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RECENT DEVELOPMENTS AND FUTURE TRENDS IN INDUSTRIAL WASTEWATER TECHNOLOGY

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Summary - Industry today is faced with increasingly stringent effluent requirements. At the same time the cost of energy and chemicals is rising at unprecedented rates. In order to develop cost effective solutions to future industrial wastewater treatment, innovative approaches are required. In most cases this will involve pollutant control at the source and modifications to existing and conventional pollution control technology. This paper discusses present trends in those areas and some of the economic implications involved. The most cost effective solution for a specific industry will depend on the characteristics of the wastewater generated and the effluent quality requirements.

INTRODUCTION

In recent years, the major emphasis in wastewater treatment has shifted from the removal of conventional pollutants (BOD and suspended solids) to a variety of other pollutants. Removal of nitrogen and phosphorus is a requirement in many parts of the United States and Canada. Through recent Federal legislation, removal of priority pollutants to low residual levels will soon be required of all industrial discharges. Priority pollutants includes a variety of heavy metals and toxic organics. In order to achieve these objectives in a cost effective manner, a new approach to water quality management is needed. In the early 1970's the technology employed add on end of pipe processes including coagulation, filtration, and granular carbon adsorption. An economic analysis should examine costs for the benefits achieved for residual pollutant removal. Emphasis at present is being directed toward in-plant control technology or modifications to existing conventional technology.

Source Control

In most cases, source control will involve process changes or chemical substitutions to eliminate specific priority pollutants or pretreatment of the discharges containing those pollutants. Alternative technologies are shown in Figure 1. Source control of heavy metals can be achieved by precipitation with lime, sulfide and in some cases, co-precipitation with alum or iron salts. A pretreatment is required in cases where the metals are complexed. If a high removal of the total metal is required, filtration, following precipitation and sedimentation may be required. In some cases, ion exchange will be a cost effective alternative. This is particularly true in cases where metal recovery is economically achievable. Organic removal can be achieved by chemical oxidation with ozone or catalyzed hydrogen peroxide, by adsorption on granular activated carbon or macroreticular resins, or in the case of volatile constituents, stripping with air or steam. Under practical conditions, complete degradation of fairly reactive compounds such as saturated hydrocarbons an halogenated aliphatic compounds does not occur with ozone alone, but current research has shown that ozone with an additional energy source, i.e., sonification, ultra-violet radiation or a catalyst will readily decompose many refractory compounds. In many cases complete oxidation of complex organics with ozone is very expensive. However, partial chemical oxidation with ozone will frequently modify the molecular structure rendering it more biodegradable in subsequent treatment processes. For example, Yocum et al (1) showed that the BOD_5/TOC ratio increases from 0.11 to 0.98 following ozonation in polyol wastewater.

There is some evidence that partial ozonation prior to granular carbon adsorption enhances organic removal and extends the carbon life. (2)

