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Organic matter removal by powdered activated carbon added to activated sludge

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Increasingly stringent effluent criteria can be met by using tertiary treatment processes such as carbon adsorption to improve the quality of effluent from biological secondary treatment processes. It was recently shown that powdered activated carbon (PAC), when added to an activated sludge unit, is also effective in achieving high effluent quality.[1] The carbon is added to the aeration basin and removed from the effluent in the secondary clarifier. Its detention time is then equal to the sludge age.[2] Although adding carbon in this manner generally reduces the effluent chemical oxygen demand (COD) or biochemical oxygen demand (BOD) to a lesser extent than does a separate tertiary columnar adsorption unit, the reduction is realized at a much lower cost, since powdered activated carbon costs about $0.65/kg ($0.30/lb) while the price for granular carbon is approximately $1.20/kg ($0.55/lb). Robertaccio,[3] for example, showed that adding PAC at an average equilibrium concentration in the aerator of approximately 4 000 mg/l resulted in a 36 percent lower soluble effluent COD than that of a control unit receiving no powdered carbon. Passage of the activated sludge effluent through separate activated carbon columns resulted in a 68 percent COD reduction, approximately twice that obtained by adding PAC, but at a substantially higher cost. Using a PAC equilibrium concentration as high as 5.13 mg/l in an activated sludge unit, Flynn [4] achieved an effluent quality equal to that obtained using a separate biological unit and a tertiary carbon column in series but at a 25 percent lower cost.

Several mechanisms have been proposed to account for the removal of organic matter by PAC. It was concluded by Scaramelli and DiGiano [5] that the addition of PAC produces a total organic carbon (TOC) decrease in activated sludge effluent primarily as a result of physical adsorption onto the carbon, since no increase in mixed liquor suspended solids (MLSS) or oxygen uptake rate of the sludge was observed. Likewise, Hals and Benedek [6] using glucose or secondary effluent as a substrate, did not observe any increase in magnitude of the final oxygen uptake by bacteria in the presence of PAC, indicating that physical adsorption was the main removal mechanism. Kalinske,[7] on the other hand, showed that adding PAC enhanced the removal rate of a glucose substrate in batch tests during the initial phase of substrate removal. Since adsorption of glucose onto the carbon could not account for the higher rates, he postulated that the PAC enhanced the biological uptake rates. In continuous flow units he obtained slightly higher biological MLSS as a result of adding PAC. Koppe *et al.*[8] also noted that addition of activated carbon to an activated sludge unit resulted in increased removal of an otherwise slowly degradable substrate.

The tests conducted over an extended period found that both mechanisms may take place (Adams [9] and Robertaccio *et al.*[1]). The addition of carbon reduced both the biodegradable organics, as measured by the BOD test (such organics generally show a low sorptive capacity with PAC), and also the total organics, as measured by the COD and TOC tests. In several instances, the carbon also reduced the effluent suspended solids (SS), indicating that it enhanced biological flocculation and sedimentation. In one test it was even observed that at high equilibrium concentrations the PAC reduced the bacterial biomass, possibly as a result of enhanced respiration of the sludge.[9]

The extent to which organics are reduced in the activated sludge unit is affected by the equilibrium concentration of the powdered carbon in the reactor, the sludge age, and the hydraulic retention time of the unit. Most studies noted that increasing PAC dosages generally resulted in lower effluent COD and BOD concentrations. The effectiveness of the different dosages, however, varied widely with differences in the operational conditions of the activated sludge units and differences in organics present in the effluent. PAC equilibrium concentrations varying between 1 000 and 7 000 mg/l were generally studied,[2, 3] but a few studies also noted substantial organic removals at lower concentrations. At a concentration of 500 mg/l, Kalinske [6] measured a COD removal rate of 45 percent as compared to a control unit, while Adams [2] observed a 13 percent reduction and a decrease of 20 percent in effluent SS at a carbon concentration of 200 mg/l.

