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Project Summary

Determination of Activated Sludge Biokinetic Constants for Chemical and Plastic Industrial Wastewaters

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The most widely used method of wastewater treatment is biological treatment. The use of kinetic models to describe the behavior of a biological wastewater treatment process has become widely accepted practice. The most often used kinetic models include those developed by Eckenfelder, McKinney, Lawrence and McCarty, and Gaudy. Eckenfelder (first model) and McKinney use first order kinetics for substrate removal; Lawrence and McCarty, and Gaudy use the empirical Monod kinetics for substrate removal; and Eckenfelder (second order) relates the substrate removal rate as a function of the remaining substrate concentration to the initial concentration. All of these models contain kinetic constants and the usefulness of each model is a function of the reliability of the kinetic constants. However, there has not been enough information available to establish reliable values for these kinetic constants for industrial wastewaters.

Cooperative Agreement CR 806843-01-02 has determined the biokinetic constants and fate for 24 toxic organic pollutants when present in a highly biodegradable wastewater. Biokinetic constants were also determined for eight groups of three chemicals. The biokinetic constants were determined based upon biochemical oxygen demand (BOD_5), total organic carbon (TOC), chemical oxygen demand (COD), and specific organic chemicals. The normal approach for determining biokinetic constants has been to plot the average values. This approach masks the actual scatter of the data and provides an average value or 50 percent probable value for the biokinetic constants to be used in design. This study has produced a methodology for analysis of the test results from biological activated sludge systems for determining the biological variability inherent in these types of systems.

This study also investigated the possibility of predicting the fate and effluent concentrations of the various priority pollutants. It was found that good predictions for the priority pollutants can be made. In general, it can be predicted that nitrogen compounds, phenols, oxygenated compounds, polynuclear aromatics, and phthalates will be removed by biological degradation. Aromatics will be removed by both biological degradation and stripping, except when the Henry's Law Constant is in the 10^{-5} atm·m^3/mole range, then that chemical will be removed by biological degradation only. Halogenated hydrocarbons present a special problem. Some are removed by stripping, whereas, others are removed by combined biodegradation and stripping. No parameter, such as Henry's Law Constant or partition coefficient, was found that would predict which removal mechanisms would persist. Therefore, biodegradability studies must be conducted.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a

separate report of the same title (see Project Report ordering information at back).

Introduction

Provisions in the Clean Water Act clearly require the U.S. Environmental Protection Agency to promulgate regulations to protect streams and publicly owned treatment works (POTW's) and to see to it that regulatory practices are in place to protect the vast investment of public funds. This law can affect nearly all industrial manufacturing plants now discharging or planning to discharge into POTW's or a stream. An important category for which effluent guidelines are needed is waste components from chemical and plastic industries. For this category, the problem is extremely difficult because of the thousands of different chemicals produced at plants across the nation. The product lines of these plants, and thus the nature of the wastes, are not fixed and change with market needs. This industrial activity consequently produces wastewaters of great and changing variety in the types of pollutants they contain. Furthermore, a significant number of the growing list of priority pollutants is appearing in various waste streams from the manufacturing of chemicals and plastics.

Because of the immensity and tremendous variety of products and process routes from production, it is logical that a computer programming procedure would be developed to handle the definition of wastewater composition as well as alternate processing routes for the treatment of wastewater. Computer programs have been developed that can combine waste load information on each product, select various product treatability routes, combine them, design and cost-out a plant's treatment system, and, finally, allocate the estimated treatment costs to the contributing product process route. However, before plant costs can be modeled, the treatment design models must be established. Design models are available but the biokinetic parameters for the chemical and plastic industries are not available. Therefore, the determination of the biokinetic parameters becomes of vital concern to the success of the cost model.

The current best practical technology (BPT) for treatment of chemical industrial and plastic manufacturing wastes usually involves activated sludge, since biological treatment is often found to be the most cost-effective in dealing with relatively low concentrations of the types of organic materials in such wastes.

Modern approaches for the design of activated sludge employ mathematical process models depicting the relationships among factors affecting the kinetics of wastewater purification. All design models require quantitative assessment of numerical values for biokinetic constants for the activated sludge in question. These values are, in general, a function of the type of carbon source comprising the carbonaceous biochemical oxygen demand. Various models are available for use in designing activated sludge processes.