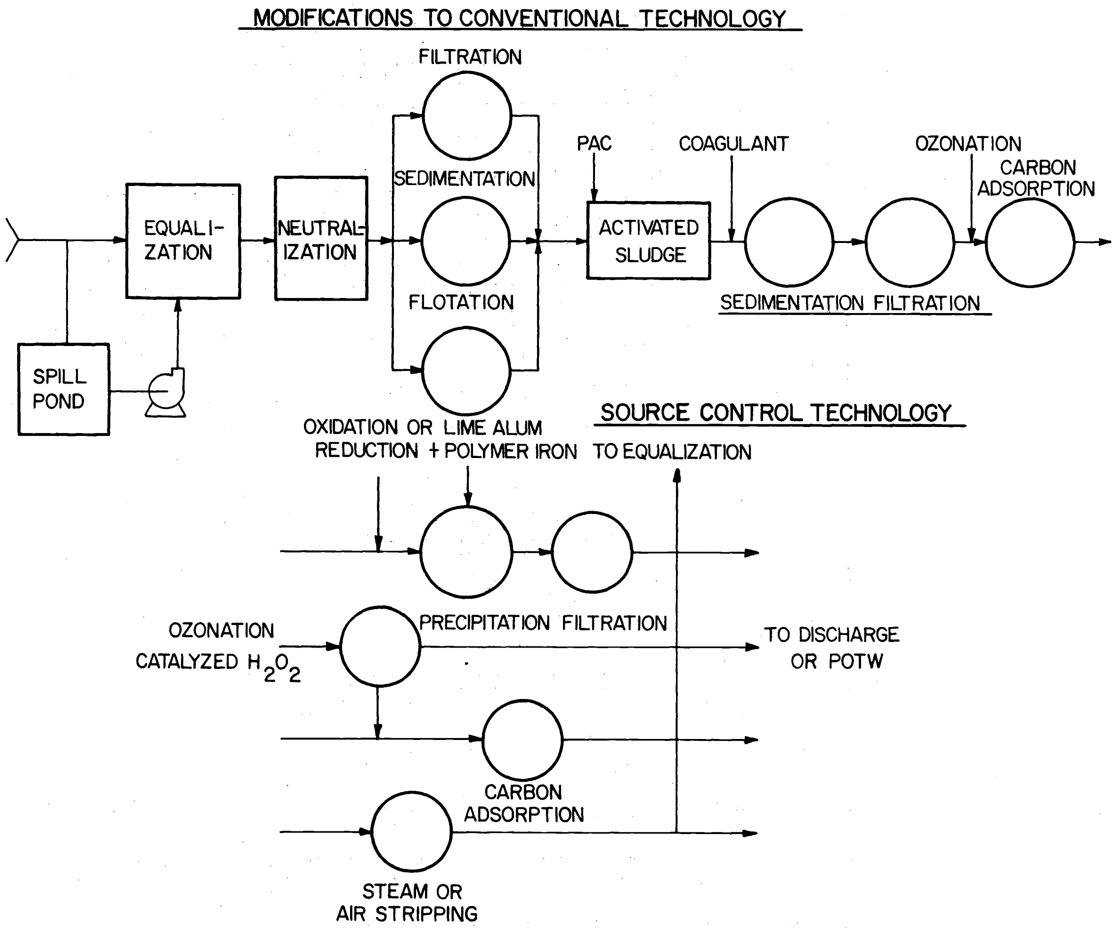

Fig. 1. Alternative technologies for removal of pollutants

Pretreatment

In order to meet future effluent limitations, improved pretreatment is required. Pretreatment should minimize variation in wastewater loading and remove pollutants which interfere with the biological process operation or pass through the system such as oil, and heavy metals. Pretreatment should therefore consider improved equalization and more effective removal of noncompatible pollutants such as oil, sulfides, heavy metals, and inhibitory organics.

Biological Wastewater Treatment

As we enter the 1980's cost effective treatment of organic wastewaters will still consider biological processes in most cases. Low energy consuming systems such as anaerbic processes, trickling filters and RBC's will find increased use where applicable. Anaerobic processes are limited to cases where potential or real toxicity does not exist such as food processing wastewaters. Trickling filters are generally limited to pretreatment of high strength industrial wastewaters. In many cases the activated sludge process will be the candidate where high effluent qualities are desired. Recent research has developed technologies for the control of both effluent quality and sludge quality. In the treatment of industrial wastewaters filimentous sludge bulking is a common problem and effective control technology has just recently been developed. (3) In most cases filimentous bulking results from an imbalance of essential nutrients or oxygen between the biological floc and the filimentous organisms. The filiments with a high surface area to volume ratio can more readily obtain nutrients than organisms within the floc which depend on the diffusion of nutrient into the floc. If the nutrients or oxygen are sufficient to fully penetrate the biological floc, the zoogleal organisms will outgrow the filiments. An estimate has been made of the dissolved oxygen level necessary to maintain a proper balance as related to organic removal rate as shown in Figure 2.

