

# PHOTODECOMPOSITION OF POLLUTANTS IN WATER

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**T**HROUGH THEIR CONCERN for both chemical and physical processes chemical engineers are ideally suited for solving water-pollution problems. Yet they have not been involved wholeheartedly in the design and operation of water treatment plants, particularly those of the municipal type. Fortunately, this situation is changing. On the industrial side, chemical and petroleum refining plants are examining their effluent streams for effects on the environment. Chemical engineers are asked to develop processes for economically separating or chemically removing contaminants from waste streams. For example, water from phase separators employed in petrochemical processes may contain oxidation products (acids, phenols, ketones, aldehydes) in ppm quantities. While heretofore such streams might be discharged into rivers or lakes, pollution restraints now require that these contaminants be removed. This cleanup of industrial wastes is progressing at a fast rate, usually with chemical engineers already employed in the plant assigned to the technical problems involved. This provides a stimulating opportunity to apply well-established chemical engineering principles to a new area. If a chemical reactor is to be used, concentrations of reactants are strangely small and analytical procedures oftentimes lacking or of inadequate accuracy. This contrasts markedly with conventional reactors where producing a product in high concentration is the objective. Nevertheless, economic considerations probably are of critical importance in the removal process for it is a cost that presumably will be added to the prices of the products of the plant.

Chemical engineers have been slower to become involved in municipal water purification, perhaps because they were not already on hand as was the case in industrial pollution problems. However, current developments are making it progressively easier for engineers with chemical training to make contributions in municipal wastewater treatment. First, the federal govern-

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ment is providing resources for research and development that were unavailable from municipalities. Second, the advent of tertiary treatment processes has meant that the feed streams (effluent from the secondary process) are better identified and less subject to large transient fluctuations. This means that quantitative concepts familiar to chemical engineers can more likely be applied to design of tertiary treatment processes. Indeed, one of the more promising tertiary treatment processes<sup>1,2</sup> is adsorption of pollutants by flowing the water through a bed of activated carbon particles. The design problem is closely related to that for removing propane, butanes and heavier components from lean natural gases by adsorption; in both cases the key objective is to predict breakthrough curves for the stream leaving the carbon beds.

The remainder of this paper is concerned with a different type of treatment, a photochemical process for removing organic pollutants from water. The first results refer to a fully identified stream, water containing detergent, as a pollutant. Subsequently, the purification of secondary effluent from a municipal wastewater treatment plant is discussed. For the latter situation, photochemical treatment may be regarded as a tertiary process. As the technical results are presented, some emphasis will also be given to the similarities and differences between the development of a water-treatment process and a more conventional chemical engineering operation.

The specifications of a tertiary treatment, with respect to organic pollutants, is to reduce the total organic carbon content (TOC) to 3 to 4 mg/liter, or its approximate equivalent, 3 to 4 ppm. In the photochemical scheme this is accomplished by oxidation of the pollutants to carbon dioxide. The heart of the process is the reactor through which the water flows and is irradiated. An *a priori* development procedure involves the same steps as for a conventional reactor for producing a desirable chemical. In ideal form these steps are:

- 1) measure rates of reaction on laboratory-scale apparatus and correlate the results in the form of a rate ex-

pression which accounts for the effects of controllable variables

2) use the rate equation and chemical engineering principles to predict the performance of potentially attractive large-scale reactors—in short, to develop a model for the reactor

3) on a pilot-plant scale measure the performance of one or more reactor types and compare the results with the predictions by the model developed in step 2

4) design an economically optimized reactor using the kinetics of step 1 and the model devised and revised in steps 2 and 3.

By training and traditional experience the chemical engineer is well-suited for this scheme of work. However, application of these concepts to municipal wastewater introduces uncertainties. Knowledge of the composition of the organic pollutants is meager. Some of the most complete analyses of secondary effluent<sup>3</sup> show the presence of acids, esters, proteins, and sugars, but up to 74% of the total organic carbon is unidentifiable. Also, the low concentrations of contaminants may hinder measurement of reaction rates by customary chemical engineering methods. For example, TOC values cannot be measured with enough accuracy to establish rates by analyzing for organic carbon in the feed and effluent from a *differential* reactor.

