



# Project Summary

## Treatment Technology for Pesticide Manufacturing Effluents: Bentazon

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Laboratory studies were conducted on the treatability of wastewater generated from the manufacture of bentazon. The wastewater was characterized for pesticide content by high performance liquid chromatography (HPLC). Toxicity determinations on bentazon and its major treatment product (dichlorobentazon) were conducted with *Daphnia magna*. Bentazon was not toxic to the daphnids at concentration of up to 50 ppm. The major known by-product of chlorination of bentazon is dichlorobentazon, which is toxic to daphnids at 50 ppm.

Emphasis was placed on the removal of bentazon from wastewater by treatment with sodium hypochlorite. The effects of variations in the pH, amount of hypochlorite, temperature, and mode of hypochlorite addition were studied. The temperature and mode of addition had little effect on the removal of bentazon. It was found that bentazon is most efficiently removed by hypochlorite when the pH is 2 or below and when a 245- to 370-fold excess of hypochlorite is used.

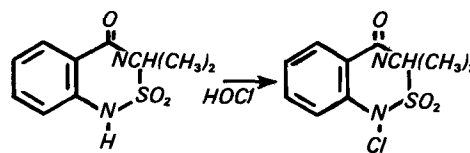
Based on assumed rates of process wastewater production, the total cost of the treatment was estimated.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, 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

This report describes a study of the treatability of wastewater resulting from the manufacture of bentazon, a postemergence herbicide. The objective of this project was to conduct a bench-scale treatability study of bentazon pesticide manufacturing wastewater using treatment with sodium hypochlorite. Pesticide removal was the principal criterion for evaluating the usefulness of each control treatment. Wastewater treatment operating conditions were chosen to simulate actual commercial units in such parameters as contact time and temperature, so that meaningful treatment cost estimates for manufacturing processes could be generated.

Under EPA's proposed Effluent Guidelines for Pesticides, bentazon may be regulated as part of Category 2 pesticides. Based on production, the allowable discharge per day is 4 lb\*, or a concentration of 2.5 ppm based on a wastewater flow of 135 gpm\* at the specific manufacturing plant tested. Preliminary studies conducted by the manufacturer have shown that oxidation with sodium hypochlorite is effective in destroying bentazon in the wastewater. Hypochlorite reacts with bentazon as shown below.



(\* )lb × 0.454 = kg; gal. × 3.785 = L.

Excess hypochlorite is destroyed with sodium bisulfite before the wastestream reaches the biotreatment facility.

The large excess of hypochlorite increases the salt content of the wastewater, and free chlorine and bisulfite can also be pollutants. Other organic materials may react with hypochlorite to form products which may be harmful.

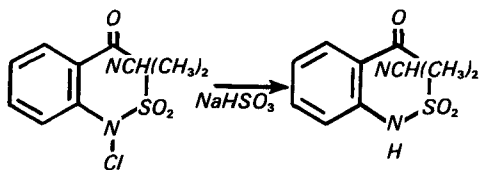
While the goal of the treatment is to reduce bentazon to the 4 lb/day level, consideration must be given to the problems of the generation of additional pollutants and requirements for compatibility with a downstream biotreatment plant.

### Treatability Studies

Samples of bentazon manufacturing wastewater were obtained from the manufacturer. Figure 1 is a diagram of the plant treatment system, showing the sampling points. Evaluation was carried out on the sample collected after the carbon unit (Sampling Point 2 in Figure 1).

