Point Toxics Control for Industrial Wastewaters

Various methods are suitable for reducing levels of toxics in wastewater. However, careful evaluation must be undertaken to select the most effective method.

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TRADITIONALLY, wastewater treatment processes have been designed to remove conventional pollutants such as BOD and suspended solids. More recently, process modifications have been made to remove nitrogen and phosphorus. In many cases, toxic organics are refractory or generated as by-products in the biological process, and physical-chemical technology add-ons are required for the reduction of those compounds or groups of compounds that exhibit inhibition or toxicity to biological wastewater treatment processes (including both carbonaceous removal and nitrification), and acute or chronic toxicity to aquatic organisms. The most common technologies include source treatment for specific pollutants, tertiary treatment following biological treatment processes, or modifications to the biological treatment technology such as the addition of powdered activated carbon (PAC) or the use of chemical oxidants (see Figure 1).

Toxicity/Technology Evaluation

A procedure has been developed for evaluating the different technologies that can be applied to point-source toxicity reduction, as shown in Figure 2. In general, this procedure is based on the assumption that the wastewaters under evaluation contain mixtures of organics and inorganics. If either organics or inorganics are absent from the wastewater, then this procedure can be modified accordingly.

Initially, an equalized sample of wastewater is analyzed for the presence of such constituents as heavy metals, oil and grease, and suspended solids that should be removed prior to biological or biological/physical-chemical treatment. Conventional technologies including coagulation, precipitation, sedimentation and flotation can be used for pretreating the wastewater. The pretreated wastewater is then evaluated in a fed batch reactor (FBR) for biodegradability and toxicity to biological treatment, includ-

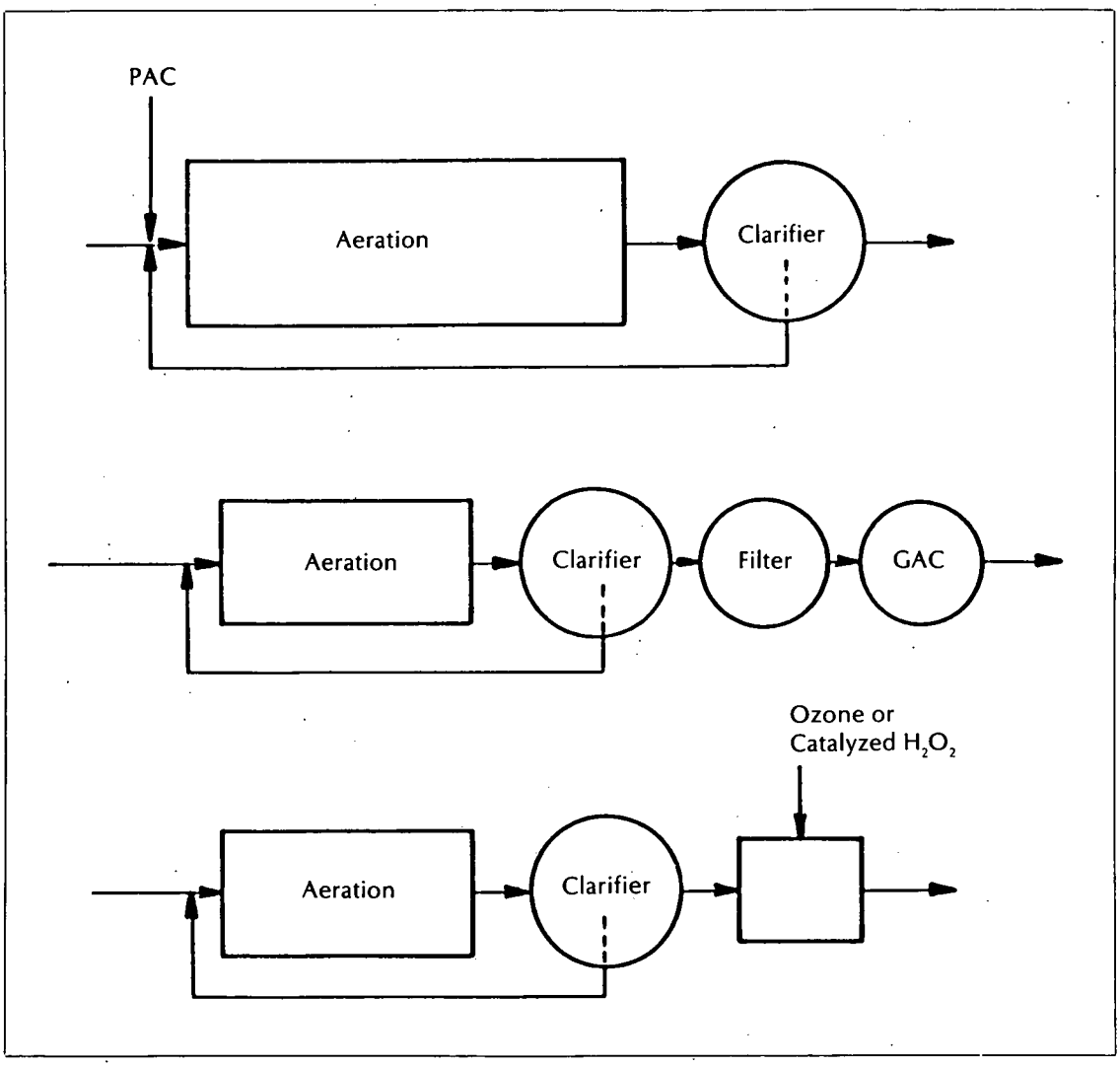

FIGURE 1. Treatment alternatives for toxicity reduction.

ing nitrification if this is required.[1]

If the wastewater is found to be non-biodegradable and toxic, it is diverted for separate treatment. If the wastewater is degradable, but exhibits a toxic threshold, it is then evaluated for toxicity reduction via biological treatment. After such treatment, the bioeffluent is then re-evaluated for both conventional pollutants, priority pollutants (if required) and bioassay (*i.e.*, LC_{50} — the dilution in which 50 percent of the test species survive after 48 or 96 hours).

If the bioeffluent fails to meet the required LC_{50}, alternative technologies are evaluated, including powdered activated carbon (PAC), chemical oxidation, polymer addition or granular activated carbon (GAC). Determination of LC_{50} following these treatments will indicate which treatment technology is applicable.

This procedure is not intended to optimize any of the candidate technologies, but rather to identify those that will help meet the required effluent quality. Further evaluation is required to develop design criteria from the various effective technologies.