#### PHOTODECOMPOSITION OF AQUEOUS DETERGENT SOLUTIONS

THE FIRST STEP IN the development scheme can be illustrated by reference to the photo-oxidation of a linear detergent molecule, dodecyl benzene sulfonate (DBS). For this special system, spectrographic analysis for DBS is sufficiently precise to permit evaluations of rates of disappearance of DBS from differential reactor data. Hence, such data for various levels of the pertinent variables, which are light intensity and DBS concentration, can be used to evaluate a rate equation. Based upon the following simplified mechanism,



the rate equation can be shown<sup>4</sup> to take the form

$$r_{\text{DBS}} = k_{\text{(DBS)}}^{1/2} (I_{\text{tot}})^{1/2} \sum_{\lambda} \left( \frac{F_{\lambda} T_{\lambda}}{F_{\text{tot}}} \right)^{1/2} \quad (4)$$

The chief assumptions in the derivation are that the stationary-state hypothesis is valid and that the kinetic constants are independent of wave length. For polychromatic light sources, the latter

#### Professor Smith emphasizes the similarities and differences between development of a water treatment process and a conventional chemical reactor.

supposition is a necessity in view of the present development of photochemistry.

While the  $1/2$ -power dependencies of the rate on pollutant concentration and light intensity, predicted by Equation (4), are verified by the experimental measurements, the level of the rate is very low; i.e., the quantum yield for the disappearance of DBS is much less than unity. In such situations, photochemists search for a photo-sensitizer. This substance readily absorbs radiation in appropriate wave length regions and becomes activated. The activated sensitizer molecule then supplies the energy required to initiate the steps in the main reaction. A typical example is the uranyl-ion sensitized photodecomposition of oxalic acid, which is widely used as a chemical actinometer.<sup>5</sup> To increase the rate of decomposition of DBS, ferric perchlorate was added in ppm amounts to the feed to the reactor. The rate is increased by about two orders of magnitude, but the mechanism of even the initial stage of decomposition of DBS becomes exceedingly complex. Oxygen concentration is a significant variable, and the rate equation must be based upon a generous amount of empiricism. The initial rate may be represented by the expression

$$(r_{\text{DBS}})_s = \frac{k_o(\text{DBS})}{[1 + K_{\text{DBS}}(\text{DBS})]^2} \frac{(O_2)(\text{Fe}^{+++})}{[1 + K_{O_2}(O_2)]^2} \left[ I_{\text{tot}} \sum_{\lambda} (\alpha_{\lambda})_s \frac{F_{\lambda} T_{\lambda}}{F_{\text{tot}}} \right]^{1.2} \quad (5)$$

An interesting aspect of Equation (5), one which is verified by the experimental data, is that the rate is a maximum at intermediate DBS and oxygen concentrations. Practically this means that it is not beneficial to use an oxygen concentration much greater than that corresponding to saturation with air. This behavior has been observed to varying degrees in all our work on photo-oxidation of organic substances, whether they be simple molecules like formic acid or the complex mixture in municipal wastewater (secondary effluents).

The initial rate, the value at zero conversion of DBS, is not enough to supply the kinetics information needed to design integral reactors for removal of a significant fraction of DBS. To accomplish this the rate must be known at all conversion levels. When the intermediates produced influence the rate of removal of the remaining reactant, the rate can be a sensitive function of con-

version, which is in addition to the effect of reactant concentration. In the case of DBS, the data suggest that intermediate compounds have a retarding effect on the rate.

Since intermediate products of DBS decomposition also may be undesirable pollutants, such as phenols, an overall measure of pollutant removal is the extent of carbon dioxide production. This can be measured accurately by stripping the dissolved gases from the product stream from the reactor and analyzing them chromatographically.

