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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · MARCH 1998

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Comparison of Catalyzed and Noncatalyzed Oxidation of Azo Dye and Effect on Biodegradability

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Catalytic and noncatalytic oxidations of diluted (0.5 g/L) aqueous azo dye (Orange II) solutions were performed at temperatures from 180 to 240 °C and oxygen partial pressure of 10 bar. The catalyst consisted of alumina and copper and zinc oxides. Dye−decay curves indicate that nearly complete removal of Orange II was achieved after 10 min at 240 °C in experiments without the catalyst while only about 3 min was needed in the presence of the catalyst at 180 °C. The TOC removal rates were found lower than those of the dye, thus implying the formation of intermediate products that are more resistant to further oxidation to carbon dioxide. On the basis of concentration−time behavior and the intermediate products identified, it is concluded that both catalytic and noncatalytic oxidations of Orange II obey a parallel consecutive reaction pathway involving free radicals. Aerobic biodegradability of Orange II solutions treated by catalytic and noncatalytic oxidation processes increases with time. The ratio of BOD_5/COD vs temperature exhibited a slight maximum at about 200 °C in the case of noncatalytic oxidation. The results of this investigation indicate that intermediate product distribution plays a dominant role in biodegradability: the solutions treated by catalytic oxidation were found to be more amenable to aerobic biodegradation, simply because smaller quantities of intermediate products were formed in this process.

Introduction

The environmental issues associated with residual color in waste streams of the dye-manufacturing and dye-consuming industries are not new, but due to the impact of dyes on the environment and stringent wastewater regulations, they have gained more attention in recent decades. There is evidence that dyehouses were concerned about levels of water pollution from discharge of waste dyebaths as early as 1893 (*1*).

Dyes are required to exhibit a high degree of chemical, photolytic, and microbiological stability in order to fulfill the fastness requirements of consumers. Consequently, dyes do not readily degrade under typical usage conditions, not even under aerobic conditions prevailing in the conventional biological treatment processes. Despite producers' interests to improve the fixation of certain dyes on specific substrates, to change the chemical structure of dyes in order to obtain more biodegradable alternatives, and to better control the dye-manufacturing and dye-consuming processes, the reactions that bind dyes onto a substrate do not always run to completion. Residual dyes, auxiliaries, and chemicals are often left in the process water and discharged with a wastewater. These effluents are discharged either to sewers, which are then treated by a municipal sewage treatment plant, or directly to rivers. The inability of these systems to function effectively makes dye-related industries incapable of responding to the current stringent legislation. Therefore, future efforts should focus on developing new and more efficient dye-containing wastewater treatment processes. Due to the encouraging results obtained with wet oxidation of various recalcitrant wastes, e.g., model aqueous solutions of anthraquinone and phthalocyanine dyes (*2*) and a monoazo monosulfonated dye—Orange II (*3*), wet oxidation is considered one of the most promising and simplest techniques for partial oxidation of parent pollutants into more biologically amenable intermediates. An attractive alternative to wet oxidation is catalytic wet oxidation, which may be effectively employed for total destruction of pollutants present in wastewater.

Wet oxidation is a liquid-phase process that takes place at elevated temperatures (200−320 °C) and pressures (20−200 bar) by means of active oxygen species, such as hydroxyl radicals. Contrary to the severe reaction conditions in wet oxidation processes, the catalytic process employs milder conditions due to the presence of a catalyst. Catalytic oxidation involves a free radical initiation on the catalyst surface while the propagation proceeds in the bulk liquid phase. From the kinetic point of view, the use of a catalyst substantially increases the oxidation rate of refractory compounds. There are a number of review articles on the wet oxidation processes (e.g., refs *4* and *5*). Recently, however, Luck (*6*) compared industrial catalytic processes to one carried out without a catalyst.