Based on the results obtained in using this procedure, specific wastewater streams can be classified relative to alternative treatment potentials as shown in Table 1. In

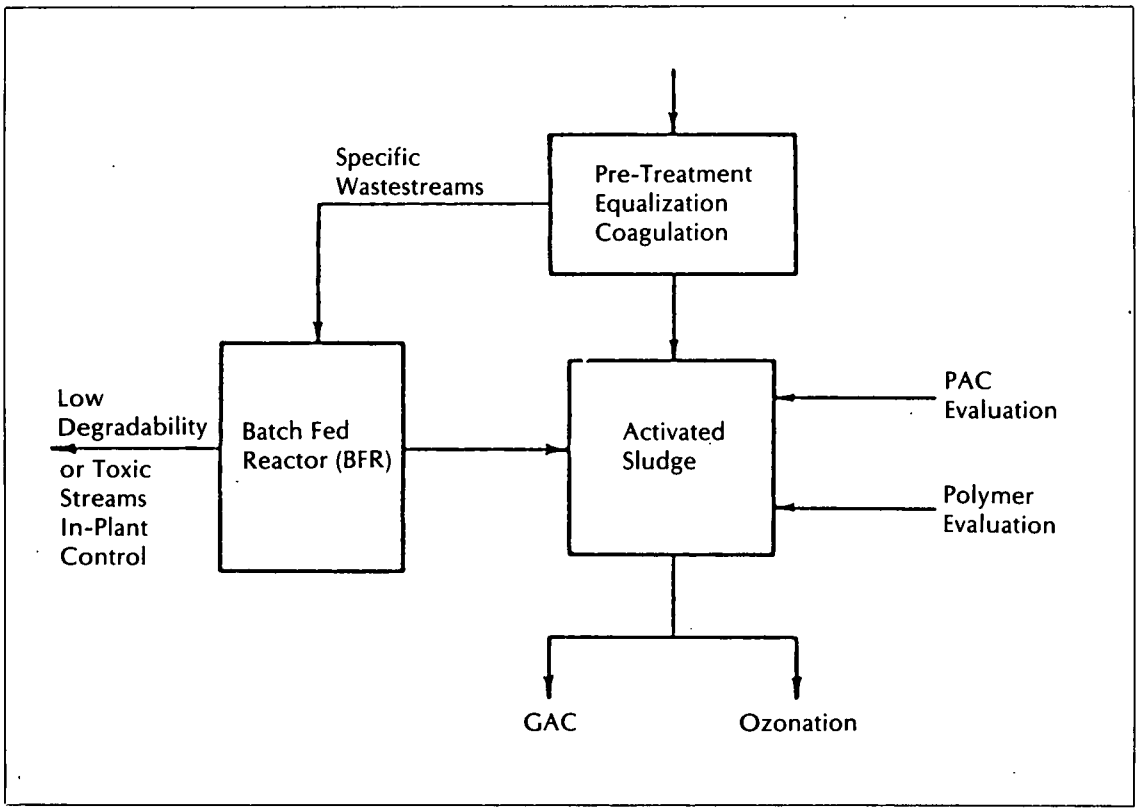

FIGURE 2. Technology evaluation procedure for point source toxicity reduction.

most cases, the maximum plant loading is that concentration of the specific stream that yields an LC_{50} of greater than 50 percent.

Source Treatment & Control

In cases of non-degradable and toxic wastewaters (Class A) or wastewaters that remain toxic after biological treatment and that can be segregated in a low-volume, high-strength stream (Class B), source treatment may provide a cost effective solution. The most common source treatment technologies are shown in Figure 3.

Chemical oxidation using catalyzed hydrogen peroxide has been successful in some cases. Table 2 presents treatment results for two wastewaters. A substantial reduction in toxicity was observed for wastewater 1. In the case of wastewater 2, very little reduction in toxicity was observed even though a substantial reduction in TOC was obtained. The use of chemical oxidation should be determined on a case by case basis.

Wet air oxidation (WAO) has been successfully applied in a number of applications. WAO is based on a liquid phase reaction between organic material in the wastewater and air supplied by a compressor. The reaction takes place flamelessly in an enclosed vessel. The system is pressurized and the system temperature, initiated by a start-up boiler, is maintained automatically once the reaction starts. These units typically operate at 550°F and at 2,000 psig. Results for two wastewaters treated with this method are summarized in Table 3. As was in the chemical oxidation case, substantial reduction in toxicity was observed for wastewater 2, but wastewater 1 was still highly toxic after oxidation. The applicability of WAO must also be evaluated for each particular case.

Although not yet widely applied, macroreticular anion ion exchange resins may be excellent candidates for removing specific organic compounds, leaving other com-

Table 1

Classification of Wastewater Streams From a Multi-Product Chemical Complex*

	q_{max} (mg TOC/gm-hr)	48 hr LC_{50} (TOC, mg/l)	Maximum Plant Loading (TOC, mg/l)
Class A Wastestream Samples (Non-Degradable With Suspect Toxicity)			
A	<1	<8	1
B	<1	0.5	0.4
C	<1	16	5.5
D	<1	2.4	1.7
Class B Wastestream Samples (Biodegradable With Suspect Toxicity)			
E	22.4	16	4
F	30.0	14	8
G	7.9	26	10
H	5.5	7.2	3.1
Class C Wastestream Samples (Unlikely to Induce Toxicity)			
I	26.5	104	14
J	5.3	319	36
K	5.4	111	11.7
L	14.1	375	56

* Mysid shrimp test species.

Table 2

Catalyzed Hydrogen Peroxide Oxidation of Concentrated Wastestreams

Sample	TOC (mg/l)	COD (mg/l)	BOD (mg/l)	LC_{50} (%)
Wastewater 1				
Before H_2O_2	92	301	135	16.3
After H_2O_2	52	184	57	29.7
Removal (%)	43.4	38.9	57.8	—
Wastewater 2				
Before H_2O_2	2,150	2,040	300	2.4
After H_2O_2	95	850	42	3.0
Removal (%)	95.5	58.3	86.0	