The primary objective of this study was to determine the biokinetic constants needed in process modeling for predicting effluent quality and design configurations of activated sludge processes treating the waste streams from chemical and plastic manufacturing. Secondary objective was to refine the method of combining the biokinetic constants of components in a mix in order to determine the overall biokinetic constants of the mix and to establish the fate of the priority pollutants in the wastewater.

Conclusions

High treatment efficiencies (in terms of biochemical oxygen demand, BOD_5; chemical oxygen demand, COD; and total organic carbon, TOC) can be achieved by biological treatment of wastewaters containing toxic priority pollutants. This study has shown that priority pollutants can be accommodated in biological wastewater treatment processes. In addition, it was found that many of the priority pollutants were biodegraded to very low concentrations. In other cases, the priority pollutants were stripped to low levels without interfering with the biodegradation of the other organics.

The biokinetic constants of the wastewaters containing the priority pollutants are representative of a readily biodegradable .wastewater. The biokinetic constants are subject to variability, and a frequency analysis should be used in determining the biokinetic constants. A new design model provides an alternative method for accounting for the variability of the system. This new model provides designs comparable with the other design models without the variability of the biokinetic constants.

The fate and effluent concentrations of priority pollutants can be predicted with a high degree of accuracy. Parameters, such as Henry's Law Constant and Log partition coefficient, are key elements in predicting the fate of priority pollutants. Some priority pollutants are both biodegraded and stripped. These are more difficult to predict. Some means of estimating the biodegradability of priority pollutants is needed.

Recommendations

This study has investigated the biological treatment of 24 toxic organic chemicals. The study also included eight groups of three chemicals as a mixture. It is recommended that additional research be conducted using chemicals that would enhance sorption as a removal mechanism. Biodegradability and fate of additional chemicals could allow the creation of a structure/activity correlation for predicting the degradability and fate of toxic organics. Cost impacts for the correction of existing problems and the ability to anticipate adverse environmental impacts from the manufacture of chemicals would be made available through the use of such correlation.

It would also be of benefit to investigate the effects of factors other than the priority pollutants. Surface tension, sulfur compounds, inorganics, etc. may be much more detrimental to biological treatment than, so called, toxic organic chemicals.

It is recommended that the water pollution control field recognize that "toxic" organic chemicals can be treated in a biological wastewater treatment plant with no detrimental effects to the treatment process.

Experimental Methods

The general experimental plan specified bench-scale continuous flow activated sludge reactors be used to treat a synthetic wastewater containing selected chemicals normally present in chemical industry wastewaters. The bench-scale activated sludge system is shown in Figure 1. The system consisted of a stainless steel internal recycle reactor. The activated sludge reactor had a volume of 3.0 liters and the settling compartment had a volume of 3.23 liters. The reactor and settling compartment both had a stainless steel cover. The wastewater was pumped from a sealed feed tank to the reactor. The effluent from the settling unit flowed by gravity to a collection tank. The off-gas was pulled by a vacuum pump through a purge trap which contained 6 inches of Tenax and 4 inches of Silica Gel. The influent air and off-gas were measured with air-flow meters. The influent wastewater flow was regulated to provide a hydraulic