Since lower carbon dosages represent significant savings, the laboratory study described here was conducted to determine the effectiveness of low carbon equilibrium concentrations in removing organics when added to activated sludge units. Filtered activated sludge effluents, with and without the addition of carbon, were analyzed to determine which specific organic fraction was removed. The results were then used to estimate the extent to which the organic matter was removed by either physical adsorption or enhanced biological oxidation. Since the operation of the activated sludge unit was expected to affect the organic matter removals,[10] a low and a high cell residence time were selected. The effect on sludge settling and flocculation was also determined. In the last phase of the study, an extensive literature review on the addition of PAC to activated sludge units was made in order to arrive at generalized conclusions concerning the organic matter removal mechanisms.

METHODS AND MATERIALS

Six 2-l, bench-scale activated sludge units were operated simultaneously to determine the effectiveness of adding PAC. Three of the units were operated at a sludge age of 5 days and the other three at a sludge age of 10 days. In two control units, one of each age, no carbon was added. In two of the other units, a final carbon dosage of 50 mg/l was maintained in the mixed liquor; in the remaining two units, a 300 mg/l dosage was maintained. All units were operated on a batch basis, with feeding taking place every 24 hours. The mixed liquor was settled for 30 min and replaced by 1 800 ml of wastewater and 100 ml of a glucose nutrient solution containing N and P sources and several salts, resulting in a hydraulic retention time of 25.3 hours. The average wastewater COD during the test period was 550 mg/l, while the glucose contributed 370 mg/l of COD to the feed liquor mixture. PAC used in this study was a dense, lignite-based carbon. The carbon was selected on the basis of a study by Johnson *et al.*,[11] who showed that it was one of the most effective carbons on a removal cost basis for treating secondary effluent. The effects of the carbon additions were evaluated during three separate time periods. Before analyzing the effluents, the units were allowed to reach steady-state conditions during a 2-week period, after which they were monitored for 7 days. During each of the three monitoring periods, 400 ml of supernatant were collected daily. These samples were filtered through a 0.45 μm membrane filter, composited for the 7-day period, refrigerated, and analyzed for COD and TOC after the termination of the run. The specific organics determined included: proteins as glycine, measured with the ninhydrin test; carbohydrates as dextrose, measured with the phenol sulfuric acid test; and functional groups such as carboxyl, measured as acetic acid with the hydroxyl amine test; carbonyl as butanol, measured with the 2,4-dinitrophenyl hydrazine test; and aromatic hydroxyl groups as tannins, measured with the Folin-Dennis test.[12]

SLUDGE CHARACTERISTICS

During the three monitoring periods, the average F:M loading of the 5- and 10-day activated sludge units was 0.53 and 0.35 g of BOD removed per gram of mixed liquor volatile suspended solids (MLVSS) per day, respectively. The average biological MLSS was 1 213 and 1 878 mg/l, with the volatile suspended solids (VSS) representing 72 and 75 percent of the total SS, respectively. The biomass in the units receiving the PAC was determined by subtracting the PAC equilibrium concentrations. This approach was justified, since none of the PAC was visually detected in the clear supernatant after settling for 30 min. The VSS were more difficult to determine since most of the PAC is volatilized during analysis. Tests with virgin PAC showed that 79 percent of the weight was removed when heated for 1 hour at 540°C. Assuming that this percentage does not change when the PAC is added to the activated sludge units, the biological MLVSS concentrations were calculated. The results in Table I, based on eleven tests, indicate that the MLSS generally does not change substantially as a result of adding PAC. The MLVSS values tended to decrease, especially at the high carbon dosage. The decrease may indi-

TABLE I. Suspended Solids in the Activated Sludge Units to Which PAC was Added.

Sludge Age (days)	PAC Concentration (mg/l)	Biological MLSS (mg/l)	Biological MLVSS (mg/l)	Sludge Volume Index
5	0	1 213	873	41
5	50	1 228	861	39
5	300	1 190	696	33
10	0	1 878	1 412	37
10	50	1 923	1 411	37
10	300	1 873	1 179	35

cate that the addition of PAC enhanced the endogenous respiration of the sludge, resulting in a lower yield of biological solids.