In the available literature, no comparison is given on the biodegradability of intermediate products formed during the catalytic and noncatalytic wet oxidation process. This, however, can be accomplished by studying the biodegradability and adverse effects of the intermediates. An example presenting the evolution of COD and BOD_5/COD as a function of temperature in the low-pressure catalytic wet oxidation LOPROX process (*6*) has demonstrated that this dependence increases with temperature. In other words, the biodegradability of treated effluents increases with temperature. At around 200 °C, the value of the BOD_5/COD ratio is already higher than 0.5, which implies that the effluents are readily biodegradable.

The purpose of this study was to determine noncatalytic and catalytic oxidation effects on the aerobic biodegradability of Orange II aqueous solutions. The homogeneous wet oxidation experiments with Orange II have been described in great detail in a recent paper of Donlagić and Levec (*3*). They have found that Orange II decomposes thermally and oxidatively into intermediates obeying a parallel consecutive reaction pathway. Bandara et al. (*7*) and Kulla et al. (*8*) found Orange II aqueous solutions to be nonbiodegradable. To accomplish the task and to compare the results with those obtained by ozonation of Orange II solutions (*9*−*11*), the BOD_5/COD ratio was used. Despite the analytical problems reported and the lack of literature information, the assessment of the BOD_5/COD ratio seems to be the most ap-

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S0013-936X(97)00643-3 CCC: $15.00
Published on Web 03/15/1998

propriate simply because the differences between the influent and effluent values of BOD_5 and COD have been predominantly used for determining the efficiency of biotreatment plants. Because these parameters alone provide little information about the oxidation pathways and the ultimate fate of the parent compound, particular emphasis was given to the formation and identification of intermediate products in the effluents of both processes.

Experimental Section

Apparatus and Procedure. Oxidation experiments were performed in a 2-L stainless steel autoclave reactor (Parr Instrument Company, Moline, IL) equipped with a magnetically driven turbine type impeller and temperature and pressure control units. The experimental setup is described in detail elsewhere (*12*).

The experiments were carried out in a temperature range of 180−240 °C, oxygen partial pressure of 10 bar, and the Orange II mass concentration of 0.5 g/L (i.e., 274 ppm of organic carbon). The mass concentration of the catalyst was 5 g/L. The total pressure was the sum of the oxygen partial pressure and the water vapor pressure at the temperatures employed. The oxidation experiments were performed in the absence of mass transfer limitations (*3*).

In a typical run, a certain amount of recrystallized (*13*) Orange II (Aldrich) was loaded in an adding device of the autoclave. By placing Orange II in the adding device, we prevent thermal degradation of the dye which would otherwise occur in the solution during its heating to the reaction temperature (*3*). In wet oxidation experiments, the reactor was filled with 1.5 L of distilled water, and during the process of heating to 70 °C, nitrogen was sparged continuously through it. Once the water in the reactor reached the desired reaction temperature, a constant stream of oxygen (1.0 L/min) was introduced into the reactor, and a few minutes later the bottom of the dye adding device was opened by means of pressurized oxygen. Simultaneously, the impeller was turned. In catalytic experiments, a given amount of the catalyst was first suspended in 1.5 L of distilled water in the reactor. To activate the catalyst, oxygen at the metered flow rate was continuously sparged through the suspension after the reactor content reached the temperature of 70 °C. Otherwise, the procedure is the same as in the noncatalytic oxidation experiments. The time of opening the dye adding device and turning on the impeller was considered as the starting point of an experiment ($t = 0$). Approximately 10 mL of representative samples of the aqueous solution were withdrawn periodically and analyzed for the residual content of Orange II, total organic carbon (TOC), and intermediates. Since larger volumes were needed to determine the chemical (COD) and biochemical oxygen demand (BOD), separate experiments were performed for this purpose at identical conditions.

Catalyst. The catalytic wet oxidation of Orange II aqueous solutions was studied using a commercially available catalyst comprising 42 wt % of CuO, 47 wt % of ZnO, and 10 wt % of Al_2O_3 (Süd-Chemie AG, Munich) pretreated for 2 h at 860 °C in an oxygen stream (*12*).

