicolumn adsorption system utilizing carbon in a countercurrent fashion. Contact time is held constant in this scale-up method.

Hager and Reilly (9) reported that the clarification-adsorption process offers advantages over biological treatment which are difficult to quantify in terms of dollars and cents but are of increasing importance to treatment plant operators and the general public who see and use treated effluents.

The value of the isotherm data presented by Hager (19, 20) from his Adsorption Isotherm Survey of Industrial Wastewaters is in its use as a reference when considering treatment alternatives available for a specified industrial wastewater problem. The data provide preliminary indications as to the utility of carbon adsorption for treatment of wastewaters from 104 manufacturing operations. Hager (20) presented design parameters covering solvent features of adsorption systems installed in 15 plants included in the 104 manufacturing operations. He proposed that adsorption must be considered with other treatment processes to optimize economics in relation to desired treatment objectives.

The design of granular carbon systems can be difficult and time-consuming (65). The usual approach involves a four-step progression--powdered carbon isotherms, laboratory column tests, pilot-scale tests, and finally design of the commercial unit.

Zanitsch (204) discussed and described in detail adsorption system components. He stated that the design engineer has considerable flexibility in selecting the type of granular carbon system best suited for a specific situation. As a result, capital and operating costs of a system vary with the design selected. Care must be taken to optimize the capital and operating costs before a final decision is made.

Lukchis (205) discussed the factors influencing equipment design for carbon adsorption systems. He stated that simplicity is the key to the design of commercial beds. Adsorbers seem to perform best when the quantity and complexity of vessel intervals are kept to a minimum. Vessel costs tend to increase dramatically with the diameter. The minimum diameter of adsorber beds is set by pressure drop limitations.

Design of the carbon column should be such as to ensure that the adsorptive capacity of the carbon is utilized as fully as possible before regeneration (145). Design factors include type of carbon, mesh size of carbon, length of column, cross sectional area of column, and water flow rate. Flow rate and column length together determine contact time. Optimization of design parameters

is essential; e.g., a fine mesh carbon will provide a short contact time, but this is best obtained by reducing the column length and thus reducing head loss.

Contact or residence time is the major design parameter for the adsorption systems (65). The optimum residence time determines size of the adsorbers and volume of the carbon bed. Regeneration equipment should be sized according to the rate of carbon consumption required to maintain an acceptable product. Hutchins (65) reported that minor design and operating parameters include linear flow rate, impurity concentration, composition in feed product, pH, temperature, and viscosity. Additional factors are properties of the adsorbent, such as, particle size, adsorptive capacity, pore size distribution, and chemical nature of the adsorbent surface. Some of these factors are interrelated; therefore, both adsorption and regeneration sections of the system should be larger than the optimum size based on estimated residence time and carbon consumption.

Lukchis (206) presented a simplified process design procedure for regenerative adsorption processes. Design of multicomponent systems is similar but considerably more complex. Desorption is the key step in the performance of regenerative adsorption systems. It involves simultaneous mass and heat transfer passing through a packed bed of adsorbent under carefully controlled conditions.

Carbon losses affect the operating costs of a granular carbon thermal regeneration system (189). To minimize the amount of carbon lost as a result of attrition, the adsorption, regeneration, and carbon handling system must be adequately designed.

It has been noted in various treatment systems that long-term column adsorption treatment studies generally result in developing carbon dosage rates lower than that determined based on isotherm testing (89). Biological degradation in carbon columns can reduce the carbon exhaustion rate in an operating plant by as much as 30%. It was also noted that capital cost is primarily a function of the amount of water to be treated.

The carbon capacity determined from continuous flow column studies is 10-80% greater than that predicted by the batch isotherm tests for the cases studied (83). This difference is attributed to the higher concentration gradient and biological degradation which prevail in columnar studies.

Weber et al. (38) reported that biological activity in carbon columns results in partial regeneration of the carbon, thereby increasing the capacity. The biological activity seems to enhance overall capacity for removal of organics, thus affording longer periods of effective operation than might be predicted. The biodegradable organics undergo anaerobic decomposition inside the carbon pores and release low molecular weight intermediate products typical to anaerobic processes. These products may be further degraded aerobically if sufficient oxygen and aerobic biota are present or else escape with the effluent. To eliminate excessive fouling of columns due to aerobic biological growth, expanded-bed operation is advocated.