The sludge settling rates obtained during the first and third monitoring periods, measured in triplicate in 1-l cylinders with a 1 rpm stirring speed, were very high. The 10-day sludge generally settled less rapidly than the 5-day sludge despite the fact that the sludge flocs of the latter were observed to be larger. The difference in settling rate between the sludges of the two different ages became more noticeable at higher MLSS concentrations. The measured settling velocities did not show that adding PAC had a definite effect, although some increase in rates were observed for the low sludge age.

The sludge volume indexes (SVI) listed in Table I were all less than 100; this showed that the sludge had very good settling properties. All indexes decreased slightly as a result of adding PAC, with the highest initial index decreasing the most. A similar trend was noted in the literature.[2, 3, 13, 14] Since high SVI's generally correspond with high F:M ratios or low sludge ages, the largest improvements in sludge settling characteristics will be observed under those conditions.

REMOVAL OF ORGANIC MATTER

Analysis of the organic matter in the effluent of the six units after it was filtered through a 0.45 μm membrane showed that increasing PAC dosages resulted in lower effluent concentrations. The results in Figure 1 indicate that both the 5- and 10-day sludge units removed approximately 15 percent of the COD when PAC is added at a level of 50 mg/l and 25 percent at 300 mg/l. The COD removal increases less than proportionally with increasing carbon dosages because of the decreasing equilibrium concentration.

Since the removal of organic matter in the activated sludge units to which PAC was added

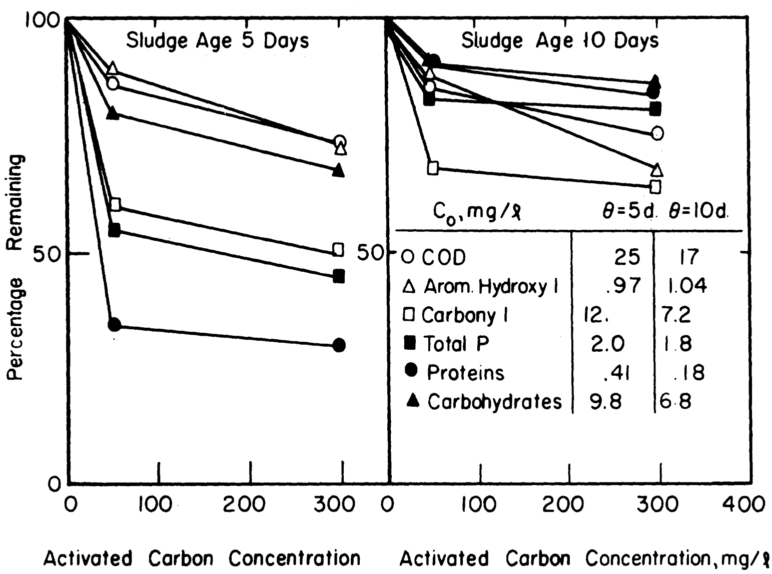

FIGURE 1. Removal of different organic constituents from the effluent of the activated sludge units receiving different PAC additions.

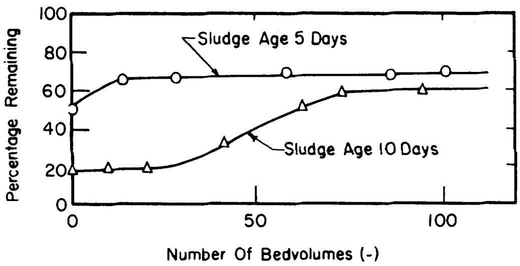

FIGURE 2. Removal of organic matter from the effluents of the control activated sludge units in upflow powdered activated carbon columns.