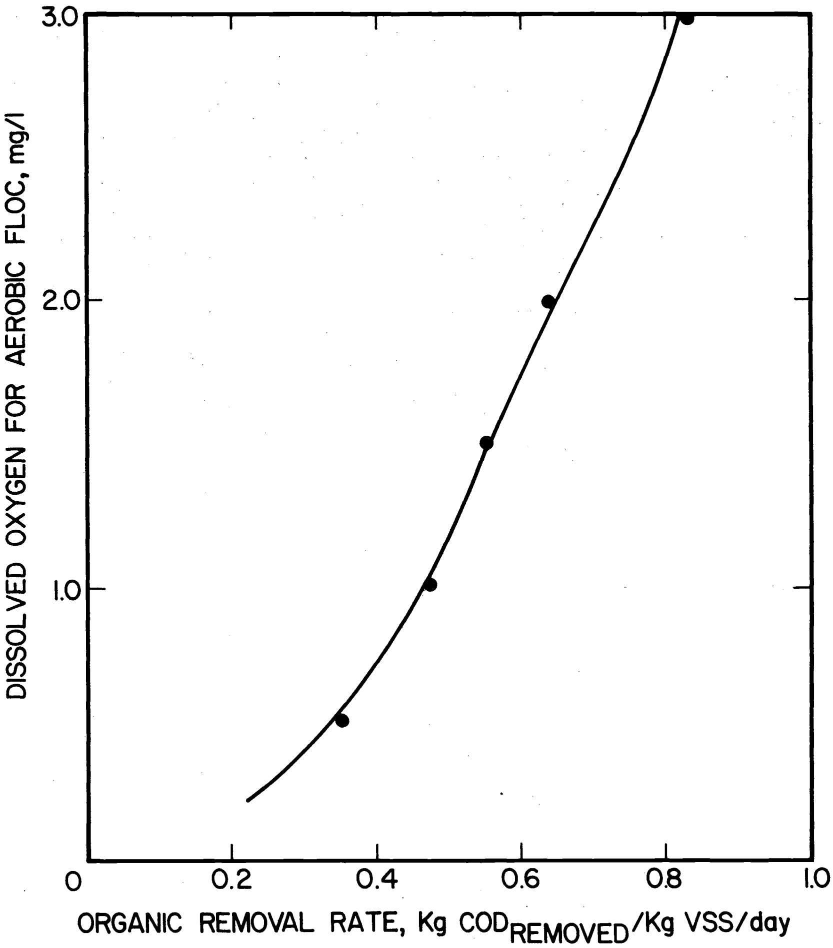

Fig. 2. Relationship between organic removal rate and aeration basin dissolved oxygen for completely mixer activated sludge (3)

It is generally considered uneconomical from energy considerations to maintain dissolved oxygen levels greater than 2.5 mg/l. This in turn will dictate a maximum organic loading to the process irrespective of the biodegradation rate characteristics of the wastewater. It is this fact which favors the use of high purity oxygen processes for readily degradable wastewaters since high dissolved oxygen levels (>6 mg/l) can be maintained without serious economic penalty. Insufficient levels of nitrogen have also been observed to cause filimentous bulking. At a pulp and paper mill, low nitrogen levels caused filimentous bulking within 36 hours. Restoration of sufficient nitrogen (a reduced concentration of 1.5 mg/l) restored the sludge settling characteristics over three sludge ages.

Chudoba et al (4) observed filimentous bulking at low organic loadings in completely mixed systems. At low residual BOD levels, diffusion and consumption limits the floc obtaining organics and overall growth favors the filiments. It should be noted, however, that this condition is limited to wastewaters containing only readily degradable organics such as food processing. In other wastewaters, the more readily degradable organics are removed rapidly so that low residuals are relatively refractory and not available to the filimentous organisms. This problem can be overcome by multistaging the biological process so that a high loading is maintained in the first stage, thus favoring the zoogleal floc growth. A study at an organic chemicals plant in Louisiana showed that filimentous bulking could be controlled by the use of an anoxic stage prior to the aeration basin. Three systems were run in parallel; a conventional air system, an oxygen system and an air system with an anoxic zone. The settling properties of the respective sludges indicated that the oxygen system yielded the best settling sludge while the air system demonstrated serious filimentous bulking. The anoxic-aerobic system had few filiments, but exhibited poorer flocculation and settling than the oxygen system.

In a well designed and operated municipal activated sludge plant effluent suspended solids are rarely a problem. Settleable solids in the range of 20-30 mg/l are readily achievable. In the treatment of soluble industrial wastewaters however, there are several factors which will drastically affect the effluent suspended solids. In addition, this increase in effluent suspended solids is usually dispersed and non-setteable.

The factors which relate to effluent suspended solids are temperature, dissolved inorganic solids and surface tension.

It has been observed that the effluent suspended solids will increase as the temperature decreases. For example, the effluent suspended solids during summer operation at the Union Carbide plant in South Charleston, West Virginia, averaged 42 mg/l and 104 mg/l during winter operation. An increase in total dissolved solids will usually cause an increase in effluent suspended solids. In most cases these solids have been identified as dispersed bacteria. Results from an organic chemicals wastewater are shown in Figure 3. A statistical evaluation of plant operating data at a drinking mill showed that increased surfactant usage within the mill resulted in an increase in effluent suspended solids.