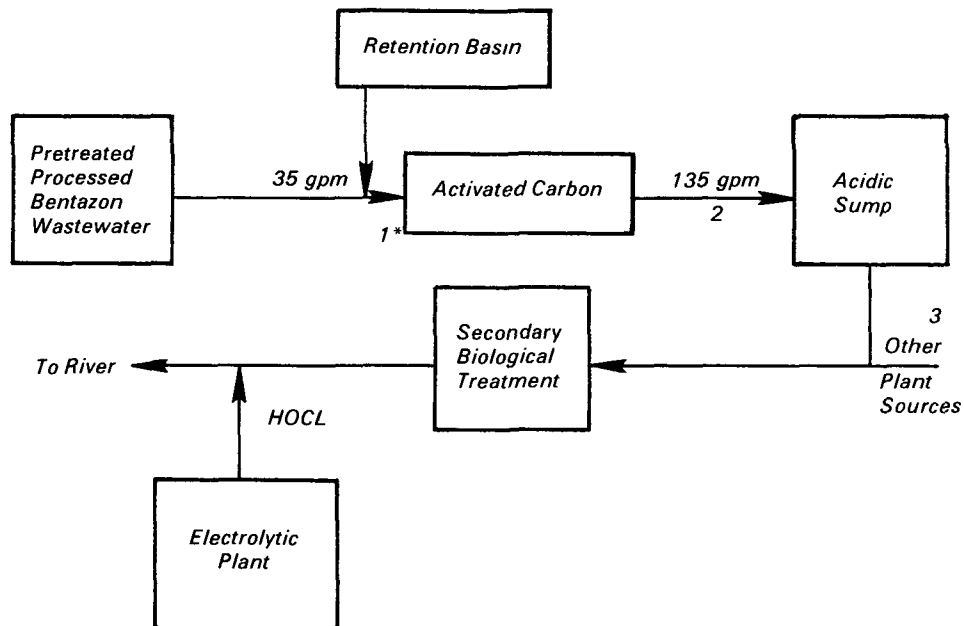
Preliminary treatability studies by the manufacturer have shown that a 40:1 molar excess of hypochlorite over bentazon was necessary at 24°C and pH 6.0 to achieve a 95% reduction in bentazon level. This large HOCl excess was required at both acid and alkaline pH. Since hypochlorite is not selective in its action, wastewater containing other amine bodies, by consuming additional reagent, will require an even larger hypochlorite excess (90:1). Note that the desired conversion was achieved at the expense of increasing the salt content of the wastewater.

Excess hypochlorite must be destroyed before the wastestream reaches the water biotreatment facility. Sodium bisulfite has been used successfully in eliminating free chlorine, although it has been shown that this reagent also regenerates bentazon from its N-chloro analog.



A technique must be developed for destroying free chlorine which will not regenerate bentazon because it interferes with the operation of the biosystem.

Free chlorine and excess bisulfite can be pollutants. Other organic materials react with hypochlorite to form products which may also be harmful. This is particularly true for amines which can form



(\*) One of three sampling points.

Figure 1. Wastewater treatment system.

potentially toxic and explosive N-chloro compounds.

The bentazon waste stream entering the activated carbon unit is expected to have the following characteristics: pH, 1.0-2.0; temperature, ambient; and bentazon content, 50-300 ppm.

The carbon columns step in the current treatment process removes 50-75% of the bentazon and about 95% of the monochlorobenzene from the wastewater. Therefore, the bentazon content of the wastewater used in this study should be between 38 and 150 ppm, based on the manufacturer's information.

### Treatment of Standard Bentazon Solutions with Aqueous Sodium Hypochlorite

A standard solution containing 55.2 ppm (within the 38-150 ppm range expected) bentazon was made up in 1 L of water. This solution, in 100 mL portions, was used for preliminary experiments. Initially, a 200-fold excess of hypochlorite (2 moles hypochlorite to 1 mole bentazon) was utilized, timed aliquots of 10 mL were "quenched" in sodium bisulfite (bisulfite) to neutralize excess hypochlorite, and the bentazon was determined by HPLC. Five separate experiments were performed:

- (1) Reagent blank (100 mL water). Treated directly with hypochlorite.

- (2) Dilution blank. Bentazon solution with water in place of hypochlorite and bisulfite.
- (3) Neutral pH. Bentazon solution treated directly with hypochlorite.
- (4) Acidic pH. Bentazon solution adjusted to pH 4 with HCl before addition of hypochlorite.
- (5) Basic pH. Bentazon solution adjusted to pH 10 with NaOH before addition of hypochlorite.

In all cases, the bentazon disappeared within 10 min, but was "regenerated" after a period of time, slowly disappearing again from solution. This suggests that a rapid reversible reaction occurs which slowly equilibrates, followed by the less rapid formation of the final treatment product. The disappearance of bentazon was more rapid from neutral and acid solutions.