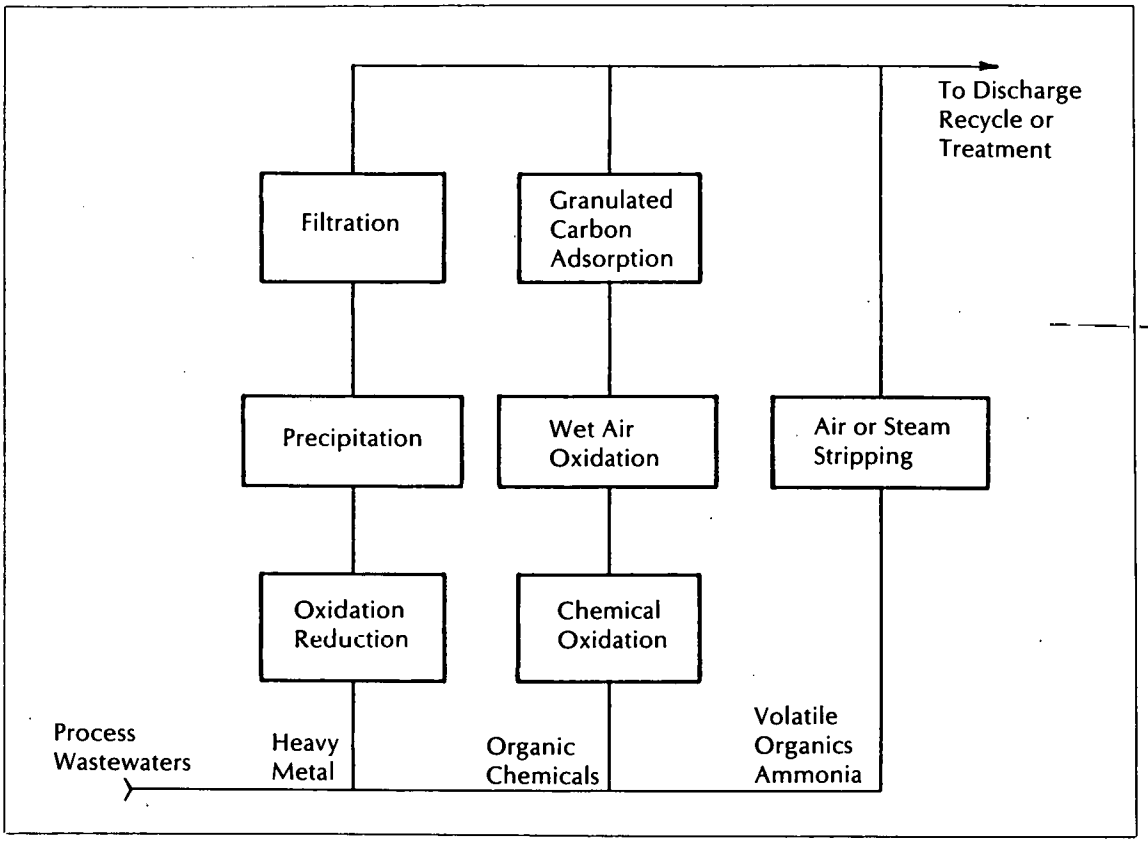

FIGURE 3. In-plant technologies for toxicity reduction of specific wastestreams.

Table 3

Wet Air Oxidation of Concentrated Wastewater Streams

	Wastewater 1	Wastewater 2
Influent COD, g/l	28.8	198.2
% Removal	79.1	86.3
Influent BOD, mg/l	228	82,500
% Removal	99.5	83.8
Influent Color APHA	1×10^6	—
% Removal	98.5	—
LC_{50} Influent*	1.1	3.2
LC_{50} Effluent*	4.1	87

Oxidation Temperature 260°C for 60 min.

* 48 hr LC_{50} mysid shrimp at 1:25 dilution.

pounds to be removed via more conventional means. Such resins are highly specific and, thus, can be formulated to remove one compound or a class of compounds. Evaluation and application of this technology requires a great deal more information about the specific compounds involved in toxicity and a significantly more sophisticated analysis than most other processes. If properly tested and applied, however, resin columns can be quite cost-effective with or without solvent recovery and reuse.

In some instances, process changes or the substitution of raw materials may result in substantial toxicity reduction by moving a wastewater stream from Class A to Class B or Class C (non-toxic wastewaters). These alternatives should be an integral part of any toxicity reduction program.

Heavy Metals Removal

Heavy metals are found in a variety of

Table 4

Effect of Metal Removal on Toxicity Reduction

	48-hr LC_{50}%	% Improvement	Cu mg/l	Cr mg/l	Zn mg/l	Ni mg/l
Secondary Effluent	16	—	0.24	0.50	0.16	0.71
After Alum Flocculation	21	31	0.06	0.35	0.07	0.52
After Hydroxide Precipitation	24	50	0.03	0.25	0.03	0.49

industrial wastewaters, including plating, chemical and petrochemical, and paint and pigment manufacture. These metals must be removed prior to biological treatment in order to avoid toxicity and the accumulation of metals in the biological sludge. The removal of metals may be accomplished via source treatment or chemical precipitation.

Heavy metals have been shown to contribute to effluent toxicity and significant improvements in LC_{50} result when metals concentrations are reduced. Table 4 presents the results of a series of toxicity tests using Mysid shrimp before and after metals precipitation. There was significant improvement in LC_{50} relating directly to metal concentration reduction.

Although conventional treatment technologies for most inorganic pollutants are well established, extreme treatment requirements or unusual wastewater constituents may prevent their traditional application due to their costliness and/or inefficiency. Advanced technologies such as ion exchange or reverse osmosis are usually not appropriate, particularly in the presence of fouling substances or high background salt levels. In addition, extreme treatment requirements may result in necessitating the use of such a process as microfiltration as a polishing step.

Biological Treatment

A majority of the toxic organics can be removed using biological treatment. The actual removal of the toxic organics, however, may occur through one or more mechanisms — sorption, stripping or biodegradation. Table 5 identifies several organics and the mechanisms that can be applied for their removal.

Sorption. Limited sorption on biological solids occurs for a variety of organics, and this phenomenon is not a primary mechanism of organic removal in the majority of cases. An exception is Lindane, as reported by Jones and Weber who showed that while no biodegradation occurred, there was significant sorption.[2] It is probable that other pesticides will respond in a similar manner in biological wastewater treatment processes.

While sorption on biomass does not seem to be a significant removal mechanism for toxic organics, sorption on suspended solids in primary treatment may occur when toxic organics are present in municipal wastewater. The importance of this phenomenon is the fate of the organics during subsequent sludge handling operations. In some cases, toxicity to anaerobic digestion may result, thus restricting land disposal alternatives.

While sorption of organics on biomass is usually not significant, heavy metals will complex with the cell wall and bioaccumulate. While low concentrations of metals in the wastewater do not generally inhibit the efficiency of organic removal, their accumulation on the sludges can have a marked effect on subsequent sludge treatment and disposal operations.

Stripping. Volatile organic carbon (VOC) will air-strip in such biological treatment processes as trickling filters, activated sludge and aerated lagoons. Depending on the VOC in question, both air-stripping and biodegradation may occur (see Figure 4). The

Table 5

Comparison of Removal Mechanisms for Various Priority Pollutants in Activated Sludge

Biodegradation*	Biodegradation & Stripping**	Stripping***	Refractory****
Nitrobenzene	Ethyl Acetate	1,2-Dichloroethane	bis (2-ethylhexyl) Phthalate
2,4-Dichlorobenzene	Benzene	1,1,1-Trichloroethane	
2,4-Dinitrobenzene	1,2-Dichlorobenzene	1,1,2,2,-Tetrachloroethane	
Acrolein	Methylene Chloride	1,2-Dichloropropane	
Acrylonitrile	Toluene	Trichloroethylene	
Pentachlorophenol	Ethylbenzene		
Phenol	Chloroform		
Phenanthrene	Carbon Tetrachloride		
Naphthalene			
Benzidine			

*Compounds that exhibit greater than 95 percent biodegradation.
**Compounds that exhibit between 5 & 50 percent removal by stripping & total removal of greater than 95 percent.
***Compounds that exhibit greater than 95 percent removal by stripping.
****Compounds that exhibit less than 80 percent total removal.