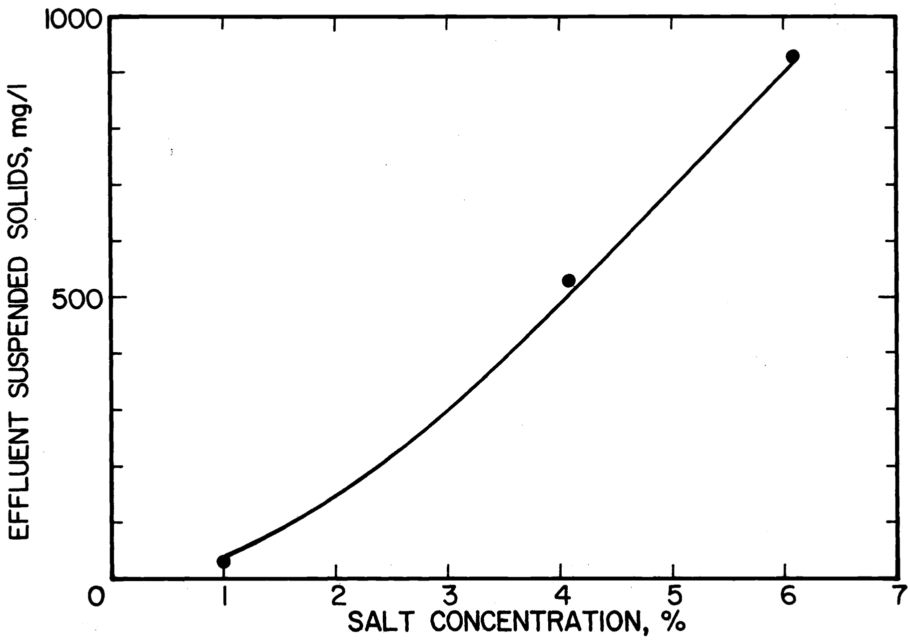

Fig. 3. Effect of inorganic salt concentration on effluent suspended solids (5)

Most effluent discharge permits in the United States require effluent suspended solids of less than 40 mg/l. In order to meet these requirements coagulation is required for solids removal. Present practices involves the addition of coagulant prior to the final clarifier. Common coagulants include cationic polyelectrolytes, alum or iron salts. If high dosages of alum or iron are required, the increased costs of sludge handling favors the use of polymers. Two years operation at the Tennessee Eastman plant has demonstrated the effectiveness of polymer addition. (6) The prounouced effect of temperature on effluent suspended solids and resulting coagulant requirements is shown in Figure 4. It is apparent that minimizing heat losses in the biological process is an important economic consideration for effluent suspended solids control. Approaches include the use of subsurface aerators rather than surface aerators, basins and the injection of waste stream.

High temperature will also cause operating problems. In a recent study (7) the aeration basin temperature was varied from 95°F to 125°F. This resulted in a marked deterioration in sludge settling properties. The protozoan population disappeared above a temperature of 105°F and biological flocculation deteriorated as evidenced by the decrease in zone settling velocity as shown in Figure 5.

Priority Pollutants

Recently the U.S. EPA defined a variety of toxic organics and heavy metals as priority pollutants which must be removed from effluents prior to discharge to water courses. Investigations have been conducted to define the fate of these pollutants in conventional biological wastewater treatment plants. In general, removal in existing technology is more cost effective than preremoval or add on technology.

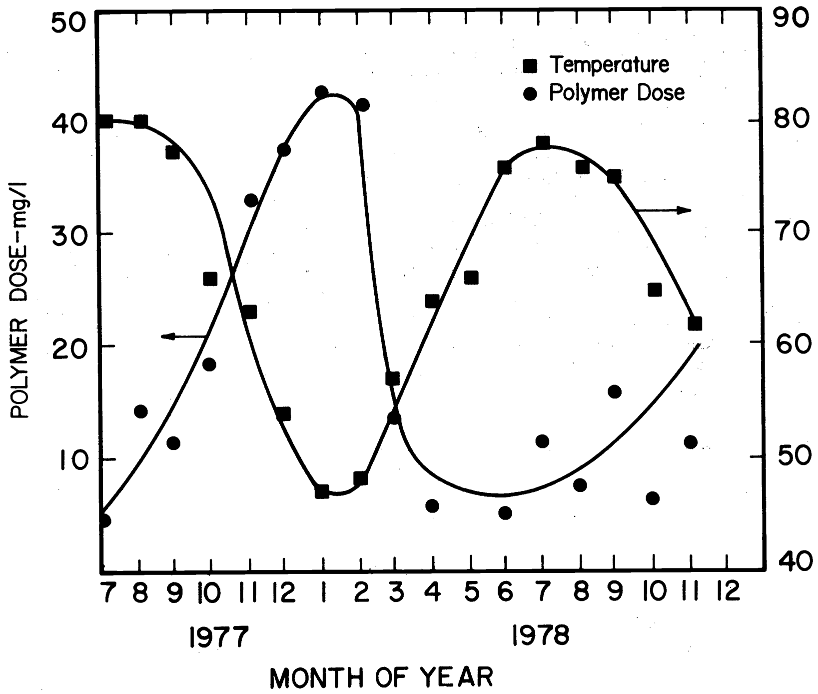

Fig. 4. Comparison of aeration basin temperature and polymer dose requred to achieve 40 mg/l suspended solids