could be the result of both physical adsorption and enhanced biological degradation, separate tests were necessary to determine the magnitude of the removal by physical adsorption alone. Adsorption isotherm tests were conducted with the powdered carbon and the effluent of the control units. Variable results were obtained, possibly because of the difficulty in removing the PAC from the samples. Column studies were therefore conducted, making it possible to obtain a clear effluent without membrane filtration prior to analysis; it is realized, however, that the kinetics of the two methods are different. The column tests were conducted with lignite-based carbon packed to a height of 50 mm. The empty bed detention time in the column was 2 min. The upflow mode caused the bed to expand approximately 100 percent. The columns were initially flushed with distilled water to remove the very small fines. Figure 2 shows that only 34 percent of the COD of the effluent organic matter from the 5-day unit was removed, while the removal with the 10-day unit was as large as 80 percent before partial breakthrough occurred. Since the COD removal rates in both the 5- and 10-day activated sludge units are 25 percent at the highest PAC concentration it may be tentatively concluded that adding PAC to the 5-day unit enhances the removal of organics that would not be removed by physical adsorption alone.

Analysis of the effluents of the two control units with different sludge ages revealed that the organic content was different (Figure 1). The effluent of the 5-day unit had relatively high concentrations of carbohydrates, carbonyl compounds, and amino acids relative to the COD, while that of the 10-day unit had relatively high concentrations of aromatic hydroxyls. The amino acids exhibited the largest relative decrease with increasing sludge age.

Previous studies in this laboratory have indicated that increasing detention times result in the removal of low molecular weight polar compounds such as free volatile fatty acids and amino acids [15] excreted as intermediates during substrate removal.[16] It was also shown that after removal of these intermediate compounds, bacteria excrete high molecular weight, humic carbohydrate-like substances. After extended degradation, however, even the concentration of this fraction is reduced, which may explain the lower relative carbohydrate concentration in the effluent of the 10-day unit. Increased aeration, on the other hand, resulted in a relative increase in the concentrations of aromatic hydroxyl compounds associated with an intermediate molecular weight fulvic-like material.[17] It was shown in subsequent studies that activated carbon treatment of secondary effluent is effective in removing the fulvic-like material having a molecular weight ranging from 500 to 10 000.[12] The high molecular weight, humic carbohydrate-like fraction was found to be less effectively removed by activated carbon possibly because its molecular weight prevents effective penetration into the carbon micropores. Relatively small removal rates were also observed for the low molecular weight compounds because of their polar character. The observed removal pattern was primarily the result of physical adsorption processes, since biological growth was not observed in the test.

A similar pattern was observed for the removal of specific organic fractions in the effluent of the 10-day sludge units to which PAC was added (Figure 1). The highest removal rates were observed for the aromatic hydroxyl and carbonyl compounds while lower removal rates were noted for carbohydrates and proteins. The former compounds are generally associated with the intermediate molecular weight fulvic fraction. Since this fraction is relatively well oxygenated as reflected by its low COD:TOC ratio, removal of this fraction causes an increase in COD:TOC ratios in the effluent of the PAC-activated sludge units. The use of 50 mg/l and 300 mg/l PAC concentrations caused the COD:TOC ratios in the effluent of the 10-day units to increase from 2.5 to 2.8 and 2.7, respectively. Similar PAC additions to the 5-day units caused an increase from 2.8 to 2.9 at both PAC concentrations. The low removal rate for high molecular weight carbohydrates and low molecular weight amino acids is consistent with earlier studies. The simi-

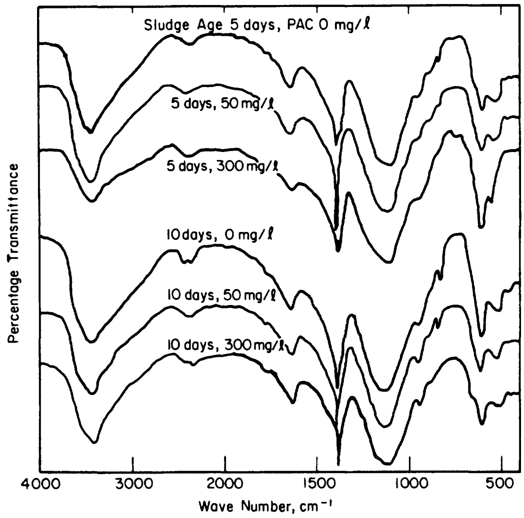

FIGURE 3. Infrared spectra of the organics in the effluents of the different activated sludge units.

larity in removal patterns would suggest that the removal of organic matter in the 10-day unit to which PAC was added is primarily the result of physical adsorption.

