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UV-Ozonation of Paraquat

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The use of ultraviolet (UV) irradiation in the presence of O_2 or O_3 was investigated as a method for degrading paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) prior to soil disposal. A solution of 1500 ppm of formulated paraquat was slowly degraded after 7 h in a unit containing 66 low-pressure mercury vapor lamps with a maximum energy output at 254 nm. Addition of acetone as a photosensitizer accelerated the rate of oxidative cleavage of paraquat in laboratory-scale studies. Loss of ^{14}C from [*methyl*-^{14}C]-paraquat was observed in paraquat solutions at 150 ppm but not 1500 ppm. Reaction products identified from paraquat were 4-carboxy-1-methylpyridinium ion at 1500 ppm by high-pressure liquid chromatography; 4-picolinic acid, hydroxy-4-picolinic acid, succinic acid, *N*-formylglycine, malic acid, and oxalic acid as their Me_3Si derivatives; and 4,4′-bipyridyl in dilute solutions by gas chromatography–mass spectrometry.

Paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) is a broad spectrum contact herbicide effective against grasses and most broad-leaved plant species. Reactions responsible for decomposing or inactivating paraquat have been reviewed extensively (Calderbank, 1968; Calderbank and Slade, 1976; Summers, 1980). In solution, paraquat is subject to photodecomposition and microbial metabolism. Dilute aqueous solutions of paraquat are rapidly photochemically degraded to methylamine and 4-carboxy-1-methylpyridinium ion (Slade, 1965). *Aerobacter aerogenes*, *Agrobacterium tumefaciens*, *Pseudomonas fluorescens*, and *Bacillus cereus* in culture solution used paraquat as a sole source of nitrogen (Tu and Bollen, 1968). In soils paraquat is rapidly inactivated by adsorption to clay minerals (Calderbank and Slade, 1976). In the bound state it is believed that paraquat is not available to living organisms (Riley et al., 1976) and is stable to most soil chemical processes (Hance, 1967). Early long-term soil persistence studies (Fryer et al., 1975) indicated essentially no loss of paraquat residues based on almost quantitative recovery from previous applications. When this study was continued for a longer period (Hance et al., 1980), a 10% per year loss rate was reported based on paraquat residues in soils, regardless of when it was applied. The half-life was calculated to be about 6.6 years.

Field trials with a 66-lamp ultraviolet (UV) unit to pretreat pesticide waste water prior to land disposal showed that paraquat was more slowly degraded than atrazine and 2,4-D (Kearney et al., 1984). The objective of the present study was to investigate (1) the effect of a photosensitizer on the rate of decomposition of formulated paraquat solutions and (2) the products resulting from UV-ozonation of dilute and concentrated paraquat solutions.

METHODS AND MATERIALS

Rate Studies. Formulated paraquat (ortho paraquat +, 29.1% ai, 70.9% inerts) was purchased from the Ortho Agricultural Chemicals Division, Chevron Chemical Co.,

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Richmond, CA 94804. Purified paraquat (99.8%) was a gift from the Chevron Chemical Co. [*methyl*-^{14}C]Paraquat (specific activity 7.91 mCi/mM) was purchased from Pathfinder Laboratories Inc., St. Louis, MO 63141.

A study was conducted on the degradation of 1500 ppm formulated paraquat for 8 h in a 66-lamp UV unit using O_2 or O_3 fed directly into the lamp chamber. Loss of parent material was measured by gas chromatography. Enriched ozone was fed into the lamp chamber with a Model GTC-1B ozone generator (Griffin Technics Corp., 66 Route 46, Lodi, NJ 07644) at a rate of 32 g per h from an O_2 feed gas (manufacturer's estimate).

Previous studies with the 66-lamp UV unit (Pure Water Systems, Inc., Fairfield, NJ 07006) and a description of the unit are cited elsewhere (Kearney et al., 1983a). The unit contains low-pressure mercury vapor lamps with a maximum energy output at 254 nm, with an additional emission at 185 nm. Each lamp is encased in a long quartz tube and the tubes are arranged so that each lamp is located 1.27 cm from each adjacent lamp. The lamps are housed in a stainless steel cylinder, approximately 40 cm in diameter. The total output of the lamp unit is about 2,244 W. The flame ionization gas chromatographic procedures used to measure paraquat residues in UV-ozonation studies have also been described previously (Kearney et al., 1984).