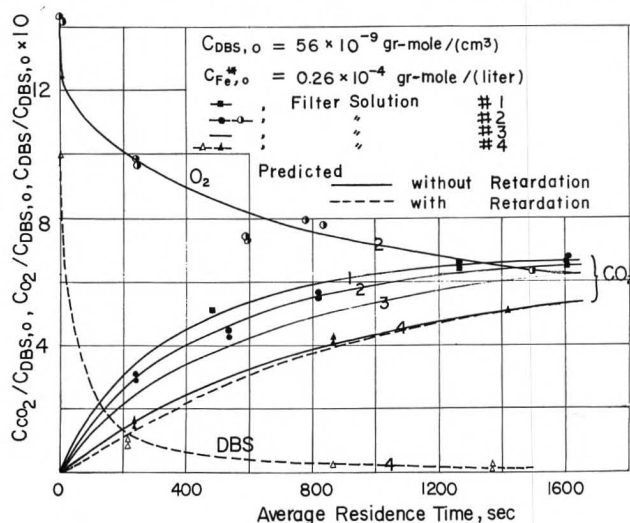


Figure 1. — Effect of Light Intensity on Product Composition

Figure 1 shows how the oxygen, carbon dioxide, and DBS concentrations change with average residence time in a tubular-flow photoreactor. The carbon dioxide curves are shown for several light intensities. The intensity was reduced by placing a filter solution between the radiation source and the reactor. The important quantity is the intensity of absorbed radiation. This is given by the summations of  $T$  (transmission of filter solution) multiplied by the absorptivity,  $\alpha$ , of the DBS solution and the energy distribution of the source,  $F/F_{tot}$ . Results for the four filter solutions are as follows:

Table 1. Light Absorption vs. Filter Solution

Summation term in Eq. 5

Filter Solution	liter/g mole-cm
1	1704.
2	1316.
3	973.
4	608.

Figure 1 shows several interesting results. While the carbon dioxide produced decreases with

reduced light intensity, all the data point to the same maximum of 7 molecules of carbon dioxide produced per molecule of DBS. Since the conversion of DBS to some product is nearly complete after 1400 seconds, this result means that a maximum of seven of the total of eighteen carbon atoms are converted to carbon dioxide. Ultra-violet and infra-red analysis of the product streams indicated that the remaining fragments of the DBS molecule were low molecular-weight, oxygenated compounds, including acids and aldehydes. It is significant to note that the photochemical treatment destroys the refractory aromatic ring structure.

The solid lines in Figure 1 are the results of the second step in the *a priori* development procedure listed earlier. Using rate equations for carbon dioxide formation, and DBS disappearance [the latter is Equation (5)], and a model<sup>4</sup> for the tubular reactor, concentrations were predicted as a function of average residence time. The model accounted for intensity distribution and for laminar flow in the reactor. The effect of conversion of DBS in retarding the rate is only significant for the lowest light intensity, filter solution 4. At higher light intensities the rate of disappearance of DBS was complete in less than 100 seconds. This means that essentially all of the carbon dioxide was produced in a reaction environment in which all of the DBS had disappeared into intermediate products. The solid and dotted curves for filter solution 4 indicate the relatively small effect of retardation on carbon production. Only the retarded curve is given for DBS concentration for clarity. The result when rate retardation is not accounted for is a curve much above the dotted one. The agreement between data points and predicted curves is a measure of the success of the reactor model.

With this background on removal of a pure-component pollutant, we proceed to the more complex problem of treating secondary effluent.