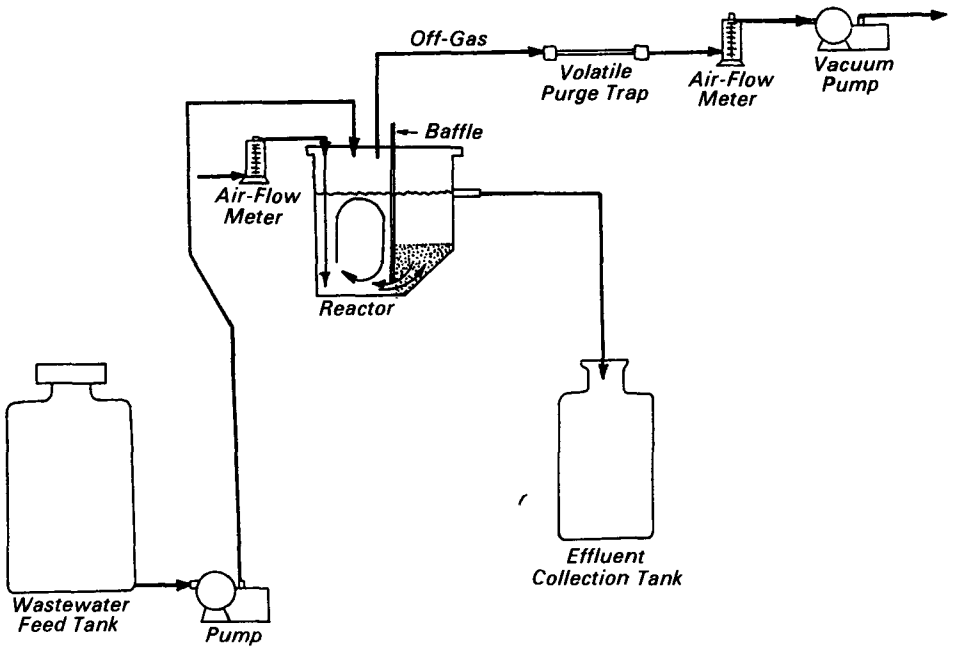

Figure 1. Bench-scale activated sludge pilot plants.

detention time of 8 hours in the activated sludge reactor. All parts of the experimental apparatus were constructed of materials to minimize contamination.

Two types of experimental studies were conducted with the previously described stainless steel reactors. A nonbiological system was operated to determine the strippability of the chemical compound. In this system, the reactor and settling compartment were filled with distilled water. The feed tank contained the wastewater. The wastewater was pumped to the reactor and the level of TOC and specific compound present in the reactor was observed as a function of time. When the wastewater had been completely diluted-in, influent, effluent, and off-gas samples were collected for specific compound analyses.

The second experimental system was a biological activated sludge system. Activated sludge for initial seeding was obtained from a local municipal activated sludge plant. Three individual systems were acclimated to each synthetic wastewater containing the pollutant to be evaluated. The activated sludge systems were operated at mean cell residence times (SRT) of 2, 4, and 6 days. After acclimation, influent, effluent, mixed liquor and off-gas samples were collected over a 60-day period for analyses. All three reactors were operated at a hydraulic detention time of 8 hours.

The synthetic wastewater referred to as the "base mix" contained ethylene glycol, ethyl alcohol, glucose, glutamic acid, acetic acid, phenol, ammonium sulfate, phosphoric acid, and salts. The specific chemical compound to be studied was added to this base mix. The specific compound and the corresponding initial BOD_5, TOC, and COD are shown in Table 1.

Results and Evaluation

Treatment efficiencies when measured in terms of BOD_5, TOC, and COD were very high for all systems in this study. The mean BOD_5 did not exceed 10.0 mg/l for any system. Generally, the mean BOD_5 was below 5.0 mg/l. This indicates that the "base mix" was highly biodegradable. This factor did create problems in obtaining data for determining biokinetic constants. The ideal situation is one in which the effluent BOD_5 varies over a wide range. However, with the wastewaters used in this study, even an SRT of 2 days produced a very low effluent BOD_5. Therefore, SRT values of 2, 4, and 6 days produced effluent BOD_5's with very little difference. The high treatment efficiencies also indicated that the priority pollutants used in this study had very little or no effect on the biological treatment of the wastewater. Even when the priority pollutant was not biodegraded, it did not affect the treatment efficiency.

It was found that the specific chemicals were removed by several mechanisms. These included stripping, biodegradation, and sorption. The percent removed by each mechanism is shown in Table 2.

The normal approach for analyzing and presenting biological system data is to plot the average values at each μ_n or SRT. This approach masks the actual scatter of the data and provides an average value or 50 percent probable value for the biokinetic constants to be used in design. Use of these biokinetic constants will provide a system capable of achieving the desired effluent quality only 50 percent of the time. The allowed statistical variability of the effluent discharge criteria must be evaluated to determine the appropriate biokinetic constants to use for design. Designing to meet a specific effluent quality 95 percent of the time will require a significantly larger reactor volume than that required for 50 percent of the time and will require use of the 95 percent probable biokinetic constants, as shown in the following example.

Using Eckenfelder's design model and the following design conditions the impacts of data variability for the acrylonitrile - containing wastewater can be demonstrated.