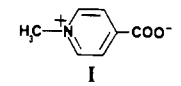
Laboratory small-volume studies (200–1000 mL) were conducted in a 450-W quartz mercury lamp (Hanovia Cat. No. 679-A36) housed in a water-cooled quartz-walled immersion well and a 300-mL reaction vessel fitted with a gas inlet tube. Ozone was generated in situ by slowly bubbling oxygen into the reaction vessel during the irradiation period. To determine whether any fragmentation of the methyl–nitrogen bond occurred, a solution containing 1500 ppm formulated paraquat with 0.1 μCi [*methyl*-^{14}C]paraquat was irradiated in the 450-W lamp unit for 1 h in the presence of O_2 and the loss of ^{14}C was measured by liquid scintillation counting. The same conditions were used in a second experiment with a 150 ppm solution with 0.1 μCi labeled paraquat. In both studies loss of the parent paraquat was measured by gas chromatography after 1 h.

Longer term experiments were undertaken to determine whether acetone served as a photosensitizer and accelerated the degradation of formulated paraquat. A 150 ppm solution of formulated paraquat with 0.1 μCi labeled paraquat was irradiated in the presence of 1% acetone for 6 h and loss of ^{14}C was measured hourly. An identical experiment was conducted in the absence of acetone.

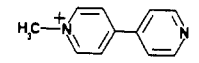
A second long-term study of 8 h was conducted on a 1500 ppm formulated paraquat solution with 0.1 μCi of labeled paraquat in the presence and absence of 5% acetone and loss of ^{14}C and parent compound were measured.

An experiment was undertaken to determine the effect of concentration on the rate of disappearance of paraquat by UV-ozonation. A concentration series of 100, 300, 600, 900, and 1200 ppm was prepared, and loss of parent compound was measured by HPLC by using the ion pair method (Gill et al., 1983) at 20-min intervals for the 300, 600, and 900 ppm concentrations, 5-min intervals for the 100 ppm concentration, and 1-h intervals for the 1200 ppm concentration. The time required for 90% loss at each concentration was calculated from those rate studies.

Product Studies. Reference samples of 4-carboxy-1-methyl pyridinium ion (I), monoquat (II), and monopyridone (III) were supplied by the Plant Protection Division, Imperial Chemical Industries Limited, Jealott's Hill Research Station, United Kingdom. Their structures are shown below. The labeled paraquat was purified by TLC on a cellulose-coated plate (MN-300 cellulose uniplates, 250 micron layer, Analtech Inc., Newark, DE 19711) with a solvent system of butanol–acetic acid–H_2O (4:1:2) and gave a product of >99% radiochemical purity.



I



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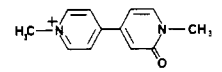

III

A 200-mL solution of 20 ppm purified paraquat was irradiated for 30 min in the presence of oxygen, the reaction mixture made acid with dilute HCl and extracted three times with 1 L of ethyl acetate, and the extract volume reduced in a rotary evaporator and to dryness under N_2. Trimethylsilyl (Me_3Si) derivatives were prepared and analyzed by use of a gas chromatograph–mass spectrometer as described previously (Kearney et al., 1983b). The mass spectrometer is a Finnigan 4021 with an Incos data system, operated in the electron impact mode, with an electron energy of 70 eV. The gas chromatograph oven temperature was held for 1 min at 90 °C and then programmed from 90 to 230 °C at 5 °C/min.

A solution containing 200 mL of a 1500 ppm paraquat with 1 μCi of the [*methyl*-^{14}C]paraquat and 5% acetone was subjected to UV-O_3 and sampled after 0, 1, 2, and 3 h. The loss of ^{14}C from the solutions was monitored by removing 1-mL aliquots and measuring radioactivity via liquid scintillation counting. The volume of each timed sample was reduced under N_2 and spotted on cellulose TLC plates and developed with butanol–acetic acid–H_2O (4:1:2). On another plate all of the cellulose above the paraquat band (R_f 0.35) was scraped, eluted with 10% methanol, and reduced to 0.1 mL for comparison with suspected products by high-pressure liquid chromatography (HPLC). Another solvent system was examined by using butanol–acetic acid–H_2O–diethylamine (4:1:2:1) plus 0.2% heptanesulfonate. In nonlabeled studies, the iodoplatinate reagent (Randerath, 1966), which is sensitive and selective for compounds containing a tertiary or quaternary nitrogen, was used to detect standards. HPLC was performed on a 5-μm C-18 reverse-phase column (Waters Associates, Milford, MA) with H_2O and acetonitrile as solvents in a sequence of 0–5 min of 100% H_2O, 5–15 min of linear gradient to 100% acetonitrile, and 15–20 min of 100% acetonitrile. In some studies the ion-pair method with Na heptanesulfonate (Gill et al., 1983) was employed to detect products I, II, and III.