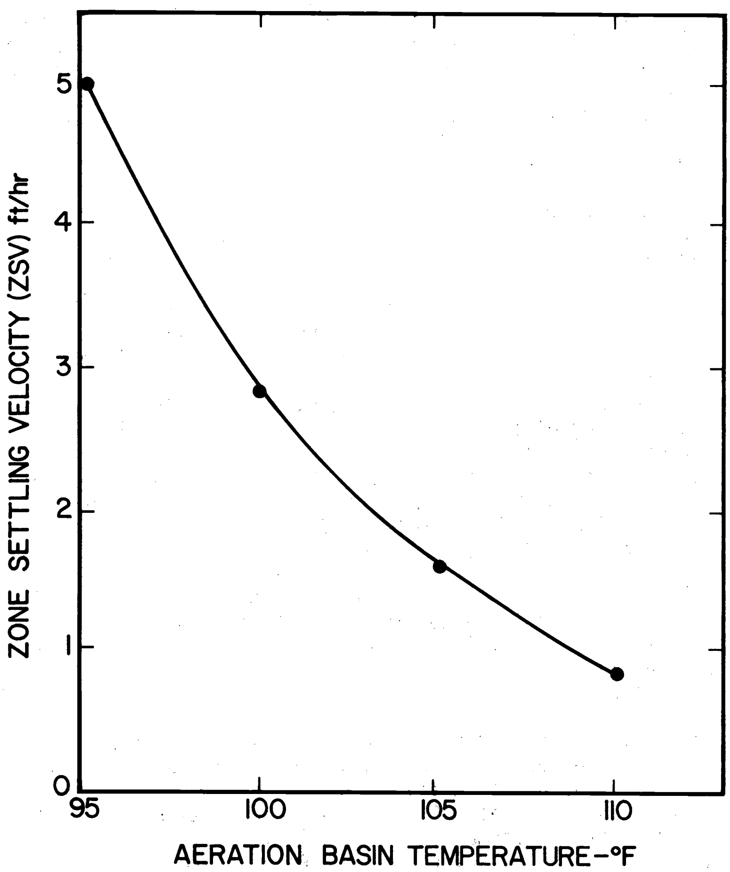

Fig. 5. Zone settling velocity as a function of temperture at a MLSS concentration of 5,000 m/l

A recent study (8) has shown that many of the organic priority pollutants are removed to low residual levels in the activated sludge process. Results from a petroleum refinery is summarized in Table 1.

TABLE 1

REMOVAL OF PRIORITY POLLUTANTS BY THE ACTIVATED SLUDGE PROCESS

Compound Class	Concentration, ppb	Average Percent Removal by Activated Sludge
Alkanes	11-683	99.65
Cycloalkanes	21-71	99.81
Alkylated benzenes	5-187	99.97
Tetralins	11-104	99.98
Aklylated Naphthalenes	21-448	99.93
Alkylated Benxothiophenes and Dibenzothiophenes	8-32	99.88
Alkylated PNA's	3-168	99.86

It is significant to note that priority pollutant removal in the activated sludge process can occur by three mechanisms, namely, stripping, adsorption to the biological floc, or biological degradation. In the case of biodegradation, little is known of degradation by-products, if any. Accumulation of these materials in the sludge would cause problems relative to sludge disposal alternatives.

Several factors need to be considered in the removal of priority pollutants in biological systems, however. In some cases long acclimation periods are required. Tabak and Barth (9) showed that six weeks acclimation was required to effect the biodegradation of benzidine.

Investigations must also be made to ensure that oxidation by-products are not toxic. Winter operation needs to be considered since the degradation rate is a function of basin temperature. It has also been shown in a number of cases that inhibition is increased at decreasing operating temperatures.

Recent emphasis on improved organic removal particularly refractory organics and priority pollutants has led to the application of powdered activated carbon to the activated sludge (PAC) process. In several industrial catagories the U.S. EPA has defined PAC as the basis for future water quality standards.

Investigation of PAC systems have centered around several process enhancement subjects. These include the enhancement of a system to receive shock loads or temperature changes, improved non-biodegradable organics removal, improved removal of priority pollutants, improved color removal, enhancing nitrification, and the resistance to biologically toxic or static substances, improving the hydraulic capacity of existing systems, suppressing foaming, improving sludge handling, and reducing sludge bulking. A flow sheet for a PAC system is shown in Figure 6. The major problem yet to be solved is proving the efficiency of carbon recovery.

The effect of PAC addition on effluent COD and suspended solids to an activated sludge plant treating a petroleum refinery wastewater is shown in Figure 7. Considerable data has been developed on the application of PAC in the chemical and petroleum refinery industries. Considerable improvement was observed in the overall variability in effluent COD and suspended solids as well as the median levels. Improvement in the removal of priority pollutants is shown in Table 2.