The continued adsorption activity of carbon well beyond its expected

capacity has been observed by Perrotti and Rodman (207). This may be due to the desorption effect produced by exo-enzyme activity. The mechanism of this activity is still not fully understood, however.

Bishop et al. (208) conducted pilot-plant studies of a physical/chemical process using granular activated carbon to treat raw wastewaters. In all cases, a nonsorbable fraction was found to exist. The nonsorbable fraction increased with the loading and the development of biological activity in the columns.

Based on pilot study results, Weber et al. (38) and Hopkins et al. (39) suggested that carbon columns become saturated rather quickly with some fraction of the organic material which hinders total organic removal. Thus, the main columns "leak" organics, and the polishing column is suggested as a possible solution. It evidently picks up organics which are only weakly sorbed.

Joyce et al (25) reported on a pilot-plant study to determine the economic practicality of using granular activated carbon adsorption to treat secondary effluents. The data indicated an organic residual averaging 15-20 mg/liter COD in the effluent. This supports the conclusion that a nonsorbable material was present in the wastewater.

The leakage of organic matter through activated carbon columns was first noted by Joyce and Sukenik (198). Such a leakage was also reported by Parkhurst et al. (40), who observed that a certain fraction of the organic matter of an activated sludge effluent was not removed in carbon columns. The presence of this nonadsorbable fraction has been illustrated in batch adsorption studies (209). Increasing the amounts of activated carbon beyond a certain dosage did not further decrease the equilibrium concentrations. Bishop et al. (185) stated that low molecular weight compounds, e.g., sugars, glycols, amino acids, hydroxyl acids, which may be present in the effluent, are too polar to be adsorbed and would therefore pass through activated carbon columns.

Parkhurst et al. (40) also reported a leakage of organic compounds through activated carbon columns. The exact nature of the leakage is unknown, but both Joyce et al. (25) and Parkhurst et al. (40) reported a strong indication that the leakage was comprised partially of nonadsorbable bacterial cell fragments and partially of small organic molecules which were extensively hydrolyzed in the biological treatment stage and thus rendered more soluble and less subject to adsorption.

Pilot studies conducted at several refineries indicated a persistent "leakage" of BOD organics when fixed-bed carbon columns were applied as a single treatment system (83). Thus, the series of biological-carbon systems will probably be the most prevalent application of carbon for refinery wastewater treatment.

Bishop et al. (53) reported that after removal of colloidal substances by clarification and filtration, carbon physically adsorbed most of the dissolved organics. In continuous treatment, the buildup of soluble organic material on the carbon rapidly promoted substantial biological activity within the adsorption system and degraded the product effluent.

Bishop et al. (185) reported that some, if not all, of the organic material that penetrates carbon columns might be colloidal in nature, either organic colloids such as fragments of bacterial cell walls and undigested particles or low molecular weight organic substances adsorbed on mineral colloids. Another class of organic substances refractory to carbon treatment consists of strongly hydrophilic (polar) organic molecules, e.g., highly oxygenated organic compounds. Although these strongly hydrophilic organics tend to remain in the water phase during adsorption, most should be biodegradable and, therefore, not present in well bio-oxidized secondary effluents. The organic portion of the colloidal material or suspended solids in the effluents should therefore constitute the major portion of organics refractory to carbon adsorption.

In continuous 9-month pilot-scale studies, Friedman et al. (196) found that aerobic expanded-bed activated carbon columns effectively and economically treated a chemically coagulated and clarified primary effluent to produce a high-quality final effluent. The primary objective was to study the effects of biological activity in expanded beds of carbon-treating primary effluent. More organics were removed with aerobic operation than anaerobic operation. Furthermore, quality of the effluent was much more consistent in the aerobic system. Anaerobic effluents consistently contained 8-13 mg/liter of hydrogen sulfide, but effluents from aerobic columns were essentially free of hydrogen sulfide. Effectiveness of the expanded-bed adsorbers was enhanced by occasional air scrubbing and backwashing to remove excess biomass and to precipitate coagulant from the column beds.