F = 10 MGD
S_i = 200 mg/l BOD_5
S_e = 5mg/l BOD_5
X = 1000 mg/l volatile suspended solids

The activated sludge reactor volumes are determined as follows:

$$V = \frac{F\,S_i(S_i - S_e)}{X\,K_e'\,S_e}$$

Using the 50 percent line or $K_e' = 31$, the required reactor volume will be:

$$V = \frac{10 \times 10^6 \times 200 \times (200 - 5)}{1000 \times 31 \times 5}$$

$$V = 2{,}516{,}000 \text{ gallons}$$

This reactor volume of 2,516,000 gallons should provide an effluent soluble BOD_5 (S_e) of 5 mg/l 50 percent of the time. Using the 95 percent line or $K_e' = 11$, the required reactor volume will be:

$$V = \frac{10 \times 10^6 \times 200 \times (200 - 5)}{1000 \times 11 \times 5}$$

$$V = 7{,}091{,}000 \text{ gallons}$$

Table 1. *Wastewater Concentrations*

Group	Chemical	Wastewater concentrations, mg/l BOD_5	TOC	COD
I	Tetrachloroethane	244	224	496
	Nitrobenzene	255	253	668
	2,4 dichlorophenol	298	234	572
	Combined	314	246	574
II	Acrylonitrile	192	189	483
	Acrolein	219	190	477
	1,2 dichloropropane	247	199	480
	Combined	279	197	565
III	Benzene	212	132	441
	Methylene chloride	287	170	480
	Ethyl acetate	259	145	450
	Combined	248	133	400
IV	1,2 dichlorobenzene	162	152	416
	1,2 dichloroethane	201	187	460
	Phenol	277	163	486
	Combined	268	176	454
V	2,4 dinitrophenol	245	203	551
	1,3 dichlorobenzene	178	136	379
	1,1,1 trichloroethane	244	183	530
	Combined	227	143	429
VI	Pentachlorophenol	265	153	470
	Trichloroethylene	295	179	530
	Bis (2-ethylhexyl) phthalate	271	159	528
	Combined	270	169	574
VII	Toluene	180	129	416
	Ethylbenzene	236	143	520
	Phenanthrene	270	166	510
	Combined	217	147	470
VIII	Chloroform	240	155	363
	Carbon tetrachloride	257	162	387
	Naphthalene	219	163	390
	Combined	317	170	409
Control	"Base Mix"	266	170	460

This reactor volume of 7,091,000 gallons is almost three times the previous reactor volume and should provide an effluent soluble BOD_5 (S_e) of 5 mg/l 95 percent of the time. Using the 75 percent line or K_e' = 19, the required reactor volume will be 4,105,000 gallons. If the reactor volume was designed at 2,516,000 gallons, the following probability of occurrence of S_e could be expected:

Probability Level %	S_e (mg/l)
50	5
75	8
95	14

The variability analysis approach presented indicated that K_d was a true biokinetic constant. μ_{max} was also treated as a true biokinetic constant, and since $\mu_{max} = K \cdot Y_t$ and Y_t was found to be a variable biokinetic coefficient, μ_{max} and K could not both be treated as constants. If $Y_t = \mu_{max}/K$ varies, μ_{max}, K, or both must vary. If both μ_{max} and K vary, the prediction of these coefficients becomes more difficult. The decision to make μ_{max} a biokinetic constant and K a variable biokinetic coefficient depending on the variable biokinetic coefficient Y_t simplifies the prediction of μ_{max} and K. The following reasoning was used in the selection of μ_{max} as a biokinetic constant.

K is simply the maximum U, and U was found to vary at constant μ_n or μ. At μ_{max}, U would be equal to K and could be expected to be variable. Also in a heterogeneous population such as in the activated sludge process treating a particular wastewater, several different kinds of bacteria will actually be in predominance; however, shifts in the ratios of these specific micro-organisms in predominance can change. As these population dynamic shifts occur Y_t changes, and thus, the mixed liquor solids (X) changes. The specific substrate utilization rate (U) could be expected to change as X changes; however, μ_{max} should not change. As μ_n or μ approaches μ_{max}, the microorganisms with lower μ_{max} values than the existing μ_n or μ will be washed out of the system. Therefore, the microoranisms with the greatest μ_{max} will predominate at the μ_{max} condition of the system. At this absolute μ_{max} which could be considered to be a constant, many microorganisms will have been washed out of the system, but several microorganisms will still remain. These few organisms may still provide a variable maximum U or K value but with lower variability since the few remaining organisms should provide less variability. All the other substrate utilization terms (K_s and K_e' or K_e) were also found to be variable in a manner similar to the true yield. Even at very constant controlled μ_n's or SRT's, all the substrate utilization characteristic descriptors were found to be variable. Based on this reasoning, Y_t, K_e', K_e, K_s and K are all considered to be variable biokinetic coefficients, while K_d and μ_{max} are considered to be biokinetic constants. The variability observed in these biokinetic coefficients during the treatability study can and should be considered during scale-up design to achieve specific effluent discharge criteria.