RESULTS AND DISCUSSION

Rate Studies. The disappearance of formulated paraquat (1500 ppm) in the 66-lamp unit in the presence of O_2 and O_3 is shown in Figure 1. As in the previous study (Kearney et al., 1984), significant oxidation of paraquat at 1500 ppm did not occur in the presence of oxygen during 7 h. When ozone was fed directly into the chamber, 32.8% of the paraquat was destroyed during the same time period. There is considerable heat buildup in the unit on long runs, and temperatures of 54–55 °C are not uncommon after several hours. Many factors govern the solubility of ozone in water, one being temperature. Dissolved ozone residuals decrease with increasing temperature due to

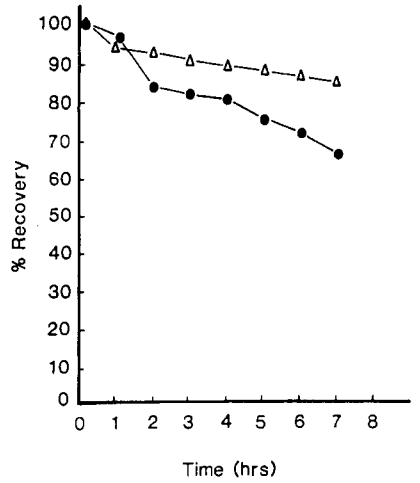

Figure 1. Degradation of 1500 ppm formulated paraquat with time in a 66-lamp UV unit with O_2 (Δ-Δ) or O_3 (•-•) fed directly into the lamp chamber.

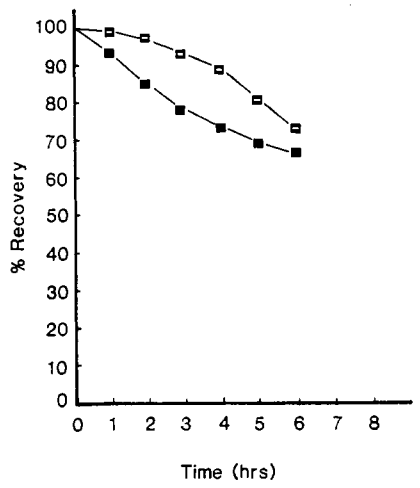

Figure 2. Loss of ^{14}C from [*methyl*-^{14}C]paraquat (150 ppm formulated paraquat) via UV-ozonation ± acetone: ■-■, 1% acetone; □-□, no acetone in a 450-W laboratory scale lamp unit.

thermal decomposition (Hewes and Davison, 1971), which could adversely affect the overall degradation process. When the experiment was repeated in the 450-W quartz lamp unit for 60 min with 1500 ppm of formulated (*methyl*-^{14}C]paraquat and 1 μCi of [*methyl*-^{14}C]paraquat, no loss of ^{14}C was recorded (100.5% recovery) and 87.9% paraquat was detected via GLC. If the concentration was decreased to 150 ppm formulated paraquat, no loss of ^{14}C (102.1% recovery) was observed and 88% of the starting material was recovered.

In longer term experiments with 150 ppm formulated [*methyl*-^{14}C]paraquat in the small lamp unit, there was measurable cleavage of the methyl–nitrogen bond as measured by ^{14}C loss (Figure 2) and loss of paraquat. The addition of acetone accelerated both reactions. After 6 h only 3.1% and a nondetectable level (<1.0 ppm) of paraquat were measured by GLC in the 0 and 1% acetone solutions, respectively.