Culp and Shuckrow (210) presented a comparison of the major physical/chemical treatment research efforts focusing on the identification of common problems which exist. It is obvious from this review that more research is needed where carbon columns are loaded with wastewaters having organic concentrations greater than 50-100 mg/liter TOC. Successful techniques for hydrogen sulfide control must be demonstrated before physical/chemical systems with granular carbon columns can reach full acceptance. This review also suggested the need for additional research on carbon capacity and the relationship of biological activity in carbon columns to that capacity.

Eckenfelder et al. (211) compared the performance of aerobic, anaerobic, and sterile columns fed with a synthetic waste containing compounds of varying biodegradability. They concluded that anaerobic growth causes a reduction in carbon adsorption capacity, while aerobic growth may or may not enhance adsorption capacity depending on the biodegradability and the concentration of the wastewater.

The presence of biodegradable organics can result in biological activity in carbon columns, which can have beneficial or adverse effects on adsorption capacity depending on the concentration and other parameters (179). In industrial applications, the concentration of organics is generally rather high, and operation time between successive regenerations is too short to allow a significant buildup of active biota in the columns.

Rizzo and Schade (212) noted hydrogen sulfide generation in carbon columns during pilot tests but reported that this could be controlled by frequent back-

washing. Shuckrow (56) indicated hydrogen sulfide was a major problem in pilot-plant operations treating a strong municipal wastewater. This study documented the nonsorbable residual that might be present in wastewater and the difficulties that may be encountered in controlling the hydrogen sulfide. Clearly, based on this work, great care must be exercised in the design of physical/chemical treatment systems. To proceed with such activities without extensive pilot-plant testing risks substantial operational difficulties in full-scale systems.

Suhr and Culp (213) noted that under certain conditions granular carbon beds provide favorable conditions for the production of hydrogen sulfide gas, which has an unpleasant odor and which may contribute to corrosion of metals and damage concrete. They presented a list of measures which could be taken in plant design to provide flexibility for dealing with problems of hydrogen sulfide production. They also presented some remedial measures available in the operation of carbon facilities.

A laboratory study by Pressley et al. (214) showed that breakpoint chlorination with proper pH control and mixing provided a physical/chemical method for removing ammonia from wastewaters by oxidizing NH_4^+ to nitrogen gas. Bishop et al. (53) reported that use of breakpoint chlorination for ammonia removal produced an overall total nitrogen removal of 86% during their study. The average residual total nitrogen of about 2.8 mg/liter contained approximately 1 mg/liter of ammonia-nitrogen. A second application of chlorine after carbon adsorption could be employed to further reduce the total nitrogen to about 2 mg/liter. Harr and Mastropietro (215) reported that breakpoint chlorination followed by activated carbon filtration was an effective method for the removal of ammonia nitrogen from wastewater.

In the treatment of aqueous wastes, granular carbon has been the form most used with adsorber configurations being: fixed beds in parallel or series, or moving beds with either, and upflow or downflow distribution system (8, 42, 145). Based on pilot-scale tests under field conditions, Hopkins et al. (39) concluded that both packed and expanded carbon beds were equivalent in removal of soluble organics from secondary effluents. Expanded beds had the advantage of lower power and maintenance requirements, although suspended solids were more effectively removed by packed beds.

Weber (164) clearly demonstrated the advantages of the fluid-column method for contacting carbon with wastewaters over the packed-column method. Weber reported that very high capacities, with resulting economies, can be realized for activated carbon in fluidized columns under proper operating conditions.

Moving bed systems are finding wider application in continuous uses of granular activated carbon because of their greater efficiency and reduced labor requirements compared to fixed-bed systems (135). Movement of the carbon countercurrent to the flow gives an extremely efficient use of the carbon capacity.