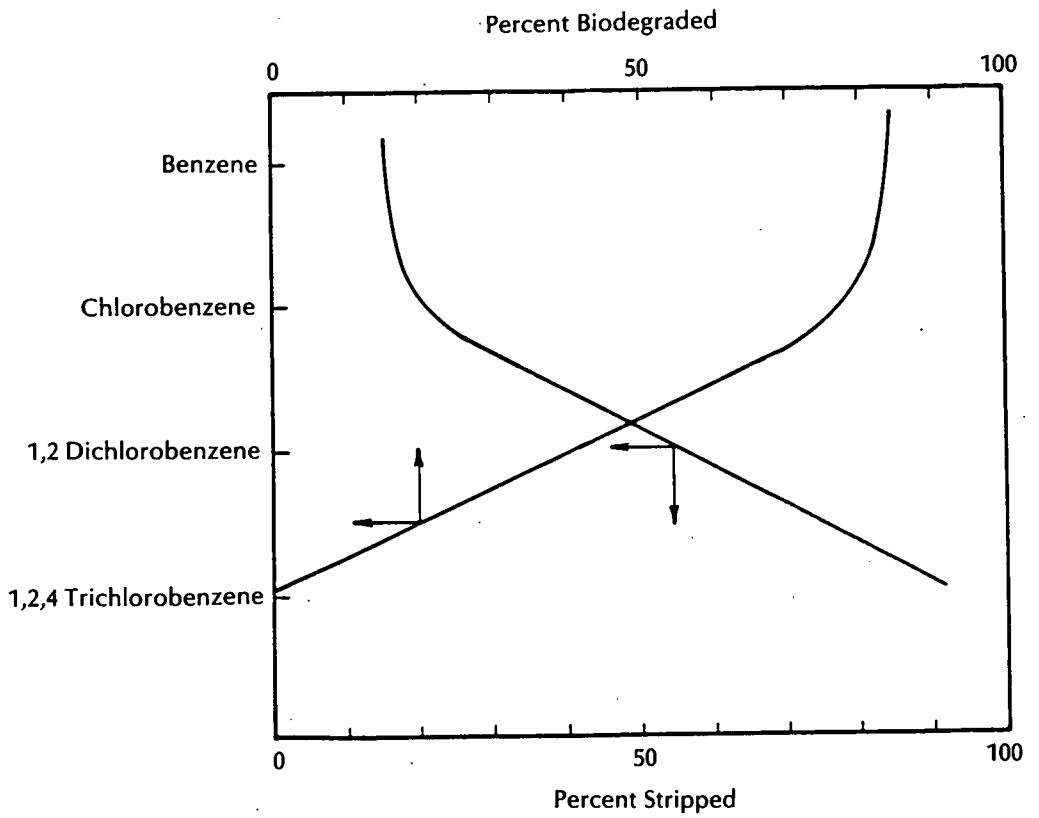

FIGURE 4. Stripping and biodegradation of organics in the activated sludge process.

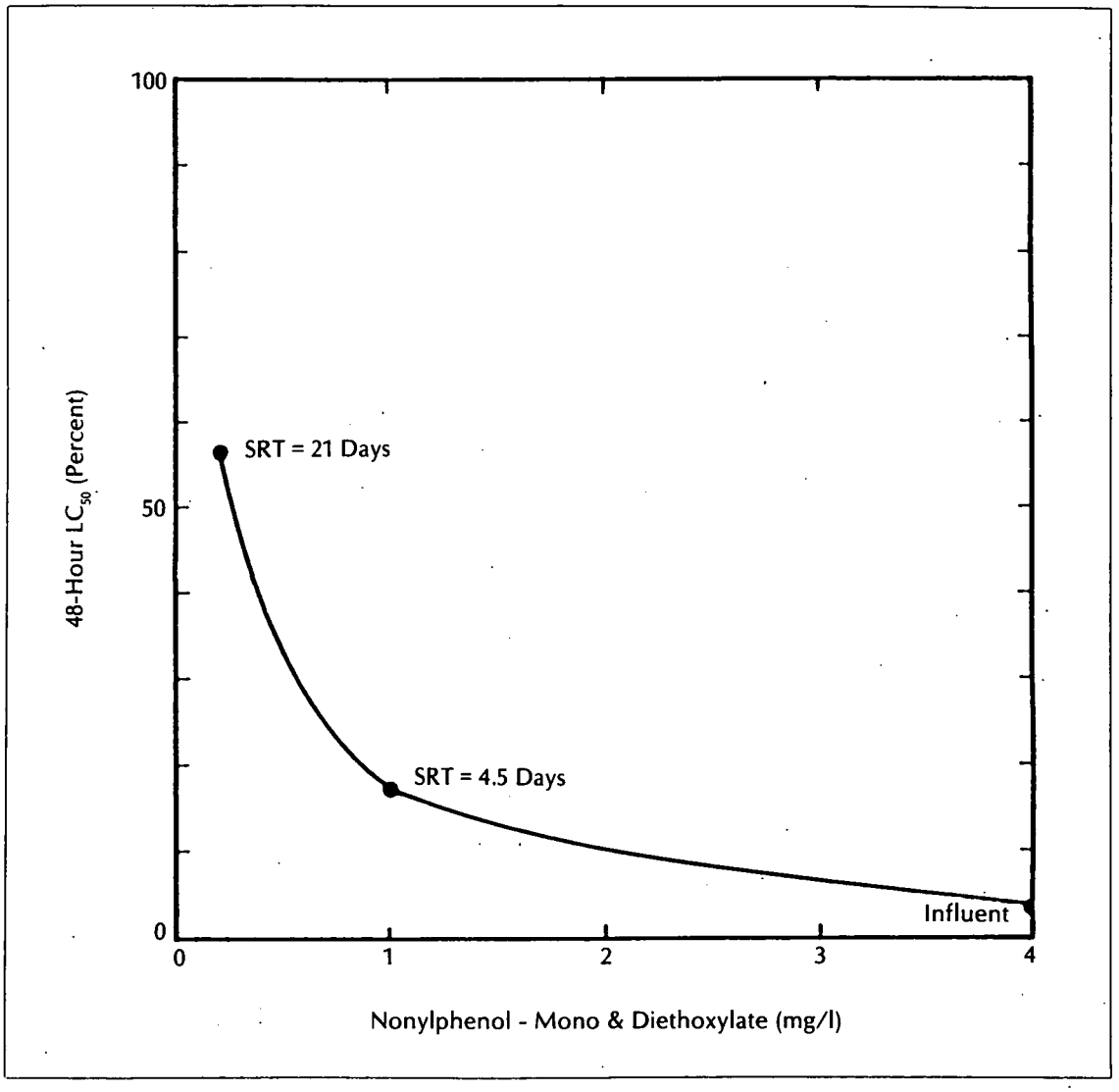

FIGURE 5. The effect of SRT on toxicity reduction for nonyl phenolics.

stripping of VOC in biological treatment processing is currently receiving considerable attention in the United States since current legislation severely limits permissible emissions of VOC.