To determine whether acetone sensitized the oxidative loss of formulated [*methyl*-^{14}C]paraquat at 1500 ppm, an experiment was conducted on the loss of ^{14}C and paraquat in the presence and absence of 5% acetone (Figure 3). At an initial concentration of 1500 ppm of paraquat there is no loss of ^{14}C after 8 h and about a 10% loss of paraquat in the absence of acetone. These trends are similar to the results noted in the 66-lamp unit in Figure 1. In the presence of 5% acetone over 90% of the paraquat in the

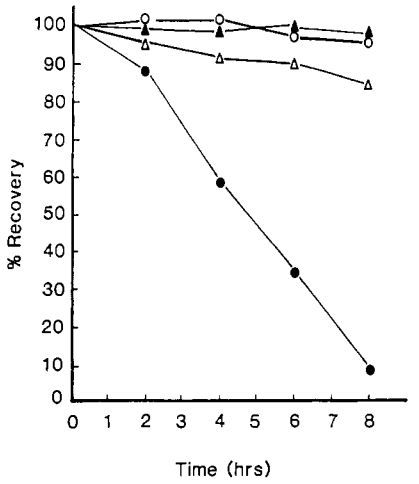

Figure 3. Degradation of formulated paraquat (1500 ppm) as measured by loss of ^{14}C from [*methyl*-^{14}C]paraquat and by GLC analysis with time in a 450-W laboratory scale lamp unit ± acetone (5%): O-O, loss of ^{14}C with 5% acetone; ▲-▲, loss of ^{14}C with no acetone; •-•, loss of paraquat with 5% acetone; Δ-Δ, loss of paraquat without acetone.

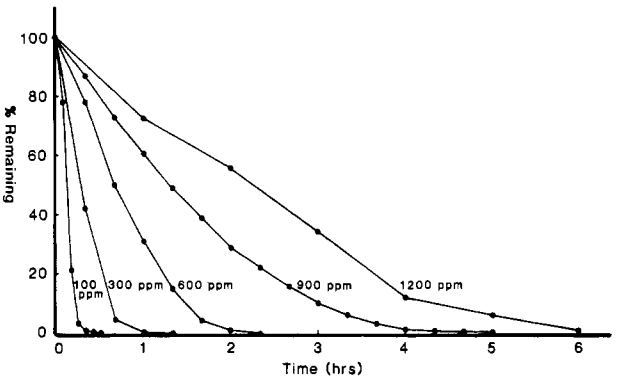

Figure 4. Loss of paraquat as a function of concentration with time (100, 300, 600, 900, 1200 ppm) via UV-ozonation in a 450-W laboratory scale lamp unit as measured by ion pair HPLC.

formulated solution was degraded in 8 h. The loss of paraquat from 100, 300, 600, 900, and 1200 ppm solutions plus 5% acetone is shown in Figure 4. The time required for degradation of paraquat decreased as concentration was progressively lowered. This has important implications from a disposal standpoint, since the time required to lower the concentration of any potential pollutant will affect cost. It is difficult to translate the data to a waste situation in a strict quantitative sense, since the reactions are complex and the waste solutions are often heterogeneous. A useful parameter is the time required to degrade 90% of the compound. For this specific study, a plot of paraquat concentration vs. time required for 90% loss was a straight line ($C = 137 + 4.22$ m, $r^2 = 0.98$**).

Product Studies. A chromatogram showing the distribution of products extracted with ethyl acetate and derivatized with Me_3Si from an acidified solution of 20 ppm of paraquat after 30 min of UV-ozonation is shown in Figure 5. A detailed discussion of the gas chromatographic and mass spectral parameters of these compounds is found elsewhere (Ruth et al.). The largest identified peak was the Me_3Si derivative of 4-picolinic acid (isonicotinic acid) with a molecular ion at m/z 195. Two other ring-containing compounds were identified as the 4,4′-bipyridine (m/z 156) and a hydroxylated 4-picolinic acid (m/z 283). The four remaining identified products were all organic acids and included the bis(trimethylsilyl) ester of succinic acid (m/z 262), the bis(trimethylsilyl) ester of