In addition to the variability analysis for the existing models, a new model has been presented. This model provides an approach in which there is no variability of the biokinetic constants. All variability can be handled as influent variability and normal procedures can be used. The new design model provides design values comparable with the other design models.

This study has also looked at the possibility of predicting the fate and effluent concentrations of the various priority pollutants. It has been found that good predictions for the priority pollutants can be made. In general, it can be predicted that nitrogen compounds, phenols, oxygenated compounds, polynuclear aromatics, and phthalates will be removed by biological degradation. Aromatics will be removed by both biological degradation and stripping, except when the Henry's Law Constant is in the 10^{-5} atm·m^3/mole range, then that chemical will be removed by biological degradation only. Halogenated hydrocarbons present a special problem. Some are removed by stripping, whereas, others are removed by combined biodegradation and stripping. No parameter, such as Henry's Law Constant or partition coefficient, was found that would predict which removal mechanisms would persist. It was also found that the type of reactor could be a factor. Therefore, biodegradability studies must be conducted. If the biodegradability is high, the chemical will be both stripped and biodegraded.

It was also found that biodegradability and stripping constants could be developed for each priority pollutant and used very successfully in predicting the effluent

Table 2. *Removal Mechanisms of Toxic Organics*

Compound	Percent Treatment Achieved					
	Single Units			Combined Units		
	Strip.*	Sorption	Biol.**	Strip.	Sorption	Biol.
Nitrogen Compounds						
Acrylonitrile			99.9			90.0
Phenols						
Phenol			99.9			99.9
2,4-DNP			99.3			99.2
2,4-DCP			95.2			77.1
PCP		0.58	97.3			97.8
Aromatics						
1,2-DCB	21.7		78.2			99.9
1,3-DCB	-	-	-	-	-	-
Nitrobenzene			97.8			33.8
Benzene	2.0		97.9	2.0		97.2
Toluene	5.1	0.02	94.9	6.2		93.7
Ethylbenzene	5.2	0.19	94.6	7.5		92.4
Halogenated Hydrocarbons						
Methylene Chloride	8.0		91.7	2.0		97.2
1,2-DCE	99.5	0.50		75.0		25.0
1,1,1-TCE	100.0			99.7	0.30	
1,1,2,2-TCE	93.5			96.2		
1,2-DCP	99.9			99.5		
TCE	65.1	0.83	33.8	69.7		30.1
Chloroform	19.0	1.19	78.7	15.0	1.36	82.8
Carbon Tetrachloride	33.0	1.38	64.9	28.0	0.03	71.7
Oxygenated Compounds						
Acrolein			99.9			90.0
Polynuclear Aromatics						
Phenanthrene			98.2			94.7
Naphthalene			98.6			78.6
Phthalates						
Bis(2-Ethylhexyl)			76.9			85.7
Other						
Ethyl Acetate	1.0		98.8			98.9

*Strip. = Stripping.
**Biol. = Biological.

concentrations for the pollutants when combined with other priority pollutants or when the influent concentrations varied.

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The complete report consists of two parts, entitled "Determination of Activated Sludge Biokinetic Constants for Chemical and Plastic Industrial Wastewaters," (Order No. PB 83-245 233; Cost: $14.50) and "Determination of Activated Sludge Biokinetic Constants for Chemical and Plastic Industrial Wastewaters (Appendix A—Raw Data)," (Order No. PB 83-245 241; Cost: $25.00, costs subject to change)
The above reports will be available only from:
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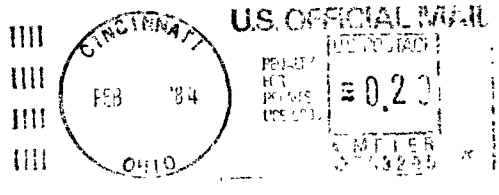

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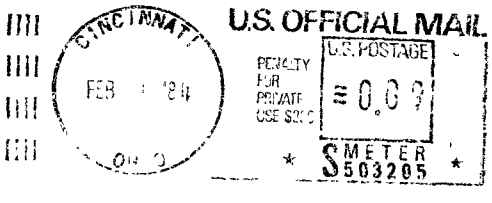

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