Biodegradation. A majority of the toxic organics will biodegrade, even though some will degrade very slowly. While biodegradation will occur in most cases, the biomass must be acclimated to the specific organic, particularly when a dissimilar biomass such as a municipal biological sludge is initially used to treat the wastewater. Depending on the organic, total acclimation may take a considerable period of time. Tabak and Barth treated benzidine starting with municipal activated sludge and required six weeks to attain complete acclimation.[3]

While acclimation may take as much as several weeks, Watkin found that the biomass possesses a "genetic memory."[1] The addition of dichlorophenol (DCP) was discontinued to an activated sludge reactor for ten sludge ages. After resuming the feeding of DCP to the reactor, biodegradation occurred immediately, although initial acclimation required three weeks. In some cases, a readily degradable co-substrate is

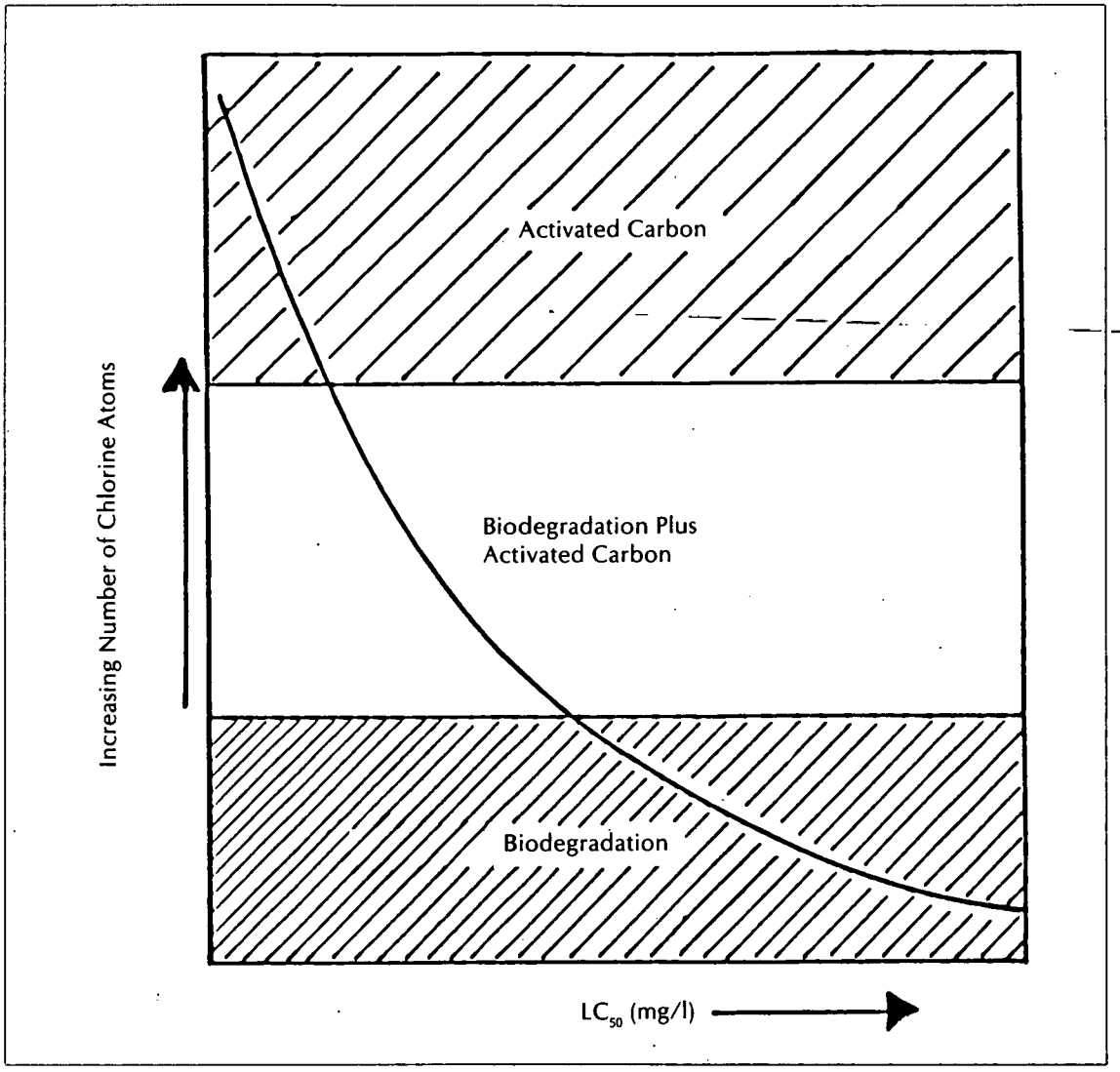

FIGURE 6. The effect of the number of chlorine atoms on biodegradation and effluent toxicity.

required to effect rapid biodegradation of a specific toxic organic. This requirement is usually not a problem for most wastewater treatment plants, since a wide variety of degradable organics are usually present. In most cases, however, achieving a low amount of organic residuals is attainable. For example, phenolics have been treated in the activated sludge process to effluent levels of less than 30 μg/l.

Some toxic organics degrade very slowly in the activated sludge process and, therefore, long solids retention times (SRTs) are required to achieve an acceptable toxicity reduction. Figure 5 shows the effect of SRT on the removal of nonylphenol and the resulting change in LC_{50}.

Increasing the number of chlorine atoms on a molecule can also progressively decrease the biodegradation rate and increase its toxicity. In these instances, the application of additional physical-chemical technologies to the biological process are required (see Figure 6). In addition, nondegradable organic by-products can accumulate in a biological treatment process. Many

Table 6

Molecular Weight Distribution of Biological Effluents

	PA & Dyestuffs		
Molecular Weight	Influent %	Bioeffluent %	Glucose Chudoba[4] %
> 10,000	—	11.5	45
500 - 10,000	—	14.5	16
< 500	100	74.0	39

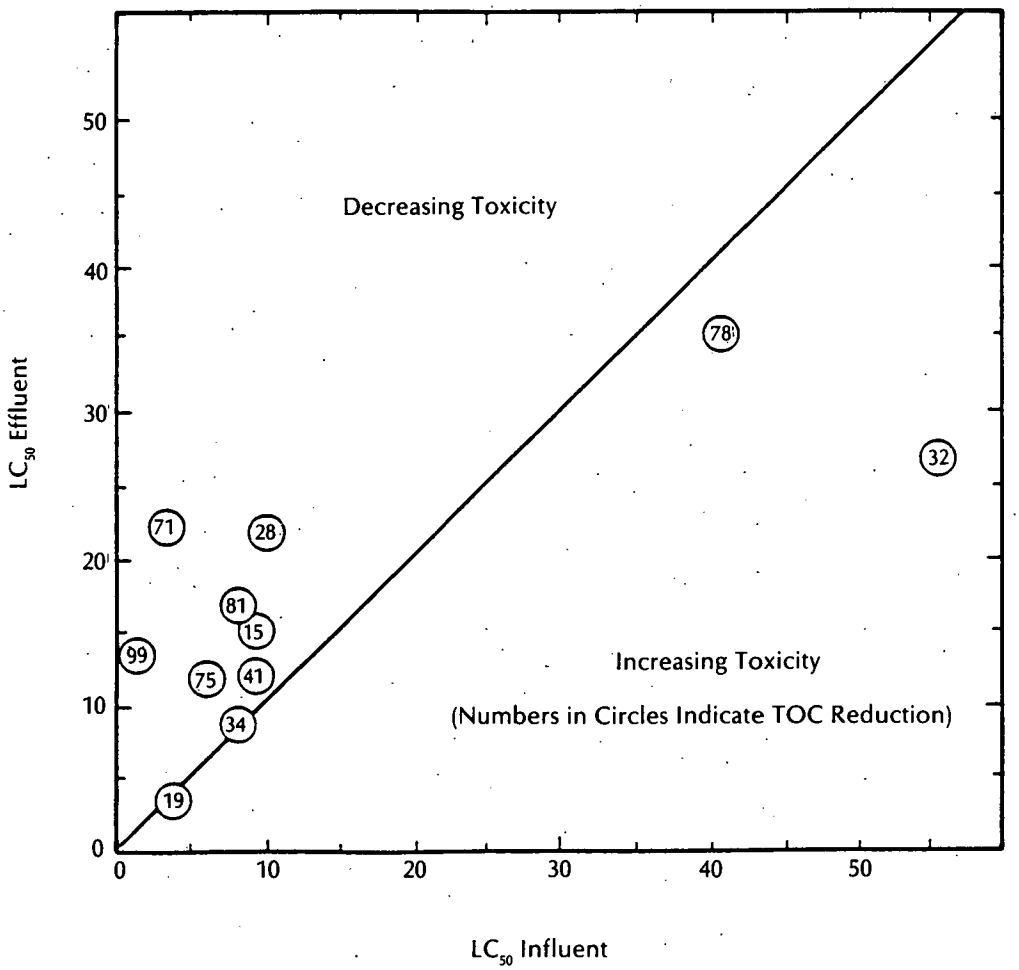

FIGURE 7. The change in toxicity using biological treatment.