Analysis. The quantity of residual Orange II in solution was determined by reversed-phase HPLC using a Hewlett-Packard 1100/DAD (set at 483 and 254 nm) system equipped with a Rheodyne 7725i injection valve (20 μL sample loop). The analyses were made using a 250 × 4.6 mm i.d. Spherisorb ODS-2 (5μm) at 40 °C. The mobile phase consisted of 0.1 M ammonium acetate (A) and acetonitrile mixed with 0.1 M ammonium acetate (B) (v/v; 80:20) at a flow rate of 1.0 mL/min; a gradient elution from 100% A to 100% B in 30 min was used.

The residual organic carbon concentrations in the samples were measured by an advanced HTCO Rosemount/Dohrmann DC-190 TOC analyzer equipped with a nondispersive infrared (NDIR) CO_2 detector.

The identification of aromatic intermediate products was performed on a Hewlett-Packard GC/MSD system running in both SCAN and SIM modes of operation. A GC was equipped with an HP-1 (Ultra-1) high-resolution capillary column (25m by 0.32 mm by 0.52 μm; HP) and interfaced directly to a quadrupole mass spectrometer (HP 5970B) as a detector. The GC was operated in an initial column temperature of 70 °C for 2 min, then increased linearly to 250 °C at a rate of 10 °C/min, and held at the upper temperature for 10 min. The GC/MSD interface was maintained at 260 °C. A helium carrier gas of ultrahigh purity was used with a flow rate of 1 mL/min. To extract analytes from aqueous samples, the solid-phase microextraction using a SPME syringe assembly (Supelco) was used. Intermediates were identified by comparing the mass spectrum of a compound with spectra of compounds stored in the NBS library. Semiquantitative evaluation of aromatic intermediates were obtained by employing a Varian 3410 high-temperature gas chromatograph equipped with a SGE (BP5−0.5 μm) column (50 m × 0.33 mm) operated with helium carrier gas of ultrahigh purity at a flow rate 1.3 mL/min and a FID R12 detector. The temperature-programming mode with an initial temperature of 70 °C held for 10 min, ramp at 20 °C/min to 310 °C, and held at this temperature for 5 min was used. Liquid samples were concentrated by the bond-elut cartridge technique (Varian). Full details are given elsewhere (*14*).

Low molecular mass organic acids were identified and evaluated by means of ionic chromatography (Dionex 4000I) using a conductivity detector. Isocratic elution of organic acid anions was optimized on the IonPac ICE-AS6 analytical column. Heptafluorobutyric acid (0.4 mM) was used as a mobile phase at a flow rate of 1 mL/min. As a suppressor, an Anion-ICE MicroMembrane Supressor with a regenerant (5 mM tetrabutylammonium hydroxide) at a flow rate of 5 mL/min was used. The sample loop volume was 20 μL. In the case of nitrite and nitrate IonPac AS4A analytical column, 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ as a mobile phase at a flow rate of 2 mL/min and suppressor (ASRS-1) with a regenerant (electrolyzed 18 MΩ·cm) at a flow rate of 3 mL/min was used. For qualitative and quantitative determination of ammonium the following conditions were used: IonPac CS12A analytical column, 30 mM H_2SO_4 as a mobile phase at a flow rate of 1 mL/min, and suppressor (CSRS-1) with a regenerant (electrolyzed 18 MΩ·cm) at a flow rate of 3 mL/min. The sample loop volume in both of the last cases was 50 μL.

The NMR $\{^1H\}$ ^{13}C CPMAS spectrum was obtained with Varian VXR 300 spectrometer. Contact time was 3 ms, and the spinning rate was 4000 Hz. TMS was used as a reference, and over 65 000 scans were co-added.

The chemical oxygen demand (COD) was determined by the closed reflux dichromate method; its concentration was measured colorimetrically and titrimetrically. The biochemical oxygen demand (BOD) was assessed by the standard dilution method using a commercially available special blend of bacterial cultures Bioseed (Interbio) as a seed source. Both COD and BOD tests were performed according to the Standard Methods for the Examination of Water and Wastewater (*15*). The mean values of six measurements are quoted as results. The tests were repeated twice. As required by the standard method, all liquid samples were neutralized before BOD assessment. The acids used for the BOD/COD assessment were the highest commercially available grade of purity as supplied by Aldrich and Fluka.