Studies by Weber and Morris (136) on equilibria adsorption indicate, as did previous kinetic studies by Weber and Morris (141), that column operation is probably to be preferred to batch or nonflow processes. Column operation

makes better use of the capacity of the carbon because much of the adsorption in this type of process occurs at solution concentrations corresponding to the plateau-like region of the adsorption isotherm; this is not true for batch operations. These workers reported that a countercurrent column operation would be even more satisfactory for removal of low levels of organics by adsorption.

It has been shown that carbon particle size should be kept as small as conditions of efficient operation allow so that high rates of adsorption may be obtained (141). If filtration of the waste through a column of granular activated carbon is contemplated, use of extremely small particles may result in excessive head losses. Use of large particles requires large quantities of carbon and long columns for providing time of contact sufficient for obtaining the desired effluent quality. Weber and Morris proposed fluidized-column operation, in which waste flows upward through an expanded bed of fine carbon, as one method of taking advantage of small particle size and yet avoiding the problem of excessive head loss and difficulty of separating the adsorbent from the solution.

Keinath (216) has shown that competitive adsorption, even in binary solutions, can lead to chromatographic displacement effects in column adsorbers treating wastewaters of varying composition. In this situation, the weakly adsorbed solute is retained by the carbon for a time and then is eluted as a rather concentrated "peak" upon prolonged contact with the feed wastewater. He further showed that fluidized-bed adsorbers are much less susceptible to this effect than more conventional packed beds--a finding that could have significant impact on adsorber design.

It is obvious that any restriction of pore openings or buildup of ash or other materials within the pore openings due to the presence of suspended or colloidal materials and their accumulation on or in the carbon particles might have an adverse effect upon the adsorptive capacity or service life of the carbon (21). Therefore, the water applied to the carbon columns should be pretreated to the highest practical chemical clarity.

In the treatment of wastes, the granular carbon system could benefit from a pretreatment stage (145). This is especially so if it reduces the organic loading to the carbon columns, removes colloidal material, and/or removes suspended matter. Experience indicates that biological filtration and chemical clarification are two systems which offer the most valuable pretreatment contributions.

Harrison (217) indicated that removal of turbidity was needed before granular carbon treatment. Culp et. al. (218) have shown that efficient solids removal before carbon adsorption produces high-quality water from secondary municipal effluents. A comparison of COD values in effluents from clarified and unclarified secondary effluents subjected to carbon adsorption indicates that organic breakthrough is associated with suspended solids.

Ford (138) stated that lack of pretreatment in removing certain constituents can have an adverse effect on activated carbon. Many of the negative

aspects experienced in the activated carbon treatment of industrial wastewaters have been attributed to poor pretreatment. Conversely, selected pretreatment can enhance carbon adsorption performance.

Westrick and Cohen (219) investigated the influence of chemical pretreatment on carbon performance by operating and evaluating three separate clarification-carbon systems simultaneously. Results obtained are obviously specific to the type of waste and conditions of operation discussed. Although slight differences in the performances of the three systems were observed, all three produced effluents in essentially the same range of quality. Carbon data analysis illustrates that even slight differences in carbon performance may be related to the economics for inclusion in the treatment process selection procedure.

Zuckerman and Molof (153) reported on efforts to maximize the effectiveness of activated carbon adsorption to yield high-quality water for reuse. The process of chemical pretreatment followed by activated carbon treatment was found to be qualitatively and economically superior to conventional tertiary treatment.

Bishop et al. (185) reported that although clarification will reduce the total organic load on a carbon column, it is unlikely that it will increase substantially the volume that can be treated before breakthrough.

Weber (42) reported that although municipal wastewater treatment experience has indicated good treatment at contact times between 30-60 minutes, significantly longer contact times are normally required for industrial waste streams. This is consistent with generally higher organic concentrations. Adsorption theory and practice indicate that treatment efficiency and economics are favored by higher concentrations. Thus, at some industrial installations, concentrated waste streams treated individually at their respective sources would optimize overall treatment system design and economics.