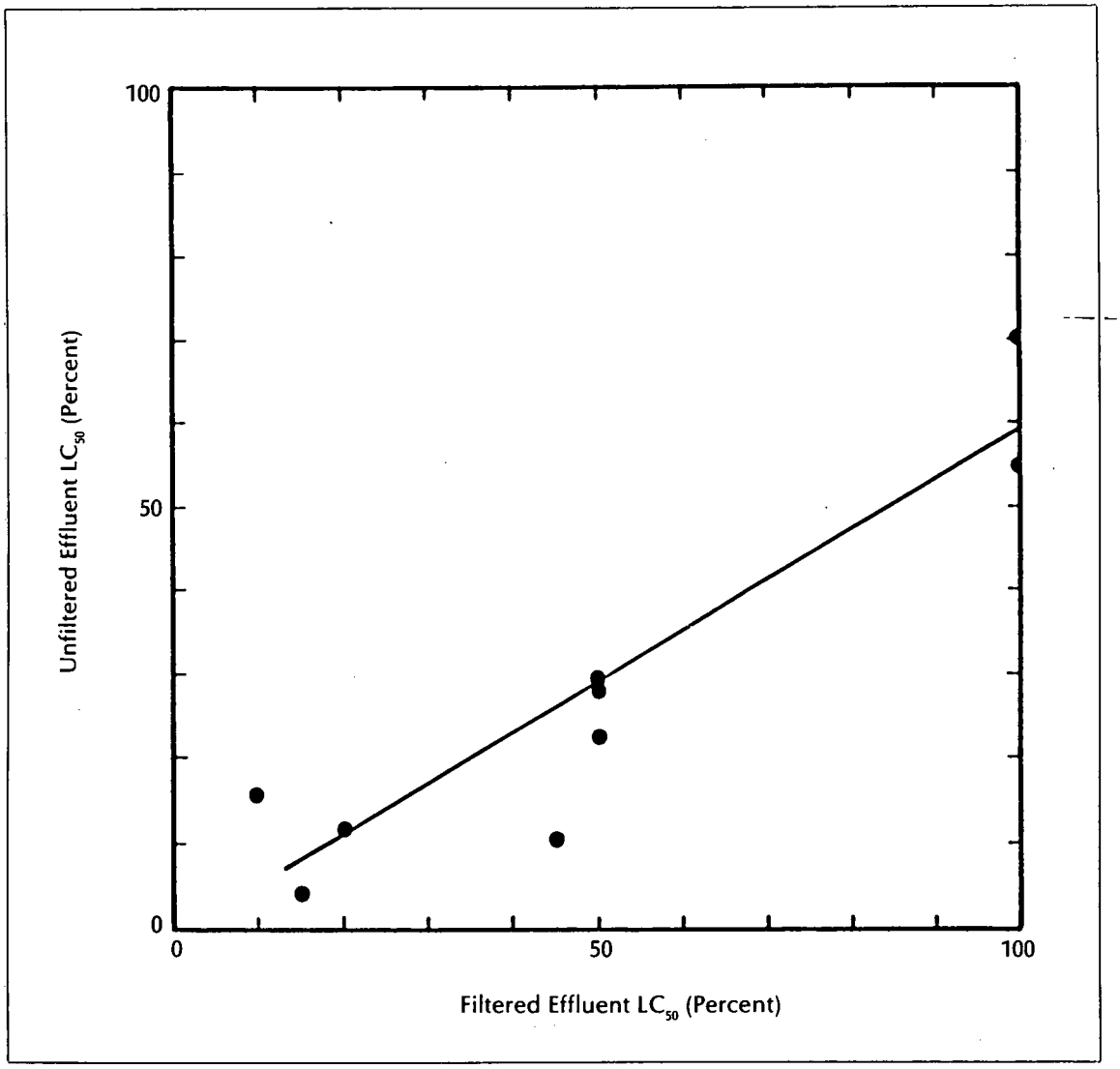

FIGURE 8. The effect of biological effluent filtration on toxicity reduction.

of these by-products possess a high molecular weight (see Table 6). In some cases, these high molecular weight fractions exhibit a greater toxicity to aquatic organisms than the lower molecular weight fractions originally present in the wastewater. Even after long periods of aeration, non-degradable organics and by-products often remain.

A study was conducted on the biological treatment of 11 organic chemicals found in wastewaters that are toxic to aquatic organisms. In each case, the wastewater was treated in order to remove all biodegradable organics. As shown in Figure 7, toxicity was reduced by biological treatment in six cases. In three cases, the toxicity levels were essentially unchanged and, in two cases, biodegradation resulted in an increase in aquatic toxicity. This area requires further study to define the effect of biological treatment on aquatic toxicity, and to optimize the biological process for aquatic toxicity removal.

Effluent suspended solids can also increase effluent toxicity in some cases. Figure 8 shows the differences in LC_{50} between a filtered and unfiltered effluent from an activated sludge plant that was treating