## PHOTOCHEMICAL TREATMENT OF SECONDARY EFFLUENT

**E**FFLUENTS FROM the biological treatment plants for municipal wastewater are likely to contain organic pollutants in several stages of oxidation. Pollutant composition of secondary effluent from a Sacramento County (California) treatment plant, described in terms of properties commonly used in water treatment technology, is given in Table 2. Chemical compositions are not

**Table 2. Typical Analysis of Reactor Feed\***  
(after filtration)

Chemical oxygen demand (COD), mg/liter	25 -40
Ammonia, mg/liter	20 -23
Total organic carbon (TOC), mg/liter	9 -14
Turbidity, Jackson Turbidity Units, JTU	0.8- 1.5
pH	7.5- 8.1
Nitrates (as N), mg/liter	0.06
Nitrites (as N), mg/liter	1.20
Organic nitrogen (as N), mg/liter	0.80
Filtrable O-phosphate (as P), mg/liter	10
Total phosphates, dissolved and suspended (as P), mg/liter	19

\*Secondary effluent from Northeast Water Treatment Plant of Sacramento County, California.

well known. Only part of the pollutants have been identified and then only according to general classifications rather than by individual chemical species. One of the more complete, published analyses is given in Table 3. The chemical engineer studying the kinetics of purification of secondary effluent has the problem of measuring and correlating the rate of disappearance of an unknown mixture present in ppm amounts. In our work the quantitative rate studies have been based upon the production of carbon dioxide, while the level of pollutant concentration is characterized by the total organic carbon content. The TOC can be measured rapidly, if not particularly accurately, down to 1-2 ppm by combusting the pollutants with oxygen and measuring the carbon dioxide produced by UV absorption. New instruments now available are sensitive to 0.1 ppm, but reproductibility and accuracy are several times that figure.

In a manner similar to that described for DBS solutions, a rate equation was first developed<sup>6</sup> for the initial rate of decomposition of pollutants. Subsequently, measurements were made when partially converted pollutants were fed to the reactor. In contrast to the results for DBS, the rate was found to be independent of the conversion of pollutants. Perhaps this is due to the partially oxidized state of the pollutants in secondary effluent. Finally, a model for the photoreactor was proposed<sup>6</sup> and used, along with the rate equation, to calculate integral reactor performance. These predicted results were compared with experimental data obtained at large conversions of pollutants, as measured by TOC.

The rate equation which best fit the data is

$$\Omega_{\text{TOC}} = \frac{2K}{R} I_{\text{tot}} \frac{(O_2)}{65 \times 10^{-9} + (O_2)} \sum_{\lambda} \frac{F_{\lambda} T_{\lambda}}{F_{\text{tot}}} [1 - e^{-2\mu_{\lambda} R}] \quad (6)$$

**Table 3. Composition of Tricking Filter Effluent**  
(Stevenage, England)<sup>3</sup>

Constituent	Analysis <sup>a</sup>	
	Soluble	Settled
Fat, acids	0.00	0.04
esters	0.00	0.02
Proteins	0.25	0.99
Amino acids	0.06	0.06
Carbohydrates	0.24	0.57
Soluble acids	1.65	1.69
Amides	not determined	
Anionic, surface-active agents	1.40	1.41
Creatinine	not determined	
Amino sugars	0.00	0.07
Muramic acids	0.00	0.01
	<b>Total</b>	<b>3.6</b>
Total carbon	14.0 <sup>b</sup>	16.5
Fraction identified	0.26	0.29
Fraction unidentified	0.74	0.71

<sup>a</sup> expressed as mg/liter of carbon.

<sup>b</sup> unidentified soluble organics were assumed to be largely anionic, high molecular weight substances.

In this semi-empirical equation the oxygen concentration must be expressed in g moles/cm<sup>3</sup>. The quantum yield was again low, corresponding to  $K = 1.4 \times 10^{-3}$  g moles/Einstein. Some of the high-conversion results are shown in Table 4. Run 1C met the specifications of a tertiary treatment process in that the TOC was reduced to 4 ppm.