A different pattern, however, was observed for the removal of specific organics in the 5-day units which received PAC. The largest reductions in organic matter concentrations were observed for proteins, phosphorus, carbonyls, and carbohydrates in order of decreasing removal rates. The fact that these compounds exhibited a low degree of physical adsorption in previous studies indicates that their significant decrease in the presence of activated sludge is biologically mediated. It has been reported that the high molecular weight fraction containing carbohydrates affects the flocculation of the sludge.[17] A decrease in this fraction may cause enhanced sludge flocculation. This effect was indeed noticed upon microscopic examination, which showed a more compact sludge floc in the units with PAC than in the sludge from the 5-day control unit. The slightly higher settling rates with subsequent SVI reductions which result from the addition of PAC agree with the above conclusions. Since earlier research in this laboratory showed the presence of hydrolyzable phosphorous compounds in the high-molecular-weight fractions, their removal may also reflect the flocculation behavior of the sludge. Since low-molecular-weight compounds such as amino acids and carbonyl compounds are excreted by bacteria as intermediates, their diffusion out of a more compact sludge floc may be limited, while their subsequent uptake is expected to be relatively rapid. This behavior could explain the relatively large removal of these compounds in the effluent of the 5-day PAC activated sludge units. The organic matter removal in the 5-day units may therefore be largely biologically mediated.

The presence of the organic compounds detected by colorimetric tests was also reflected by the various peaks in the infrared spectra of the unfractionated dried effluent organic matter from the six units (Figure 3). All spectra

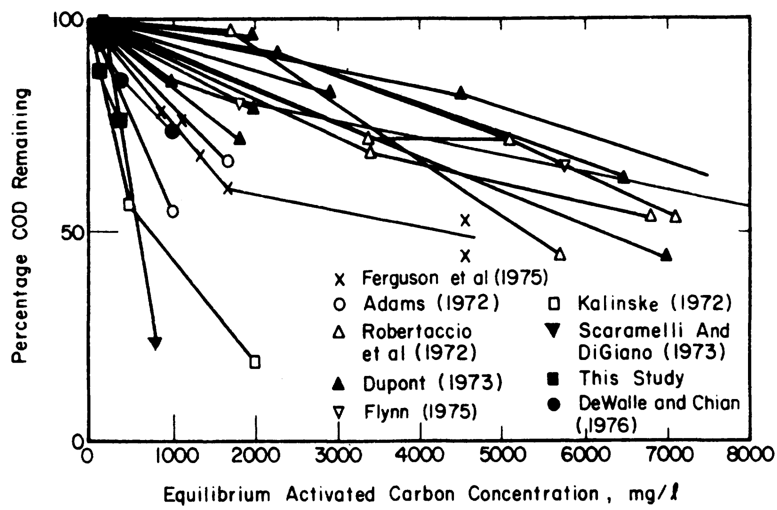

FIGURE 4. Effect of increasing PAC equilibrium concentrations on the COD organic matter remaining in the effluent of the different activated sludge units.