In a subsequent experiment, a 100 mL portion of standard bentazon solution was treated with a 333-fold excess of hypochlorite, aliquots were removed over time and analyzed. No bentazon was found in any of the aliquots (from just after hypochlorite addition up to 1 hr later).

### Treatment of Bentazon-Containing Wastewater

Aliquots of wastewater taken after the carbon unit were treated as described below.

A. Hypochlorite: 333-fold excess

Exp. No.	pH
BG-10	1
BG-19	2
BG-16	3
BG-17	4
BG-3	6

B. pH  $\approx$  1.5

Temp.	Exp. No.	Excess Hypochlorite/Bentazon
20-28°C	BG-2,10	333:1
3-7°C	BG-20	167:1
	BG-11	83:1
	BG-12	17:1
	BG-21	
	BG-13	

**333-Fold Excess Hypochlorite at pH 1 and 6**

Timed aliquots were taken after the addition of hypochlorite to 100 mL portions of the wastewater and quenched in a slight excess of bisulfite. A second aliquot was taken immediately and quenched in 3 fold amount of bisulfite to test the effect of excess bisulfite on bentazon concentration.

With the use of a 333-fold excess of hypochlorite at pH 1, the bentazon disappeared almost completely within 10 min. The amount of bisulfite excess made little difference in the amount of bentazon detected. At pH 6, the bentazon disappeared more slowly: even after 60 min, more than 55% remained. Some of the samples were not analyzed on the day the experiment was run but at a later date. The values obtained by HPLC were higher by about 25% for these samples. However, in a later re-analysis of the pH 1.5 samples, all remained at zero or low values. It is possible that the large amount of flocculent material in the quenched aliquots may interfere in the analysis, or that some bentazon is regenerated upon standing under certain conditions.

**333-Fold Hypochlorite Excess at pH 2, 3, and 4**

Timed aliquots were taken from each of three 100-mL portions of wastewater adjusted to pH 2, 3, and 4 with 10N NaOH and then reacted with a 333-fold excess of hypochlorite. All aliquots were analyzed by HPLC after quenching with bisulfite. The results are shown in Figure 2. The reaction at pH 2 was nearly identical to that at pH 1.5; i.e., bentazon disappeared immediately and was only observed in very small amounts or not at all up to 3

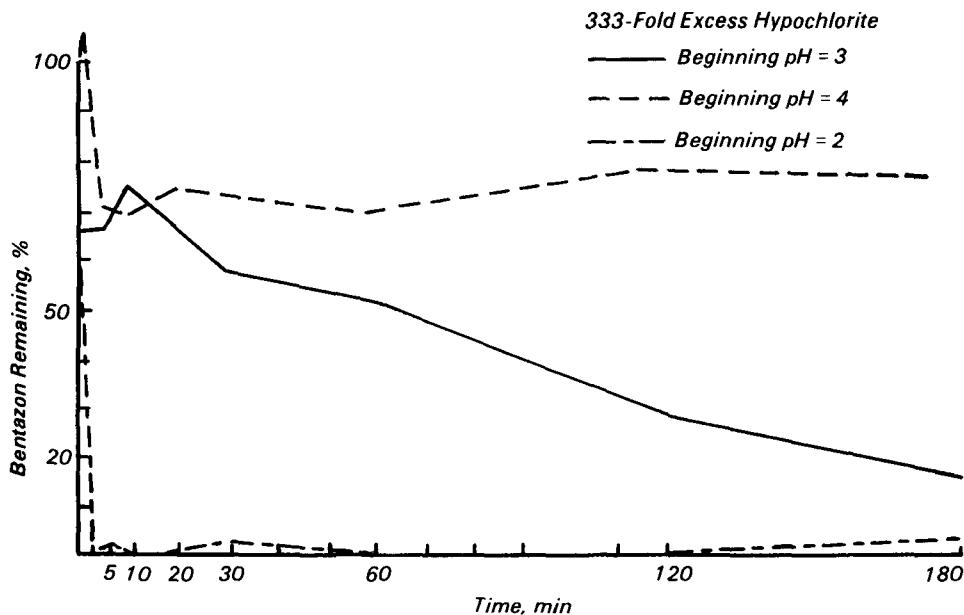


Figure 2. Bentazon-containing wastewater treated with hypochlorite at pH 2, pH 3, and pH 4.

hr. The reaction at pH 4 was more similar to the previous reaction carried out at pH 6: some bentazon disappeared early in the reaction (10 min), but about 70% remained even after 3 hr. The pH 3 reaction showed the bentazon concentration dropping off rapidly at first and then decreasing at a much slower rate to a concentration of about 20% after 3 hr. Another aliquot was taken at 5 hr: the bentazon concentration was still about 19%.