POWDERED CARBON SYSTEMS

Although knowledge of the applicability of activated carbon to wastewater treatment has been well established, limitations have been placed on the use of powdered carbon forms because of the difficulty encountered in separating them from solution and in regeneration (220). Knopp and Gitchel (221) reported that the application of powdered carbon systems to wastewater treatment has been limited by the ability to economically regenerate powdered carbon. Shell (222) observed that application of powdered activated carbon for the treatment of wastewaters is dependent upon an efficient and effective method of regeneration.

Interest in the application of powdered activated carbon (PAC) for treatment of wastewaters is based on the fact that PAC has all the inherent process advantages of a nonbiological treatment system, yet is less expensive than granular activated carbon (GAC) and requires less inventory, and can be fed on demand (222). Even with these basic process advantages, regeneration of spent PAC is necessary for most wastewater treatment applications.

Powdered activated carbon is a highly adsorptive material that can be used to treat wastewater (194). The small structure size and highly porous structure make it an ideal adsorbent. Shell (222) reviewed the advantages and characteristics of powdered activated carbon in its application to wastewater treatment and discussed various approaches to regeneration of PAC. He stated that the basic process of regeneration is not different for PAC and GAC. The carbon first drys, then bakes, and is finally reactivated. Disadvantages in regeneration of powdered carbon compared to granular carbon lie in the difficulty of dewatering the carbon before regeneration and in high losses during thermal regeneration (74).

The development of thermal regeneration of spent powdered carbon has only recently been vigorously pursued (28, 57, 163, 221, 222, 223, 224, 225, 226, 227). Results of these studies have indicated that thermal regeneration is now technically feasible and may be economically justified. A transport reactor in operation since 1971 now routinely regenerates 10 tons per day of powdered activated carbon at less than one-third of what it would cost to buy it fresh (228). Cost estimates are given. A multiple-hearth regeneration furnace has recently been installed as part of the 40-mgd PACT treatment process at the DuPont Chambers Works Plant (129).

Results of tests conducted by Bloom et al. (223) and Gitchel et al. (225) indicated that water quality produced by using regenerated activated carbon equaled the best obtained with virgin carbon. Davies and Kaplan (163) described a method for reactivating powdered carbon in which the carbon was dewatered, dried in an indirect steam dryer, and then fed to a regeneration furnace where regeneration was effected in a steam atmosphere at 750°F. using a 1-hour detention time.

Bloom et al. (223) reported that because of its large surface area, powdered carbon could be reactivated in a matter of seconds if the carbon were heated in a steam atmosphere to 1400-1600°F. A process, called the dispersed phase technique, was developed and demonstrated which takes the spent carbon slurry and reactivates the carbon without drying or removing the bulk of the water. The regenerated carbon has essentially the same activity as fresh material.

Burant and Vollstedt (29) and Knopp and Gitchel (221) have reported that the adsorptive properties of powdered carbon can be restored by partial wet air oxidation without dewatering of the sludge. Wet air oxidation is reported to regenerate the active carbon with less than 10% loss. Adams (72) reported that the wet air oxidation process is, technically, the most attractive regeneration method.

Fluidized-bed systems for powdered carbon regeneration have been evaluated on a pilot scale and appear to have promise (28, 227, 229). In this process, a bed of inert granular material such as sand is fluidized by the upward flow of hot gases, and the wet spent carbon is injected directly into the bed. Under proper operating conditions, spent carbon can be restored to an active form as effective as virgin activated carbon. Recovery of regenerated carbon has been found to be about 85% per regeneration cycle.

A new process, called the Atomized Suspension Technique (AST) for regenerating spent powdered activated carbon, has been developed and successfully demonstrated (230). This process is the first to use an oxygen-free atmosphere for regeneration. This eliminates the possibility of burning some carbon and reducing the yield. Pilot-plant results show that AST reactivates the carbon to about 95% of its original capacity with yields of better than 90%, which compares favorably with regeneration results of granular activated carbon.

Flynn and Barry (231) have presented a methodology for evaluating the choices between type of carbon (granular or powdered) and method of application. The choice between the various alternatives is dependent on waste characteristics, thus requiring laboratory experimentation to define technical feasibility, cost, and reliability.