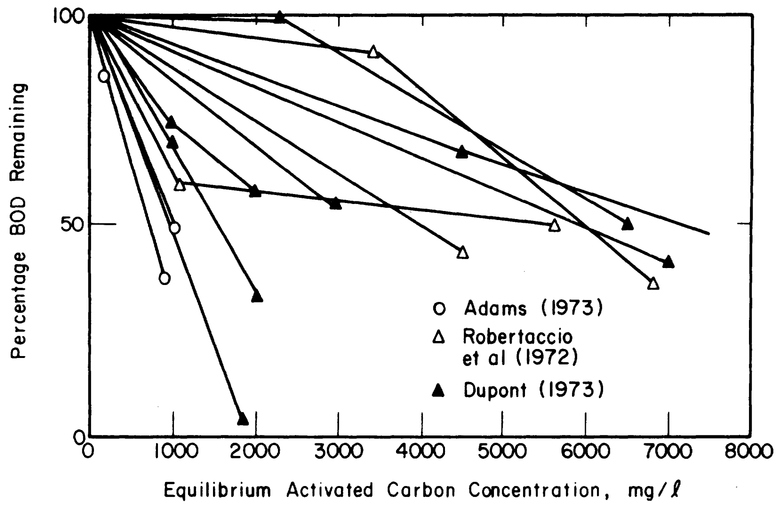

FIGURE 5. Effect of increasing PAC equilibrium concentrations on the BOD organic matter remaining in the effluent of the different activated sludge units.

are characterized by large peaks absorbing near 3 400 cm^{-1}, reflecting H bonded O-H stretching and N-H stretching, and near 1 130 cm^{-1} caused by C-O stretching of primary alcohols, generally indicating the presence of carbohydrates. The peaks at 1 640 cm^{-1} are the result of N-H bending and C-O stretching of ketones. The absence of absorbance at 1 720 cm^{-1} and the small shoulder at 1 170 cm^{-1} may indicate that some carboxyl groups are present in ester linkages. The small peak at 2 340 cm^{-1} generally reflects the presence of phosphates. Because these complex spectra result from a mixture of organic compounds, they generally show only small changes as a result of adding PAC. The most noticeable differences were observed in the spectra of the 5-day units, which showed decrease at 3 400 cm^{-1} and 1 620 cm^{-1}, reflecting the removal of amino acids and carbonyl compounds.

The last phase of the study consisted of an extensive evaluation of the results from previous PAC studies to determine whether trends similar to those described above could be observed.[1, 6, 9, 18, 19] The data in Figures 4 and 5 relate the percentage of COD and BOD removal to the equilibrium PAC concentration in the reactor. The percentage removal was selected as the indicator, since it is one of the most important parameters in determining the effectiveness of a unit. The results indicate that most COD removal percentages varied between 5 and 50 percent, about half as much as is generally observed in activated carbon columns. The COD reductions observed in the effluent of PAC activated sludge units receiving municipal wastewater was generally larger than those noted for units receiving industrial waste.[5, 14, 19] The observed BOD removals were generally in the same range as the COD removals. When the COD and BOD removals at the arbitrary concentration of 500 mg/l were related to sludge age, it was found that COD removals were generally unaffected by differences in sludge age, which agrees with the results in Figure 1. The removals observed in this study compare favorably with results from other studies, indicating that even low equilibrium concentrations can be effective. Removal rates for BOD, on the other hand, tended to decrease with increasing sludge age. This situation is to be expected, since BOD concentrations decrease with increasing sludge age, thereby decreasing the relative effectiveness of PAC additions. Since low-molecular-weight amino acids and carbonyl compounds are readily degradable, their relatively large removal percentage at low sludge ages (Figure 1) follow a pattern similar to that observed for the BOD values.

CONCLUSIONS

It was found in the present study that the addition of powdered activated carbon to activated sludge units having 5- and 10-day cell residence times resulted in decreased organic matter concentrations in the effluents, even when the PAC was added at low equilibrium concentrations. The addition of PAC was equally effective when the activated sludge unit was operated at a 5-day as compared to a 10-day cell residence time. Passing the effluents of the control units through activated carbon columns produced higher COD removal percentages for the effluent of the unit with a 10-day residence time. Organic analysis of the various effluents using colorimetric tests indicated that the organic matter decreases in the 5-day PAC units are partially biologically mediated, which may well be caused by the formation of a denser sludge particle. High-molecular-weight carbohydrates affect the formation of such flocs, which may explain their lower concentration in the effluent of the PAC activated sludge units. The reduction in concentration of low-molecular-weight amino acids and carbonyl compounds excreted by bacteria during substrate removal is probably a result of their restricted diffusion into the solution and their subsequent rapid uptake. The organic matter removal in the 10-day units is of a more physical nature because of the removal of an intermediate molecular weight fraction characterized by aromatic hydroxyl groups.