There was a distinct change in the reaction between pH 2 and pH 3. The mechanisms involved in this treatment are not known. The reaction mixture has been titrated at the end of 3 hr and still contained excess hypochlorite. The physical appearance and amount of insoluble material varied with time and conditions.

**Variations of Temperature and Hypochlorite Added to Wastewater**

The effects of variations in temperature and hypochlorite addition were evaluated in two experiments: in the first, 100 mL aliquots were treated with a 333-fold excess of hypochlorite at room temperature and near 0°C; and in the other, 100 mL aliquots were treated with a 83-fold excess of hypochlorite at room temperature and near 0°C. When a 333-fold excess of hypochlorite was added, the bentazon disappeared rapidly and was essentially gone in 5 to 10 min. When this reaction was

carried out at near zero (3-7°C), the reaction proceeded at a slower rate but resulted in the nearly complete removal of bentazon. This indicates that bentazon can be removed at temperatures as low as freezing.

The low temperature reaction using an 83-fold excess of hypochlorite proceeded much more slowly than the ambient reaction. In fact, at all points studied, more bentazon was detected than was originally present. In trials using a 167-, 83-, and 17-fold hypochlorite excess at room temperature, bentazon levels remaining in the reaction mixture were measured at levels 5 to 10 times greater than was originally present. The early appearance of what appears to be additional bentazon in experiments using less than 333:1 addition of hypochlorite is striking. There is no explanation for this phenomenon.

**Stepwise Addition of Hypochlorite to Bentazon-Containing Wastewater**

Several additional experiments were performed to determine more about the nature of the hypochlorite/bentazon reaction. First, half the amount necessary for complete reaction was added (167-fold excess), and the reaction followed for 30 min. Another 167-fold hypochlorite excess was added, and the reaction followed for another 30 min. The same behavior was

observed as before—the 167-fold excess of hypochlorite resulted in an apparent 300% increase in bentazon by HPLC. However, the second 167-fold addition caused the reaction to behave as if a 333-fold excess had been added originally; that is, the bentazon disappeared almost completely within a few minutes.

In another experiment, hypochlorite was added to the bentazon-containing wastewater in increments every 5 minutes. Aliquots were taken before each new hypochlorite addition. The bentazon increased as expected with each addition until a critical point was reached, then rapidly fell off. This point was between 245 and 370 equivalents of hypochlorite. Interestingly, the characteristic purple color of this experiment did not disappear until after the bentazon was gone.

### Fine-Tuning of Hypochlorite Addition to Bentazon-Containing Wastewater

To determine more precisely the amount of hypochlorite needed to remove bentazon from the wastewater in a reasonable amount of time (10-30 min), several concentrations were investigated between 167- and 333-fold excess hypochlorite: 200-fold excess hypochlorite to correspond to 200-fold excess studied on standard bentazon and 266-fold excess (20% less than 333-fold excess). An experiment was also carried out using a 500-fold excess (50% greater than 333-fold excess). The experiments were carried out just as previous experiments: timed aliquots were taken, quenched with bisulfite, and analyzed by HPLC. The results of these experiments are shown in Figure 3.

It can be seen that neither the 200- nor 266-fold excess hypochlorite was as effective as the 333-fold excess in removing bentazon from wastewater. The 500-fold excess was, however, quite effective in removing 98% of the bentazon in a 5 min reaction time.

The timed aliquots were analyzed by HPLC and also qualitatively by Thin Layer Chromatography (TLC). At the end of the experiment, a portion of the reaction mixture was extracted with methylene chloride and the extract analyzed by TLC. Dichlorobentazon was seen in all three reaction mixtures, the largest amount in the experiment using 266-fold excess hypochlorite. This reaction also contained the largest variety of compounds seen by TLC.