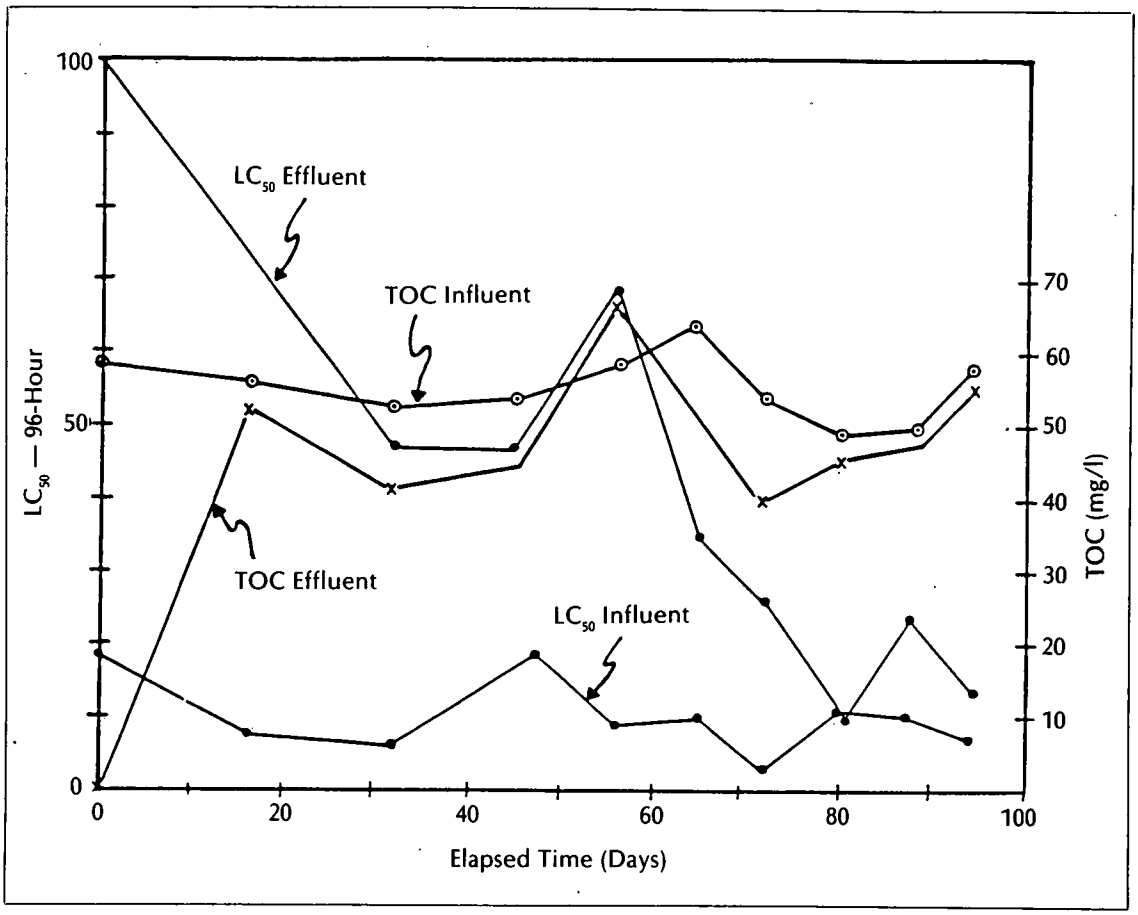

FIGURE 9. TOC and toxicity reduction using granular carbon columns.

surfactant manufacturing wastewater.

A significant part of the toxicity present in wastewater is non-biodegradable through conventional biological wastewater treatment. In the latter case, it is necessary to supplement the biological process with physical-chemical treatment. The most economically viable end-of-pipe alternatives at the present time are activated carbon adsorption or chemical oxidation.

Carbon Adsorption

Activated carbon adsorption can be applied as tertiary granular carbon columns (GAC) or as powdered activated carbon (PAC) integrated into the activated sludge process. In order to determine the applicability of carbon for the removal of organic carbon and toxicity, several factors must be considered including the type of carbon to be used and the effect of regeneration on adsorption efficiency.

Depending on the nature of the organics contributing to the toxicity, carbon efficiency for toxicity reduction may be considerably superior to TOC removal. Figure 9 depicts a carbon column operation in which TOC breakthrough occurred after 12 days of operation, while breakthrough of LC_{50} did not occur for 60 days. One possible explanation for these results is the replacement of the more strongly adsorbed toxicity causing molecules for the more weakly adsorbed non-toxic molecules. Because of these and related phenomena, it is not possible to develop design data from the laboratory isotherms, and continuous column pilot studies should be conducted to confirm carbon usage.

An alternative technology to GAC is the

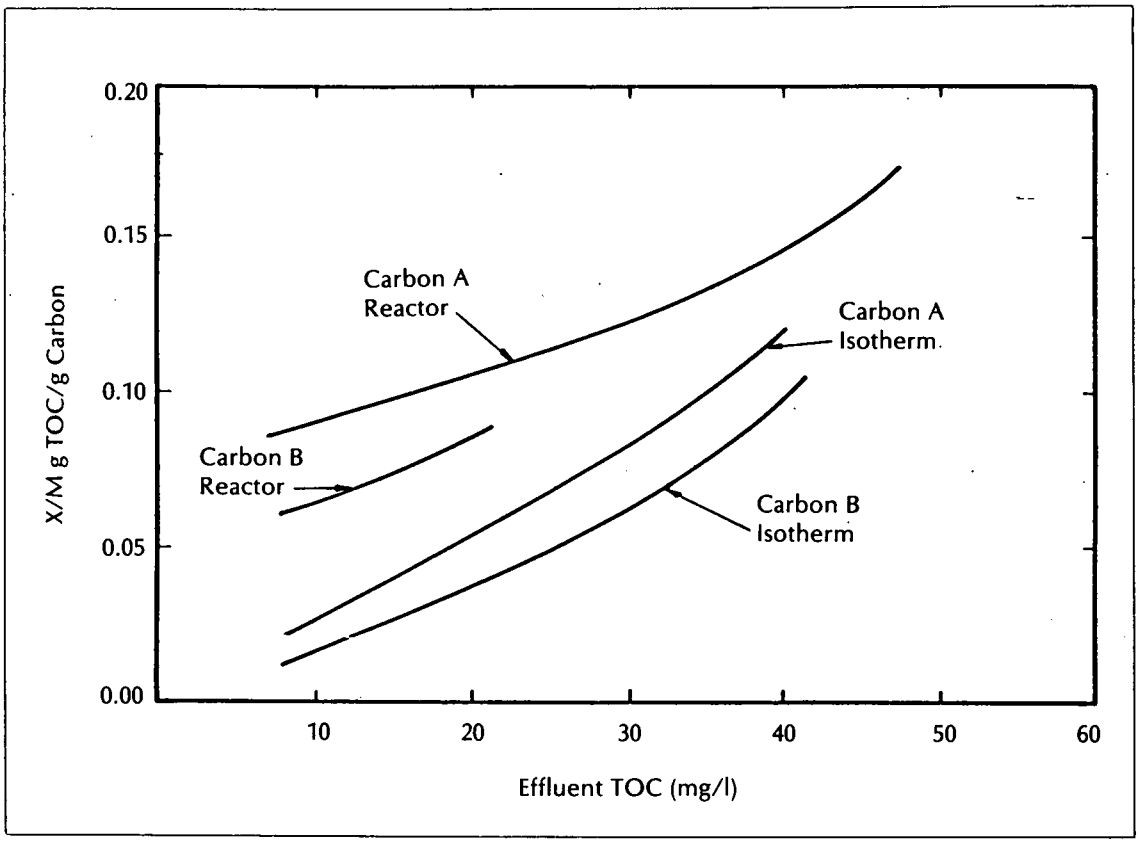

FIGURE 10. The performance relationship of PACT reactors with isotherm data.

application of powdered activated carbon (PAC) to the activated sludge process. Carbon is mixed with the influent wastewater or fed directly to the aeration basin. The carbon-biosludge mixture is settled and the sludge is recycled in the same manner as in the conventional activated sludge process. The waste-activated sludge similarly contains the carbon and biosludge.

PAC offers the advantage of being able to be integrated into existing biological treatment facilities at minimal capital cost. Since the addition of PAC enhances the ability of sludge to settle, conventional secondary clarifiers will usually be adequate even with high carbon dosages.