### ECONOMIC DESIGN

WHILE THE DATA in Table 4 show that the technical requirements for a tertiary treatment can be achieved with a photochemical process, the optimum design from an economic standpoint has not been considered. This fourth step in process development is particularly important in photochemical systems because of the electrical energy requirement. Energy costs are likely to be a dominant factor in a tertiary photochemical process. The key factor is the efficiency,  $\eta$ , of energy utilization. The data reported here were obtained in a system where the lamp and reactor were of tubular shape and placed at the foci of an elliptical reflector. For this laboratory-scale equipment it is estimated that less than 1% of the energy input to the lamp was absorbed, in the wave length regions effective for reaction, by the pollutants. Since reaction rates are proportional to absorbed radiation [Equation (6)], a ten-fold increase in efficiency would reduce costs of treatment a comparable amount. It is instructive to divide the overall efficiency into components. First, only a fraction of the energy input to the lamp appears as radiation in wave lengths

**Table 4. Integral reactor (high conversion) data**

Run #	TOC*		(O <sub>2</sub> ) in Feed*	Δ(TOC)*	Δ(O <sub>2</sub> )*	Δ(CO <sub>2</sub> )*	Residence Time V/Q, sec	Conversions, %	
	Initial	Final						Exp.	Predicted
3F.C.	780	584	1280	196	180	220	410	25.2	24.6
1C	850 <sup>a</sup>	333 <sup>b</sup>	1400	517	500	514	1560	60.9	60.8
2C	890	740	1200	150	180	167	376	16.9	18.3
4C	890	533	1380	357	300	370	1085	42.3	40.2

\*All concentrations in g moles/cm<sup>3</sup> x10<sup>9</sup>.; <sup>a</sup> 10.2 ppm; <sup>b</sup> 4.0 ppm.

suitable for photochemical reaction (usually 2000-4000 Å). This efficiency  $\eta_L$  is solely dependent upon the characteristics of the lamp. Second, only a part of the radiation emanating from the lamp reaches the reactor wall. This fraction  $\eta_{LRR}$  depends upon the geometry of the lamp-reflector-reactor system and is within the control of the designer. For example, with a tubular lamp surrounded by an annular reactor, all of the radiation leaving the reactor would impinge on the reactor wall. Finally, only a fraction of the energy striking the wall is absorbed by the solution flowing through the reactor. This efficiency  $\eta_R$  depends upon the radiation path length (reactor geometry) and the absorptivity  $\alpha_\lambda$ , or attenuation factor  $\mu_\lambda$ , of the solution. The overall efficiency is given by

$$\eta = \eta_L (\eta_{LRR}) (\eta_R) \quad (7)$$

For our laboratory reactors  $\eta_{LRR}$  and  $\eta_R$  have varied from 0.08 to 0.13 and from 0.15 to 0.25, respectively. It appears that studies on maximizing the product of these two efficiencies could lead to a significant increase in  $\eta$  and reduce the energy costs proportionally. Since rate is dependent upon the intensity of the radiation as well as its magnitude, a complicating factor is that the geometry of the lamp-reflector-reactor system affects the process costs in other ways than through the efficiency of utilization of energy.

Another possibility for improving the economics of a photochemical tertiary process is through the use of a sensitizer. Since chlorine absorbs radiation in the proper wave length range, and since this substance would probably be added to treated water for its germicidal action anyway, chlorine is a likely candidate. The effect in this case would be on the kinetics of the reactions, increasing the quantum yield  $K$  in the rate equation. However, the chemistry of the chlorine-pollutant-water mixture is complex, particularly when ir-

radiated. Hence, the form of the rate equation would probably be different than Equation (6).

**I**N SUMMARY, the attractiveness of a photochemical process for tertiary treatment will depend to a significant extent on how much the energy costs can be reduced by improved utilization of the energy input through design of the lamp-reflector-reactor system, and increased rate of pollutant removal by photosensitizers. Both of these factors are challenging chemical engineering questions that need additional attention.