Enhancement of nitrification industrial wastewaters using PAC has been demonstrated. Nitrification has not been successful in coke plant wastewaters. Inhibition has been attributed to some specific organics initially present in the wastewater or intermediate product of biooxidation. Addition of PAC resulted in complete nitrification.(11) Low carbon dosages permitted nitrite formation but still inhibited Nitrobacter while higher PAC dosages eliminated inhibition of the Nitrobacter. Results are summarized in Table 3.

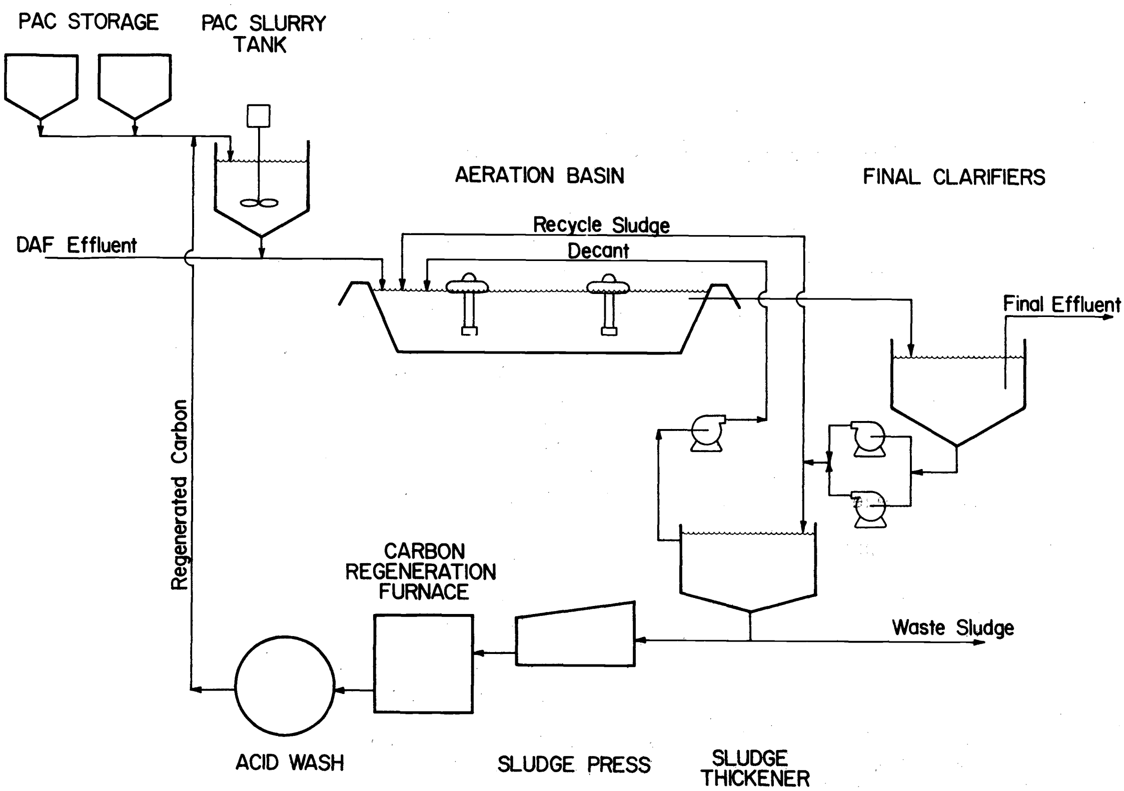

Fig. 6. PAC activated sludge flowsheet

TABLE 2

COMPARISON OF PACT AND ACTIVATED SLUDGE FOR ORGANICS REMOVAL (10)

	Effluent Concentration, mg/l	
Organic	PACT	Activated Sludge
Chlorinated Pesticides	0.017	0.35
Organo-sulfur Pesticides	0	15.0
Organo-phosphate Pesticides	1.23	3.03
PCB's	0.008	0.13