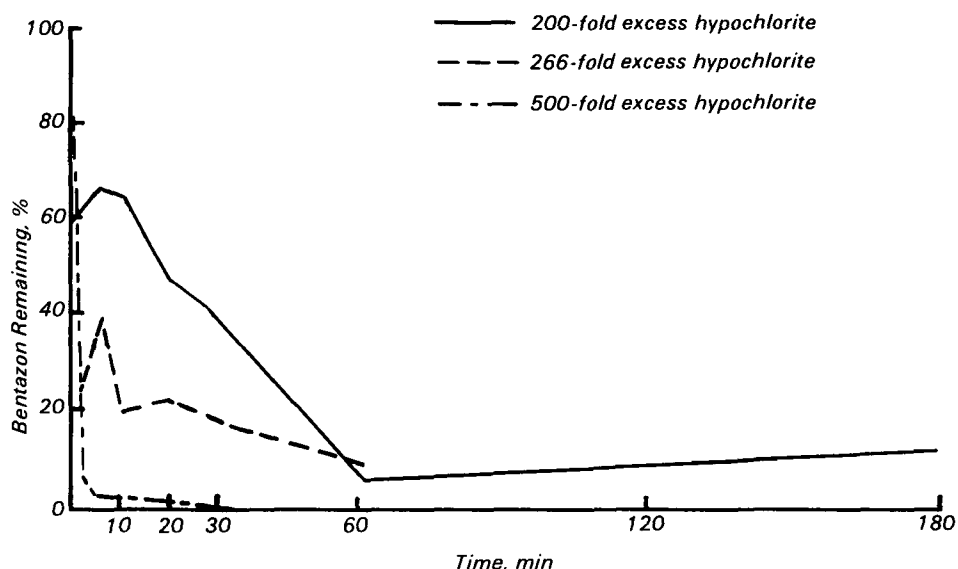


Figure 3. Addition of different hypochlorite excesses to bentazon-containing wastewater.

### Scaled-Up Treatment of Bentazon-Containing Wastewater with Hypochlorite

Using the most favorable conditions from previous experiments (low pH with addition of 333-fold excess hypochlorite), the reaction was scaled up to 1 L of wastewater. An aliquot was taken before addition of hypochlorite, immediately after hypochlorite addition, and again after 10 and 30 min. The entire reaction mixture was then quenched with bisulfite. A final aliquot was taken 10 min after bisulfite addition. The results are in Table 1. The removal of bentazon from solution was essentially the same as the corresponding 100 mL reaction.

### Identification of Dichlorobentazon as Reaction Product of Hypochlorite with Bentazon

The major product of hypochlorite with bentazon was initially assumed to be dichlorobentazon based on TLC studies of the reaction. To positively identify it as the reaction product, authentic bentazon was treated with hypochlorite, and the product isolated and characterized.

Preliminary experiments with authentic bentazon showed that under acidic conditions dichlorobentazon was seen 10 to 162 min after hypochlorite addition. Bentazon was extractable with methylene chloride from neutral and acidic, but not basic,

Table 1. Larger Scale Treatment of Bentazon-Containing Wastewater with Excess Hypochlorite

Bentazon	Time min	Bentazon Remaining, %	Temp °C	Reaction
Add hypochlorite	0	100	25	
	1	23	27 to 29.5	Color changes
	10	1.3	30	Orange, flocculant material
	30	—	30	Reddish material separates out
Add bisulfite	30	—	31	Oil globules adhere to flask walls
	40	—	32	

solutions. After testing on a small-size reaction, dichlorobentazon was isolated, using an extractive procedure.

Infrared spectra were generated for bentazon, dichlorobentazon, and isolated product using the Nicolet FT-IR. The lack of resolution in the spectrum of the product, and the complexity and similarity of bentazon and dichlorobentazon spectra made identification impossible.