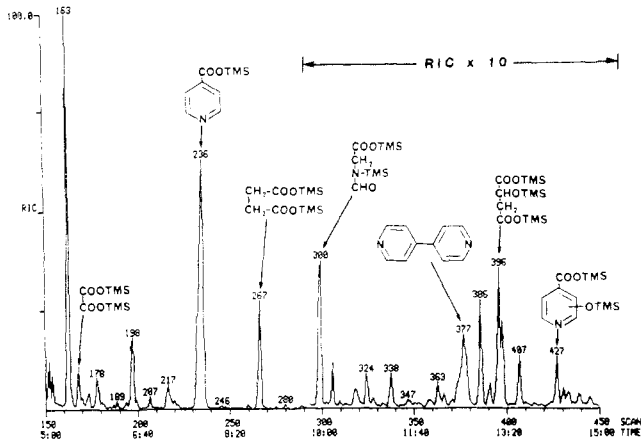

Figure 5. Reconstructed ion current (RIC) chromatogram of the Me_3Si derivatives of paraquat products obtained from UV-ozonation of a 20 ppm solution irradiated for 30 min. The vertical scale (RIC) has been expanded by a factor of 10 between scan 290 and scan 450.

oxalic acid (m/z 234), the bis(trimethylsilyl) derivative of *N*-formylglycine (m/z 247), and the tris(trimethylsilyl) derivative of malic acid (m/z 350). The 4-picolinic acid could arise by demethylation of the 4-carboxy-1-methylpyridinium ion (I) or oxidative ring cleavage of the 4,4′-bipyridine in a series of reactions similar to those described for the formation of I from paraquat (Summers, 1980). A control solution containing 20 ppm of paraquat but receiving no irradiation contained none of these compounds when the ethyl acetate extract was derivatized with Me_3Si and examined by gas chromatography interfaced with the mass spectrometer. All products were verified by comparison with authentic samples.

Identification of the quaternary ammonium compounds was achieved by cochromatography on TLC and HPLC. Products were separated on cellulose TLC plates from a 1500 ppm solution of formulated paraquat in 5% acetone. A compound at R_f 0.43 cochromatographed with the 4-carboxy-1-methylpyridinium ion (I). The solvent system containing heptanesulfonate gave the following R_f values: 0.47 for I, 0.60 for II, 0.82 for III, and 0.30 for paraquat. Compounds II and III cochromatographed with products from a paraquat reaction mixture and were detected with the iodoplatinate reagent.

Cellulose containing the spot corresponding to compound I was extracted and the extract was examined by HPLC. Without the ion pair reagent, a peak from the extract appears at 2.6 min, which cochromatographed exactly with I. Only one peak appeared when I and the extract were cochromatographed in essentially equal amounts. Reference sample II (minus one methyl group) did not exhibit a peak on HPLC and may have been lost in the void volume. Based on the ^{14}C recovery data, i.e., 99.5% after 3 h, the appearance of II would not be anticipated.

Products I, II, III, and paraquat could be resolved with the ion pair method via HPLC. The retention times were I = 2 min, II = 4.5 min, III = 4.0 min, paraquat = 6.0 min. Product I was seen frequently in the time–concentration studies. Small peaks with retention times for II and III were observed.

Previous field studies with a 66-lamp UV unit for disposal of pesticide waste waters generated at an actual farm site suggested that fragmentation of paraquat at concentrations in the range of 1500 ppm was relatively slow compared with loss rates for atrazine or 2,4-D (Kearney et al., 1984). The direct addition of ozone into the lamp chamber improved the degradation process (67% recovery after 8 h) compared with in situ ozone generation from oxygen (86% recovery after 8 h). In a laboratory study with [*methyl*-^{14}C] paraquat, only in the presence of acetone was paraquat degraded more than 90% after 8 h. At 1500 ppm no evidence exists for oxidative demethylation of paraquat and the reaction proceeds by fragmentation of one ring to yield the 4-carboxy-1-methylpyridinium ion (I). In a previous study (Farrington et al., 1969), when paraquat was reacted with a strong oxidant, such as hydrogen peroxide, the monopyridone (II) and dipyridone were produced as ring oxidation products but the major end product was I. Further oxidation of II leads to a compound tentatively identified as 4-carboxy-1-methylpyridone. Compounds I and III are reported to be microbial products of paraquat (Funderburk and Bozarth, 1967) and I is readily metabolized by soil bacteria (Wright and Cain, 1969). Most metabolic reaction products described for I retain the methyl group bonded to the nitrogen of the original pyridinium ring, with the ultimate products being formate, methylamine, and succinate (Wright and Cain, 1972a, 1972b).