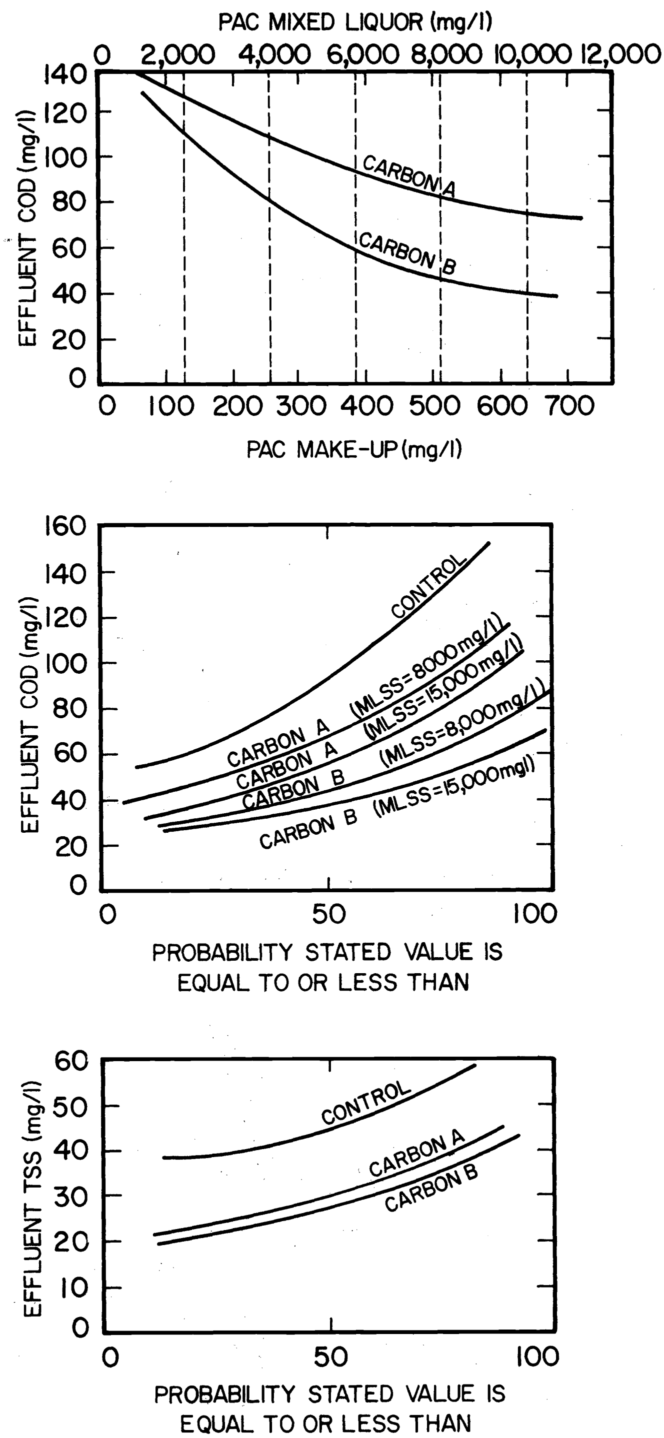

Fig. 7. Conceptual PAC relationship

ECONOMICS OF ADVANCED WASTEWATER TREATMENT

No discussion of future trends in industrial wastewater treatment technology would be complete without consideration of economics. Rapid escalation in the cost of energy and chemicals have placed emphasis on technologies which are cost effective in these areas. This includes in-plant modification, water reuse and by-product recovery and modifications to existing technologies. As an example, a comprehensive study was made on an organic chemicals plant to define the most cost effective approach to meet future effluent limitations. (12) It was shown that maximum in-plant modification would result in a 25 percent reduction in wastewater flow and a 34 percent reduction in organic loading. This, combined with the