An intensive laboratory investigation has been conducted using 11 commercial and experimental activated carbons to evaluate their physical and adsorptive properties, to select those best suited to treating municipal wastewaters, and to gain insight into properties important for this application (209). Results suggested that the best carbons for adsorbing organics from municipal wastes have a broad spectrum of pore sizes so as to accommodate the wide variety of molecules present in wastewaters. Mixtures of carbon of different pore structure characteristics might prove to be more efficient. As expected, rate of adsorption of a powdered carbon was seen to be strongly influenced by its particle size.

Obviously, properties of the powdered carbon used are of primary importance (209). The carbon must have a high adsorptive capacity for the organic pollutants, attain a close approach to equilibrium in a reasonable period of time, and be readily removed by flocculation and clarification. Studies by O'Conner et al. (232) to determine which basic carbon properties are important for treating wastewater have shown no strong correlation between COD adsorption ability and BET surface area or ability to adsorb four specific model substances.

Burns and Shell (58) reported the following advantages of powdered activated carbon over granular activated carbon:

1. Cost of powdered carbon substantially less.

2. Powdered carbon adsorption will equilibriate with soluble wastewater organics in a small fraction of the time.

3. Powdered carbon can be supplied on demand to meet varying feed organic strength.

4. Powdered carbon systems require a fraction of the carbon inventory.

5. Powdered carbon contacting system is more amenable to control of undesirable biological activity.

Soluble organic removal in a physical/chemical system treating municipal wastewater is usually assumed to be primarily by a physical adsorption mechanism. Burns and Shell (58) implied that a substantial amount of soluble organic

removal was accomplished by anaerobic biological activity in a powdered activated carbon physical/chemical treatment system. These workers also reported that laboratory test results indicated no significant effect of chemical pretreatment on organic removal.

Wallace and Burns (60) presented results from a 15-month pilot-plant study indicating the effect of biological activity, pretreatment chemicals, thermal regeneration, and countercurrent staging on soluble COD removal in a powdered activated carbon physical/chemical treatment system.

Bishop et al (185) studied the removal of organic material from secondary effluents using powdered activated carbon. Data from their studies suggested the presence of a nonadsorbable organic fraction. The authors found that with clarification and powdered carbon, treatment produced secondary effluent TOC values of 2 mg/liter or less. They concluded that treatment studies with actual wastewaters was the only dependable method of rating powdered carbon performance.

Davies and Kaplan (26) conducted studies on the effects of powdered carbon size on the efficiency of organic removal and found that, although some improvement in the adsorption rate could be obtained with finer particle sizes, the added cost of sizing and the more difficult prospect of physical handling outweighed the improvements in adsorption. The workers concluded that it was not physically possible to separate commercially available carbons to obtain particular particle sizes. They also found, in a laboratory study, that 90% of the adsorption capacity of powdered activated carbon could be realized in less than 5 minutes in most cases with turbulent mixing.

These studies by Davies and Kaplan also showed that powdered carbon could be removed from treated effluents by flocculation and settling. The workers tested a number of high-molecular-weight flocculating agents and found that nonionic polyacrylamides were most effective. These studies also showed that several high-molecular-weight polyelectrolytes were effective flocculants for carbon at a dose of 1 mg/liter. Residual carbon in the settled effluent was in the range of 10 mg/liter. Lime added in the range of 300-400 mg/liter performed about as well.

The use of powdered activated carbon in the area of municipal wastewater treatment has been reasonably well established (233). A high-quality effluent can be achieved at a relatively low cost. The process was determined to be well suited to automation and flexible in treatment of wastes of variable strength and composition. Advantages of using powdered activated carbon in treating industrial wastes are discussed. Also, several industrial wastewater treatment designs employing powdered activated carbon and the developed associated costs of treatment are presented.

The addition of powdered activated carbon to the activated sludge process is a recent innovation which has attracted attention because of its ability to remove pollutants beyond the ability of ordinary secondary treatment at a cost which is intermediate between secondary treatment and secondary treatment plus carbon columns (30, 124).