#### ACKNOWLEDGMENT

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#### NOMENCLATURE

(DBS), (O <sub>2</sub> ), etc	concentrations, g moles/cm <sup>3</sup>
Δ(TOC), Δ(O <sub>2</sub> ), etc.	difference in concentration between feed and exit streams from photoreactor, g moles/cm <sup>3</sup>
F <sub>λ</sub> , F <sub>tot</sub>	energy output of lamp, at wave length λ and total, Einsteins/sec
h	Planck's constant
I <sub>tot</sub>	total light intensity at wall of reactor without filter solutions, Einstein/sec-cm <sup>2</sup>
k, k <sub>o</sub> , K <sub>DBS</sub> , K <sub>O</sub>	rate constants defined by Equations (4) and (5)
K	quantum yield, Einsteins/g mole
Q	volumetric flow rate in reactor, cm <sup>3</sup> /sec
R	reactor radius, cm
T <sub>λ</sub>	fraction of light of wave length λ transmitted through filter solutions
V	volume of irradiated reactor, cm <sup>3</sup>
α <sub>λ</sub>	absorptivity of pollutant, cm <sup>2</sup> /g mole
(α <sub>λ</sub> ) <sub>s</sub>	absorptivity of sensitizer, cm <sup>2</sup> /g mole

(Continued on page 36)

At Florida a time sharing and remote job entry terminal system (Figure 1) is implemented on the University Computer. Our department has two IBM 2741 selectric typewriter terminals associated with this system. Our normal method of entering the subroutines just discussed would be to type them directly into the computer using a 2741 terminal. A phone call to the center is needed to reserve top priority space for our programs and then via the typewriter terminal, we have the computer compile our user programs and add them to our standard 1070 software. They are then linked and loaded into core and execution commences.

At the 1070 terminal and interface equipment, we then start the hardware poller whenever we are ready to begin and our terminal is now a voltmeter. The poller can be turned off anytime we wish to put the software program into hold.

### DEMAND FUNCTIONS

Several standard programs exist whose execution can be requested via the six decimal digit input device. All input is decoded in a standard form. The first two digits indicate the program ordinal and the last four are data to be passed to the program when it is called. The response routines are called demand functions, and Table 2 lists some of those provided.

TABLE 2—TYPICAL DEMAND FUNCTIONS

1. STOP PROGRAM
2. ERROR RESPONSE
  - A. STOP B. CONTINUE C. RESTART
3. CHANGE VALUE OF CORE WORD
4. DISPLAY VALUE OF CORE WORD
  - A. ONCE B. PERIODICALLY UPDATE
5. PUT ROUTINE ON DELAY STACK
6. TAKE ROUTINE OFF DELAY STACK

### DISCUSSION

Table 3 gives a brief summary of the system costs and typical core requirements. These costs are quite small. The operating costs will increase when we are charged for core space used, a charge not now implemented. The core required would be equivalent to a 50,000 word minicomputer with 16 bit words, certainly a large minicomputer. It is however only 10% of the University Computer's core. We can reduce the requirements substantially by removing portions of the software not needed for a particular control program.

TABLE 3—SUMMARY OF COST DATA

EQUIPMENT FROM IBM	
DATA SET	
CONTROL UNIT	\$17,000
13 BIT A/D CONVERTER	
DIGITAL PULSE CONVERTER	
100 MULTIPLEXER POINTS	
DIGITAL DISPLAY	
NONSTANDARD EQUIPMENT	
CABINETS	
RELAYS, SWITCHES, LIGHTS	\$ 4,000
POWER SUPPLIES	
TRANSDUCERS	
OPERATING STATISTICS	
CONTROLLING A DISTILLATION	\$3-5/HR
COLUMN BY ADJUSTING 3 SETPOINT	
CONTROLLERS	
CORE SPACE	100,000 8-BIT BYTES

A detailed description of the system is available from the department in the form of a pair of manuals on the system [1,2].

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2. Eschenbacher, R. C., Hardware Manual for GIPSI, Department of Chemical Engineering, University of Florida (1969).

### SMITH: Photodecomposition

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$\nu$	frequency of radiation, sec <sup>-1</sup>
$\lambda$	wave length
$\mu_{\lambda}$	attenuation coefficient of pollutants in water, cm <sup>-1</sup>
$\Omega$	rate of reaction, g moles/cm <sup>3</sup> -sec
$\eta$	overall efficiency of utilization of energy input to lamp

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