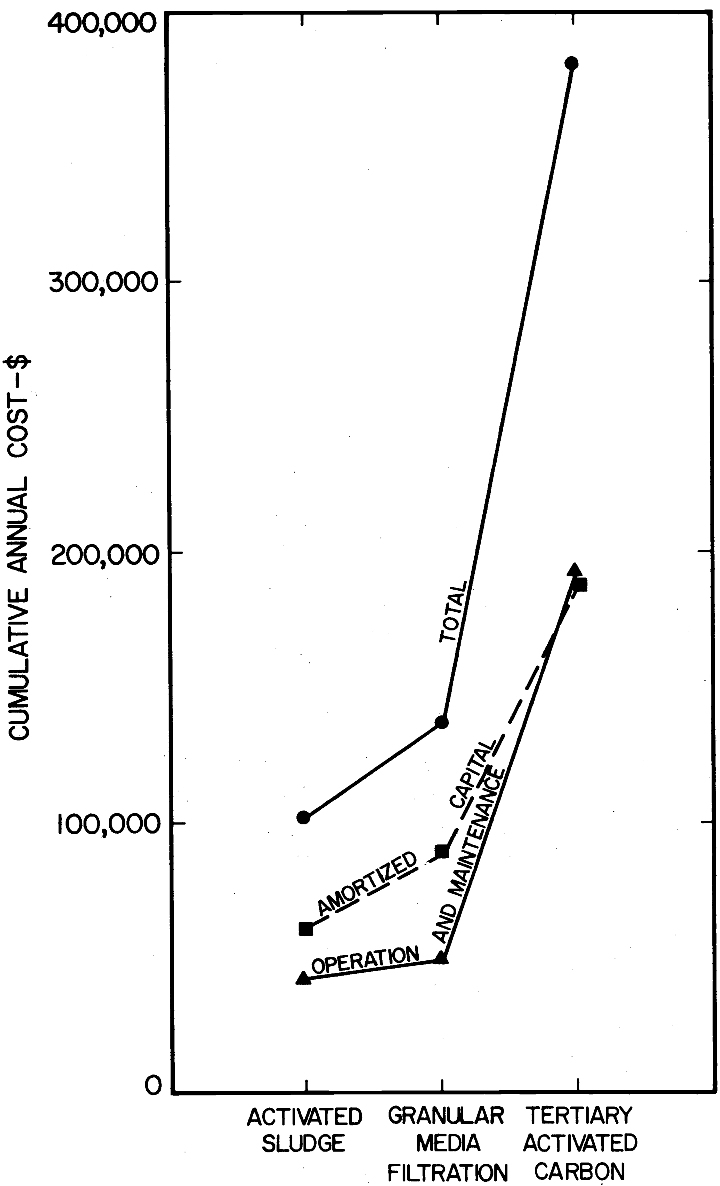

Fig. 8. Total annual costs of waste treatment-model refinery

TABLE 3

EFFECT OF PAC ON NITRIFICATION OF COKE PLANT WASTEWATERS

PAC feed mg/l	SRT days	TOC mg/l	TKN mg/l	NH_3-N mg/l	NO_2-N mg/l	NO_3-N mg/l
0	40	31	72	68	4.0	0
33	30	20	6.3	1	4.0	9.0
50	40	26	6.4	1	1.0	13.0

Influent conditions: TOC=535 mg/l, TKN=155 mg/l, NH_3-N=80 mg/l.

addition of chemical coagulation and filtration results in an effluent COD level of 22,500 lbs per day at an annual cost of 1.33 million dollars. End of pipe granular carbon adsorption to the existing facility would result in an effluent COD level of 17,850 lbs per day at an annual cost of 4.1 million dollars. The economic advantages to in-plant changes and modifications to the existing technology are obvious.

Ford and Tischler (13) developed the economics of advanced wastewaters treatment for the petroleum refining industry. Their results are shown in Figure 8. In comparing the cost effectiveness of granular vs. powdered activated carbon, Ford (14) showed a cost of \$2.02/lb COD removed for PAC and a cost of \$3.79/lb COD removed for granular carbon. An evaluation of energy requirements for advanced wastewater treatment in the petroleum refining industry is shown in Figure 9.

It is recognized that cost effectiveness will vary with industrial category depending on the concentration and characteristics of the pollutants to be removed. In most cases, however, considerations of energy and chemical usage will mitigate against end of pipe treatment whereas large volumes of wastewater at low pollutant concentrations must be considered for treatment.

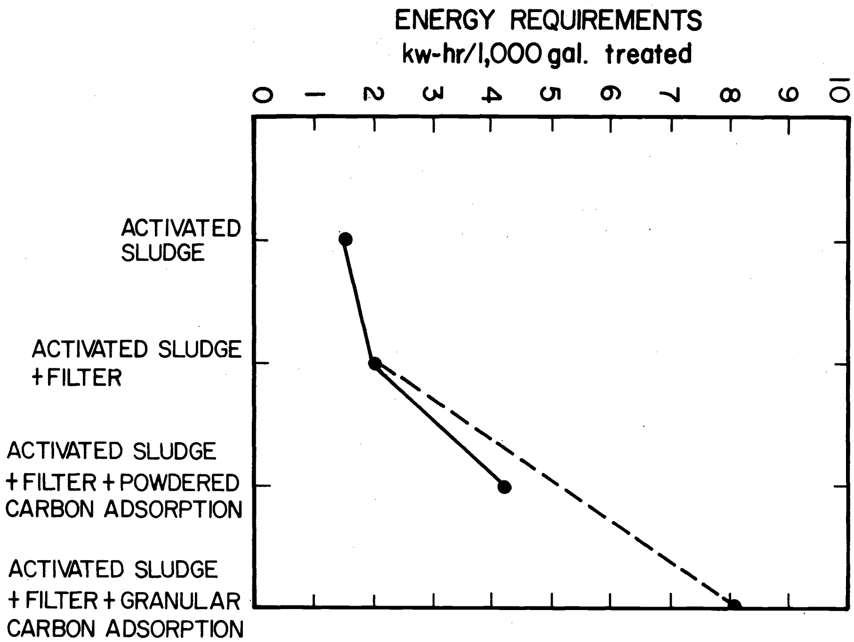

Fig. 9. Energy usage in the treatment of petroleum refinery wastewaters

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