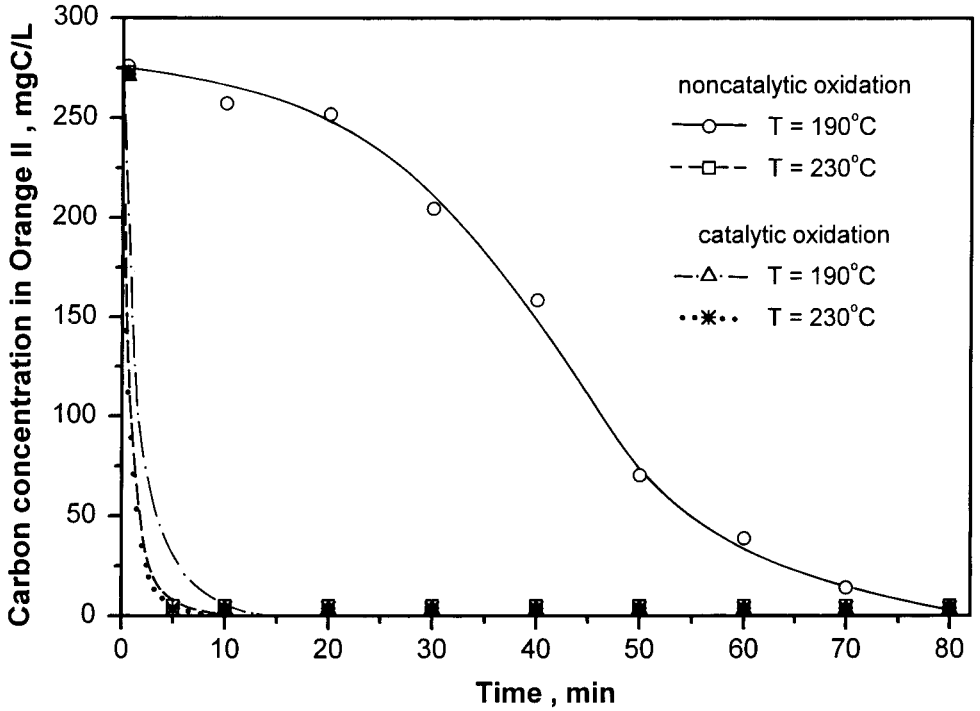

FIGURE 1. Organic carbon concentration in Orange II as a function of time in noncatalytic and catalytic experiments carried out at 10 bar of oxygen partial pressure.

Results and Discussion

Wet Oxidation. The dye−decay curves in Figure 1 indicate an extremely rapid Orange II destruction caused by the presence of the catalyst. Complete removal of dye was obtained within 5 min at 190 °C, while this was not reached without the catalyst. Moreover, in the noncatalytic oxidation carried out at the same temperature, complete removal of dye was achieved within 80 min, while at 180 °C it was not achieved at all.

The carbon in the dye−decay curve characteristic for noncatalytic oxidation performed at lower temperatures (Figure 1) suggests that there is an induction period, which is typical for a free-radical chain mechanism. This phenomenon is ascribed to the time needed for establishing a steady-state hydroperoxide radical concentration; therefore, its diminishing appearance with increased temperature seems to be logical. In the case of catalytic oxidation, the induction period was not observed. In general, the induction