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REFERENCES

1. Robertaccio, F. L., *et al.*, "Treatment of organic chemical plant waste water with the DuPont PACT process," Amer. Inst. Chem. Eng. National Meeting, Dallas, Symposium Series No. 125, Vol. 65 (1972).
2. Adams, A. D., "Improving activated sludge treatment with powdered activated carbon." *Proc. 28th Annual Purdue Industrial Waste Conference* (1972).
3. Robertaccio, F. L., "Powdered activated carbon addition to biological reactors." *Proc. 6th Mid Atlantic Industrial Waste Conference,* University of Delaware, Newark (1973).
4. Flynn, B. P., "Finding a home for the carbon: aerator (powdered) or column (granular)." *Proc. 31st Annual Purdue Industrial Waste Conference* (1976).
5. Scaramelli, A. B., and DiGiano, F. A., "Upgrading the activated sludge system by addition of powdered activated carbon." *Water Sewage Works,* **120**, 9, 90 (1970).
6. Hals, O., and Benedek, A., "Simultaneous biological treatment and activated carbon adsorption." Paper presented at the 46th Annual Water Pollution Control Federation Conference, Cleveland (1973).
7. Kalinske, A. A., "Enhancement of biological oxidation of organic waste using activated carbon in microbial suspensions." *Water Sewage Works,* **115**, 7, 62 (1972).
8. Koppe, P., *et al.*, "The biochemical oxidation of a slowly degradable substance in the presence of activated carbon: biocarbon unit." *Gesundhuts Ingenieur* (Ger.), **95**, 247 (1974).
9. Adams, A. D., "Improving activated sludge treatment with powdered activated carbon." *Proc. 6th Mid Atlantic Industrial Waste Conference,* University of Delaware, Newark (1972).
10. Kim, B. R., *et al.*, "Influence of activated sludge CRT on adsorption." *Environ. Engr. Div., ASCE,* **102**, 55 (1976).
11. Johnson, R. L., *et al.*, "Study of powdered carbons for wastewater treatment and methods for their application." U. S. Environmental Protection Agency, Water Pollution Control Research Series 17020 DNQ 09/69 (1969).
12. DeWalle, F. B., and Chian, E. S. K., "Removal of organic matter by activated carbon columns." *Environ. Engr. Div., ASCE,* **100**, EE5, 1085 (1974).
13. E. I. DuPont de Nemours Co., "DuPont PACT Process." Wilmington, Del. (1973).
14. Ferguson, J. F., *et al.*, "Combined PAC-Biological Contact Stabilization Treatment of Municipal Wastewater." Department of Civil Engineering, University of Washington, Seattle (1975).
15. Chian, E. S. K., *et al.*, "Removal of organics in sewage and secondary effluent by reverse osmosis." *Prog. Water Technol.,* **9**, 761 (1977).
16. Chian, E. S. K., and DeWalle, F., "Sequential substrate removal in activated sludge systems fed with naturally occurring wastewater." *Prog. Water Technol.,* **7**, 235 (1975).
17. DeWalle, F. B., and Chian, E. S. K., "The kinetics of formation of humic substances in activated sludge systems and their effect on flocculation." *Biotechnol. Bioeng.,* **14**, 7, 739 (1974).
18. Flynn, B. P., "A model for the powdered activated carbon activated sludge treatment system." *Proc. 30th Annual Purdue Industrial Waste Conference* (1975).
19. DeWalle, F. B., and Chian, E. S. K., "Biological regeneration of powdered activated carbon added to activated sludge units." *Water Research,* in press (1977).