The principle advantage of the DuPont PACT process (76) is that it achieves tertiary quality treatment in secondary treatment facilities. A mixing tank and pump for feeding powdered carbon slurry to the aeration tanks is all the equipment needed to upgrade an existing secondary treatment plant. Moreover, by controlling powdered carbon concentration, one has a convenient way of regulating the degree of treatment obtained (125). Lawrence and McCarty (236) reported that at a given carbon dosage, performance of the PACT system could be satisfactorily described by the use of conventional biological kinetic methods.

Data from laboratory tests indicated that addition of powdered activated carbon to the aerators of an activated sludge process would not only provide color and refractory organics removal in an effective manner but also would add stability to the activated sludge process resulting in improved and more consistent BOD removal (128). Subsequent research showed that bacteria tending to grow around carbon particles in such a manner as to reduce the dispersion of biological flocs make the sludge more dense and improve settleability of sludge in a clarifier. All of this would result in significant improvement in the activated sludge process of wastewater treatment.

Commercial processes using powdered activated carbon to enhance activated sludge wastewater treatment are available (234). Powdered activated carbon has been shown to increase the sludge settling rate, decrease the sludge volume, increase effluent clarity, and promote greater reductions in BOD and COD than bio-treatment alone. Results presented by these workers indicate that the carbon-assisted bio-unit could handle a greater flow rate or that a smaller bio-unit could be used to process the same volume of wastewater as a conventional activated sludge system.

Adams (62, 63) reported that both laboratory and full-scale evaluations have demonstrated that addition of lignite powdered activated carbon to anaerobic digesters will provide many benefits, alleviating operating problems and reducing sludge disposal costs. He stated that two properties of the lignite powdered carbons which render them most effective are density and activity. Adams suspects that by adsorbing organics and concentrating them for biodegradation, carbon helps to drive the reaction further toward completion.

Ferguson (236) demonstrated the capabilities of the PAC-biological contact stabilization process. He also compared the effectiveness of two high-surface-area powdered activated carbons with a low-surface-area PAC in the treatment process. Powdered activated carbon addition to the contact stabilization process improved removal of soluble organic matter at the PAC dosages tested. A dosage of 25 mg/liter of either high-surface-area PAC was comparable to, or slightly better than, a 75-mg/liter dosage of the low-surface-area PAC.

Thibault et al. (237) conducted a test program for the evaluation of powdered activated carbon treatment of activated sludge. Results are presented which show that low carbon levels (0-400 mg/liter) are ineffective in improving contaminant removal and sludge settling characteristics. Some improvement in clarity was noted. High carbon levels (1000-2000 mg/liter) may improve TOC and COD removals during normal operation but do not affect ammonia removal. Based on experience to date, these workers proposed that powdered activated carbon

treatment would be most effective when used on a standby basis for low-cost treatment or organic shock loadings.

Flynn (238) reported that a reliable methodology for use in the testing of powdered carbons for use in the PACT system has been established. Not surprising, those parameters which measure surface area available for adsorption seem to correlate fairly well with effluent quality. Flynn stated that any comprehensive design for a wastewater treatment plant based on powdered activated carbon addition to the activated sludge process must consider the cost of the carbon and ways of reducing it.

Flynn (239) developed a procedure for analyzing data to produce the required sludge age for a biological system with powdered carbon addition. Removals of COD and TOC due to carbon alone can be computed and indicate that the removals due to carbon apparently increase with sludge age.

Lang et al. (74) discussed and described a three-stage countercurrent contacting system that uses a fine activated carbon of a size intermediate between powdered and standard granular carbon. A preliminary engineering assessment of this system (dubbed FACET--Fine Activated Carbon Effluent Treatment) indicated that it combines some of the advantages of both conventional systems. The process has been patented (75, 76). Carbon size and concentration are chosen such that contact time requirements are short, while the size is large enough to provide fast settling without assistance of flocculation agents. Therefore, FACET permits use of simple stirred tanks as contactor-settlers and avoids need for the preclarification or frequent backwashing commonly required in granular carbon systems to prevent column pressure build-up. The suitable particle size range for FACET is 100-250 microns (140-60 mesh). This particle size is believed to be large enough to permit use of the standard multiple-hearth furnace for regeneration. The workers discussed advantages and disadvantages of FACET versus powdered and granular carbon treatment.