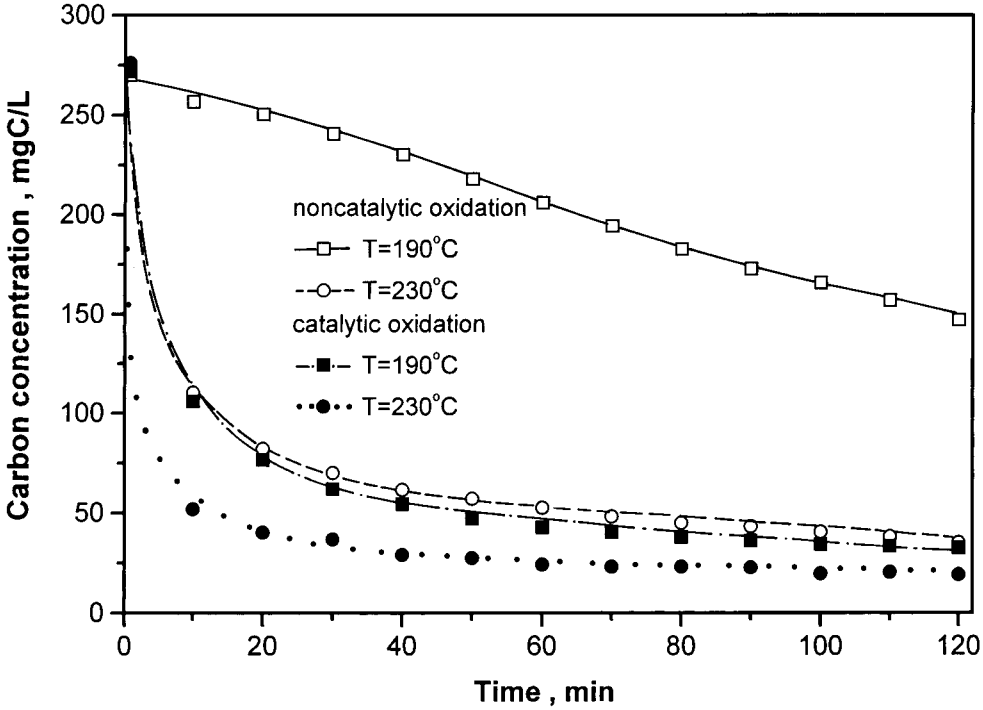

FIGURE 2. Total organic carbon in solution as a function of time in noncatalytic and catalytic experiments carried out at 10 bar of oxygen partial pressure.

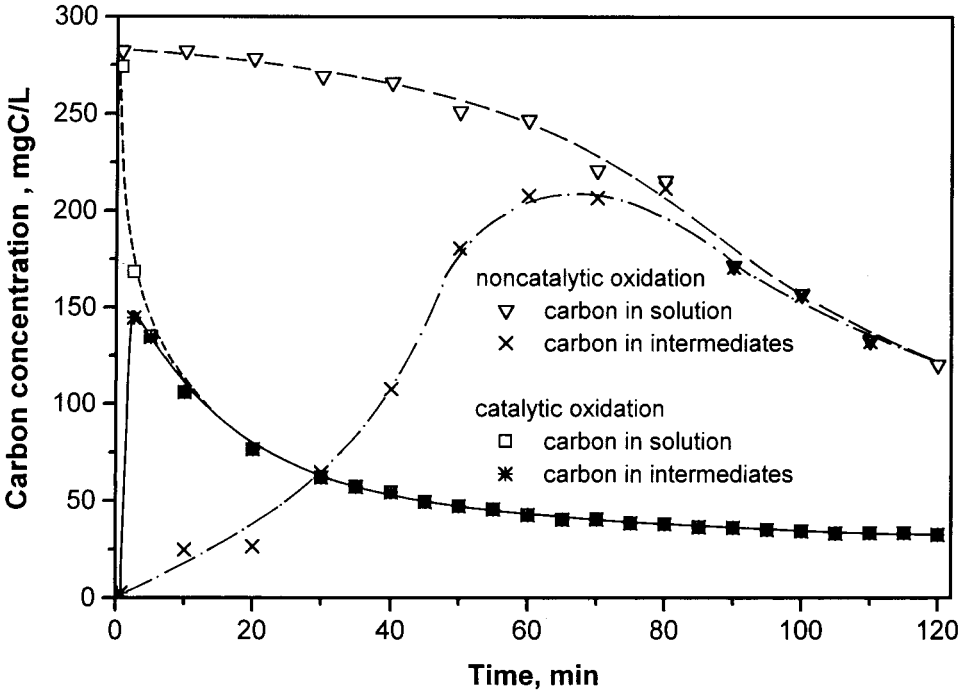

FIGURE 3. Total organic carbon in solution and in intermediates in noncatalytic and catalytic experiments as a function of time at 190 °C and 10 bar of oxygen partial pressure.