At lower concentrations in the range of 150 ppm or less there is substantial degradation of paraquat in waste water and loss of the methyl group. Three demethylated ring products were isolated and identified: 4-picolinic acid, hydroxy-4-picolinic acid, and 4,4'-bipyridyl. Ring fragmentation products identified were oxalate, succinate, malate, and *N*-formylglycine. Based on the products identified to date, a pathway is proposed for the alteration of paraquat by UV-ozonation (Figure 6).

The photooxidative reactions that occur here are extremely complex. Perhaps the most difficult question to answer concerning this process is the function of the various components: paraquat, O_2, O_3, acetone, and ultraviolet light. The complexity of the problem is perhaps best exemplified by examination of the photochemical reactions of O_2 and O_3 (Calvert and Pitts, 1966; Okabe, 1978). Irradiation at the Schumann–Range bands results in homolytic scission of oxygen, which ultimately leads to

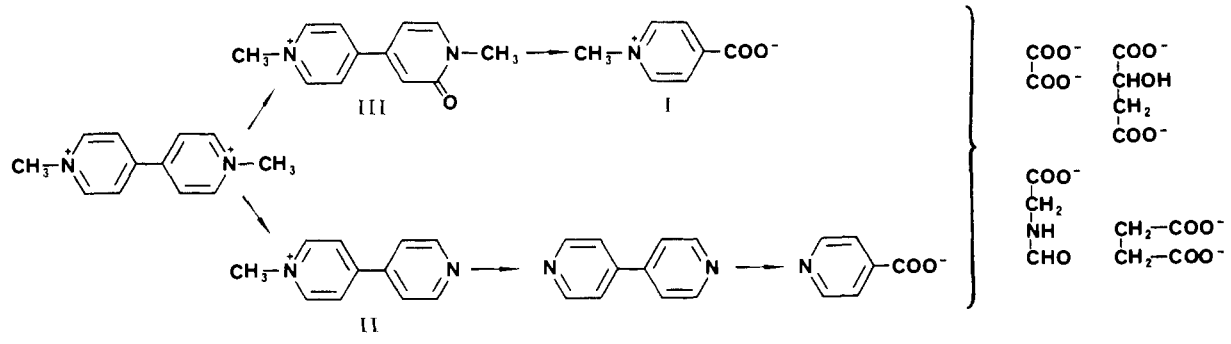

Figure 6. Proposed pathway for paraquat degradation during UV-ozonation.

the presence of the five oxygen species as shown below.

$$O_2 \xrightarrow{h\nu} 2O(^3P)$$

$$O_2 + O + M \rightarrow O_3 + M$$

$$O_3 \xrightarrow{h\nu} O(^1D) + O_2(^1\Delta)$$

Which species is responsible for the degradation of paraquat, or subsequent products in the degradation pathway of paraquat, is open to conjecture. The role of acetone as an apparent sensitizer is also unclear, as is the possible contribution of direct photolysis of paraquat in the mixture. There is no clear understanding of all of the reactions involved in the UV-ozonation process and consequently it is difficult to optimize the process. For example, the compound TNT has been the subject of numerous UV-O_3 studies. After many years of study of conditions favorable for the destruction of TNT, Wentzel et al. (1982) pointed out in an extensive review that very little is known about the optimum conditions for and the degradation mechanism of TNT. Likewise, in studies on the oxidation of tetrachloroethylene, Peyton et al. (1982) concluded that while the UV-O_3 process is still not understood from a chemical mechanistic standpoint and is not optimized for engineering applications, the process appears to be amenable to modeling, at least for certain substrates. We hope to be able to provide information on these processes upon completion of detailed mechanistic investigations that are now in progress.

The use of UV-ozonation as a pretreatment for disposing of pesticide waste water prior to microbial metabolism by indigenous or engineered soil microorganisms is limited by equipment currently available to fragment the molecule in the pretreatment phase. For large volumes of dilute rinse waters of certain pesticides, the UV-ozonation method is ideally suited to a pretreatment prior to soil disposal.

Registry No. I, 36455-39-7; paraquat, 4685-14-7; acetone, 67-64-1; 4-picolinic acid, 55-22-1; hydroxy-4-picolinic acid, 22468-26-4; succinic acid, 110-15-6; oxalic acid, 144-62-7; *N*-formylglycine, 2491-15-8; malic acid, 6915-15-7.

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