Since degradable organics adsorbed on the carbon are biodegraded in the process, it is assumed that the organic removal by the carbon sludge consists primarily of nondegradable organic carbon. This fact is confirmed by comparing adsorption through a laboratory isotherm on bioeffluent alone with TOC removal in the PACT process as shown in Figure 10. TOC removal in the PACT process is greater than that predicted by the isotherm. One explanation for this phenomenon is the longer carbon contact time in the activated sludge process, thus permitting the attainment of effluent levels closer to equilibrium than that achieved in the shorter laboratory test.

As shown in Figure 11, as the number of chlorine atoms increase, the addition of PAC becomes more effective. TOC removal by carbon adsorption may or may not correlate with the LC_{50}, depending on the specific organics responsible for the toxicity. Performance of the PACT process in treating plastics additives and dyestuff wastewaters is shown in Table 7. The addition of PAC reduces TOC and color as well as toxicity, as defined by the LC_{50}. As Table 7 shows, the carbon also removes heavy metals.

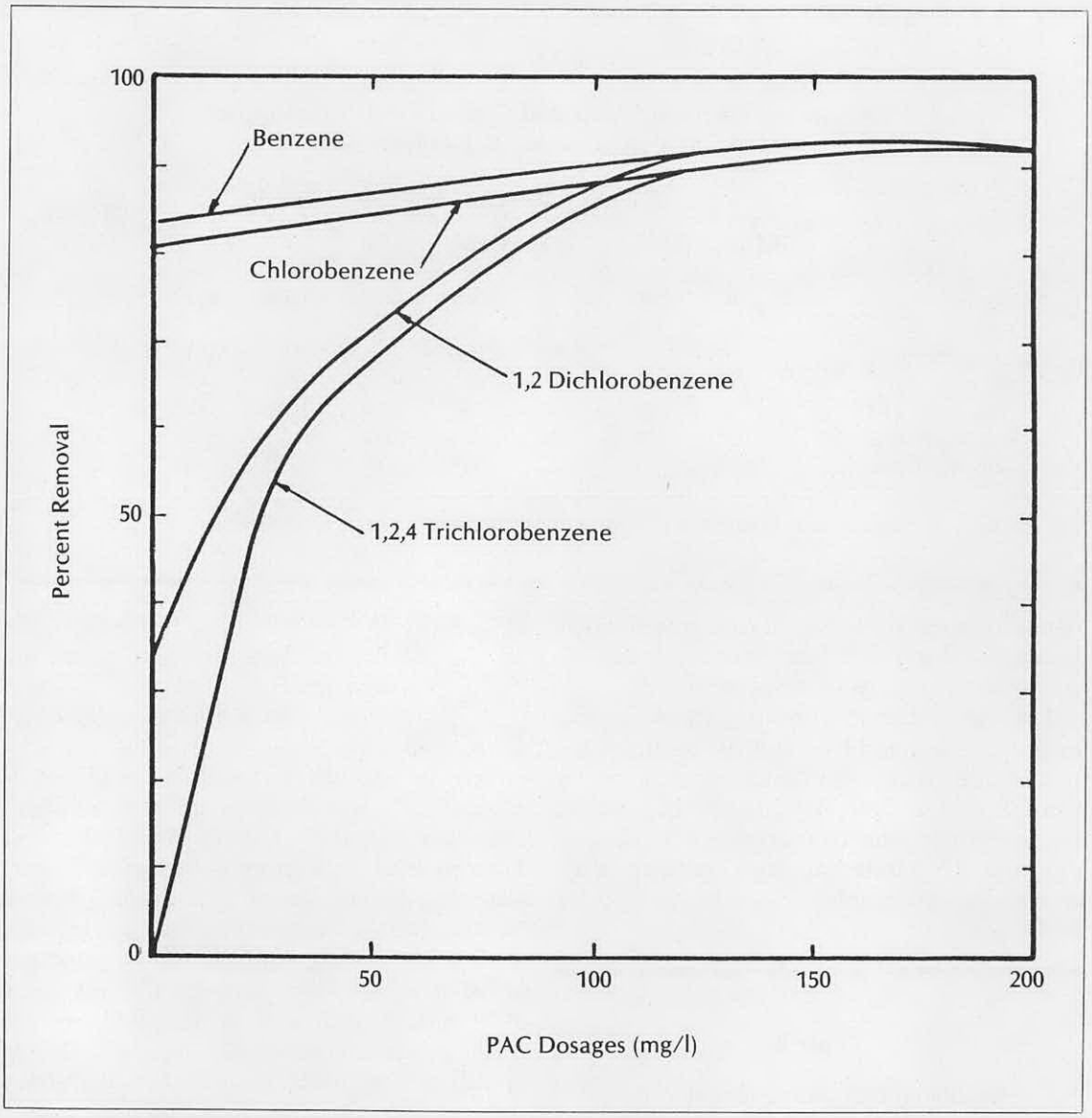

FIGURE 11. The effect of PAC dosage on chlorinated benzenes.

Heavy metals on carbon will markedly affect the adsorption efficiency so that the carbon may require an acid wash prior to reuse.

Chemical Oxidation

In some cases, toxicity reduction may be achieved by chemical oxidation. Common oxidants include permanganate, ozone and hydrogen peroxide. The chemical degradation of refractory organics may take several forms. Primary degradation, in which a structural change occurs in the parent compound, results in improved biodegradability. Acceptable degradation, in which degradation occurs to the extent that toxicity is reduced, and ultimate degradation, which results in complete destruction to CO_2, H_2O and other organics, are achievable. The use of chemical oxidants to provide the ultimate degradation of organic compounds may be extremely expensive, and requires the largest oxidant demand. However, a primary or acceptable degradation of compounds may be carried out with a much smaller oxidant

Table 7

Dosages of Powdered Activated Carbon for the Removal of Organic Carbon, Color & Heavy Metals

	Wastewater Composition (mg/l)							Bioassay
	BOD	TOC	TSS	Color	Cu	Cr	Ni	LC_{50}*
Influent	320	245	70	5,365	0.41	0.09	0.52	
Biotreatment	3	81	50	3,830	0.36	0.06	0.35	11
+50 mg/l PAC	4	68	41	2,900	0.30	0.05	0.31	25
+100 mg/l PAC	3	53	36	1,650	0.18	0.04	0.27	33
+250 mg/l PAC	2	29	34	323	0.07	0.02	0.24	>75
+500 mg/l PAC	2	17	40	125	0.04	<0.02	0.23	>87

* Percentage of wastewater in which 50 percent of aquatic organisms survive for 48 hours.

demand and, therefore, if integrated with biological treatment, may represent a more cost effective means of reducing toxicity.

The use of ozone to reduce the LC_{50} of a mixed plastics additive and dyestuff wastewater following biological treatment is summarized in Table 8. While the LC_{50} might be acceptable, the conversion of refractory organics to biodegradable organics may result in an unacceptable increase in effluent BOD.

Table 8

Results of Ozonation Treatment of Final Plant Effluent

Ozone Dosage (mg O_3/l)	48-Hour LC_{50} (%)*	TOC (mg/l)
0	5.6	152
100	49	96
300	60	108
600	87	88

* Mysid shrimp.

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