SECTION IV

DISCUSSION

An attempt has been made to review the literature pertaining to activated carbon adsorption and its use in the treatment of petroleum refining, petrochemical, and combined municipal/industrial wastewaters. There is ample evidence in the literature to suggest that activated carbon adsorption, using either granular or powdered carbon, should be considered when evaluating treatment alternatives for these wastewaters. Activated carbon adsorption, however, should not be thought of as a process which will satisfactorily remove all organic compounds from wastewater (240). There are considerable variations in the adsorptive behavior of organic compounds so that adsorption may not always provide a suitable removal process.

Many classes of organic compounds (particularly oxygenated organics) are not amenable to carbon adsorption and show up as residual BOD, COD, or TOC in carbon column effluents (35, 138). This limits the overall process efficiency of activated carbon when treating industrial wastewaters. Knowledge of the chemical composition of wastewaters is essential for determining the applicability of carbon adsorption and for the efficient design of adsorption facilities (240). The final test of the applicability of a process will be not only the efficiency but also the economy of the process or system (83).

The efficacy of utilizing carbon adsorption for the treatment of refinery and petrochemical wastewaters at any point in a process sequence can be determined only after a thorough investigation (83). There has been a tendency for investigators and equipment developers to oversimplify the process adaptability for industrial wastewater applications. Specifically, translation of data from carbon systems receiving domestic wastes into design criteria for industrial utilization has limited validity, and the use of batch isotherm information under any testing condition as a basis for process selection is imprecise.

Activated carbon treatment of industrial wastes, while promising, must be carefully evaluated before process decisions are made and capital funds are committed (35, 138). Breakthrough geometry and adsorption kinetics of multicomponent wastewaters are difficult to define; many organic compounds are not amenable to carbon adsorption; and the effects of carbon regeneration are variable and unpredictable. For these and other reasons, comprehensive testing and technical reviews are a necessary prerequisite to process commitment.

There is no single wastewater treatment system which can be applied in all cases. Each industrial operation has its own wastewater characteristics and its own effluent requirements. Availability of land, complexity of operation, cost of treatment facilities, and variations in wastes all combine to

make each wastewater treatment system unique. The optimum treatment system can be designed only after careful study of the entire problem and preliminary evaluation of several alternate designs.

To produce maximum results, a wastewater treatment system must be not only well designed but properly operated. The simple adding on of a carbon system will not make up for deficiencies in a biological system, regardless of whether those deficiencies are from improper design or operation.

New truths pertaining to the subject of activated carbon treatment become known on a continuing basis (138). However, when evaluating process concepts, developing design bases, predicting effluent quality, and finalizing management decisions in terms of constructing control systems with attendant capital commitments, one must carefully base these judgements on the known process capabilities and limitations of activated carbon.

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16. ABSTRACT A review of the literature on activated carbon adsorption as a treatment concept for petroleum refinery, petrochemical plant, and combined industrial-municipal wastewaters is presented in this report. A total of 241 references are cited. These references cover the various aspects of carbon adsorption and its application in the treatment of industrial and municipal wastewaters.

There is ample evidence in the literature reviewed to suggest that activated carbon adsorption, using either granular or powdered carbon, should be considered when evaluating treatment alternatives for industrial wastewaters. Successful applications of this mode of treatment have been claimed at numerous municipal, industrial, and combined municipal-industrial installations.

It must always be remembered, however, that there is no single wastewater treatment system which can be applied in all cases. There are enough variations in the adsorption behavior of organic compounds so that adsorption may not always provide a suitable removal process. Each industrial operation has its own effluent characteristics and requirements. Availability of land, complexity of operation, cost of treatment facilities, and variations in wastes all combine to make each wastewater treatment system unique. The optimum treatment system can be designed only after careful study of the entire problem and preliminary evaluation of several alternate designs.

17. KEY WORDS AND DOCUMENT ANALYSIS

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