The same materials were subjected to low and high resolution mass spectrometry. The major treatment product was shown to be the aromatic substituted dichloro analog of bentazon. The spectrum so generated was compared to the spectrum of dichlorobentazon standard (supplied by the manufacturer). A common fragmentation pattern was observed:  $m/e$  308 (molecular ion), 264, 229, and 187. Peak-matching the 308 signal from the treated bentazon spectrum gave a mass of 307.9787, best match  $C_{10}H_{10}N_2O_3SCl_2$ —empirical formula of dichlorobentazon. Thin layer chromatography and infrared spectrometric analysis of the HOCl-treated extract confirmed this structure assignment.

The presence of a second treatment product was indicated. This material gave rise to a mass signal at 282 (281.9303 -  $C_{12}H_4SO_2Cl_2$ ). The absence of a nitrogen atom suggested the possibility that this specie may be a fragment ion.

Characterization of other compounds was not undertaken.

### **Daphnia Bioassay**

Solutions of bentazon and dichlorobentazon were subjected to toxicity testing with *Daphnia magna*. The test procedure used is an EPA-approved acute static bioassays procedure. The bentazon was not toxic at the levels studied: 50, 5, and 0.5 ppm. The dichlorobentazon showed toxicity at all levels, and was quite toxic at 50 ppm.

### **Cost Estimate**

A cost estimate, prepared for the HOCl treatment of bentazon wastewater for the specific site sampled, showed the estimated capital cost to be \$1.3 million and yearly operating costs to be \$3.6 million.

The following assumptions were used in preparing the estimate:

- (1) 333-fold excess of HOCl (2 HOCl/1 bentazon)
- (2) 100 ppm bentazon in wastewater
- (3) 30 min residence time
- (4) Use of  $NaHSO_3$  to neutralize half of added HOCl
- (5) Operate 270 days/yr

This estimate does not take into consideration the manufacturer's comment that heat exchangers would be needed that would add \$1 million to the capital costs. Installation of a storage tank for hypochlorite would require heat exchangers to cool the hypochlorite to prevent decomposition. Because of the corrosivity of the hypochlorite, these exchangers must be made of carbon steel shell with titanium tubes.

### **Results and Conclusions**

The following results were obtained from this hypochlorite treatment study of bentazon-containing wastewater.

- (1) The analytical HPLC method was used successfully to monitor bentazon levels in wastewater samples.
- (2) Assuming a stoichiometry of 2 equivalents hypochlorite to 1 equivalent bentazon, the excess hypochlorite (5% aqueous sodium hypochlorite) required for complete bentazon removal was between 245 and 370-fold.
- (3) Bentazon disappeared rapidly as long as the wastewater pH was 2 or below with the use of a 333-fold excess of hypochlorite. A higher initial pH resulted in incomplete bentazon removal.
- (4) The effect of temperature on the reaction was of secondary importance over the temperature range which the wastewater would encounter. Water temperatures (3°-7°C) may slow the reaction a little (the smaller the excess of hypochlorite, the greater the slowing effect), but with a 333-fold excess the effect was very small.
- (5) The mode of addition of hypochlorite had no effect on the treatment process. As long as the correct excess was added, whether all at once or in portions, the final result was the same.
- (6) Dichlorobentazon was the major product of the reaction of bentazon with excess hypochlorite in acidic solutions. Other products have not been identified.
- (7) Bentazon was essentially nontoxic to *Daphnia magna* up to at least 50 ppm. The major treatment product of bentazon, dichlorobentazon, was toxic to *Daphnia magna* at 50 ppm, with some toxicity also at 5 and 0.5 ppm.
- (8) The estimated unit cost of hypochlorite treatment was

\$0.0714/gal. Annualized costs were estimated at about \$3.6 million/yr.

### **Recommendations**

The experimental findings have led to the following possibilities for future work.

- (1) Other treatment approaches could lead to a system with a product less toxic than bentazon or upgrade current treatment to produce less bentazon in wastewater.
- (2) Other treatment conditions could reduce the hypochlorite excess required for complete bentazon removal (e.g., catalysis, nature of the acidic agent).

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*Robert V. Hendriks is the EPA Project Officer (see below).*

*The complete report, entitled "Treatment Technology for Pesticide Manufacturing  
Effluents: Bentazon," (Order No. PB 85-176 816/AS; Cost: \$10.00, subject to  
change) will be available only from:*

*National Technical Information Service*

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*The EPA Project Officer can be contacted at:*

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