period is expected only at low catalyst-to-hydrocarbon ratios and in systems initially free of hydroperoxide radicals. Nevertheless, due to significant radical formation on the catalyst surface in addition to that generated by thermal decomposition of Orange II (*3*), the induction period is not expected in the heterogeneous oxidation carried out at the relatively high temperatures employed here.

The time dependence of carbon concentration in solution is depicted in Figure 2 for both the catalytic and noncatalytic oxidation experiments at two different temperatures. It can be seen that the use of the catalyst appreciably increases the carbon conversions; this effect is more pronounced at lower temperatures. These results further imply that the homogeneous disappearance rates of organic carbon are already very high at 230 °C.

While the concentration of Orange II dropped rather fast in both catalytic experiments and in the noncatalytic one carried out at 230 °C (Figure 1), the organic carbon concentration in solution still remained relatively high (Figure 2). One should be aware that the difference between the total dissolved organic carbon and the fraction of dissolved organic carbon that is attributed to Orange II accounts for the intermediate products that were formed during the course of oxidation. These differences are illustrated in Figure 3 for the catalytic and noncatalytic oxidations performed at 190 °C. In Figure 4, the results obtained at 230 °C are displayed. Comparing catalytic and noncatalytic oxidation, one can see that in the latter process much larger quantities of intermediates are produced (area under appropriate concentration vs time curve) and that the presence of the catalyst shifts the maximum of appearance toward the shorter residence times.

Intermediate Products. In a typical noncatalytic wet oxidation experiment, the following intermediates were identified: benzenesulfonic acid, naphthol, 4-hydroxybenzenesulfonic acid, 1,3-isobenzofurandione, 2-hydroxymethylbenzoic acid, 1,2-benzenedicarboxylic acid, acetic acid, formic acid, oxalic acid, and glycolic acid. The pH values of the solutions dropped within the first 40 min of oxidation from 6.4 to 3.4−2.8 and then remained almost constant. This implies that organic acids are formed at a later stage of oxidation and that the sum of their concentrations remains constant. In the experiment performed at 190 °C, formic acid was found as the prevailing organic acid while acetic acid was dominant at 230 °C (Figure 5). In the former case, the total amount of acids accounted for 15% of the organic carbon in solution, whereas in the latter case this value increased up to 55%. Donlagić and Levec (*3*) proposed the formation of the intermediates by noncatalyzed homogeneous oxidation of Orange II as a consequence of radical and ionic processes. Due to the appearance of hydroxylated aromatic intermediates, they concluded that the radical mechanism is the prevailing process.

On the other hand, in a catalytic wet oxidation experiment, acetic, formic, glycolic, lactic, and malic acids were identified. It seems that the catalyst is responsible for formation of large-chain acids such as lactic and malic acid. Acids occurrence in the case of the catalytic experiment carried out at 190 °C is shown on the left coordinate in Figure 6. In the experiments at 190 and 230 °C, the acetic acid was found dominant. At 190 °C, the total amount of acids made up 45% of the organic carbon in solution. When the experiment was carried out at 230 °C, this value was only slightly higher, 51%. These results imply that the intermediate products formed during the catalytic oxidation are predominantly in the form of acids when comparing the product distribution of the catalytic and noncatalytic processes at the same residence time. At 230 °C practically no difference was found between the two processes. Thus, one may conclude that the catalyst would be employed more effectively at lower temperatures. Acids distribution in catalytic and noncatalytic oxidation runs is further discussed by Donlagić and Levec (*16*). Contrary to the noncatalytic oxidation, the pH remains constant between 6 and 7; this may be due to the adsorption of hydrogen ions onto the catalyst surface. It seems, however, that acetic acid is one of the last intermediates before the final product (carbon dioxide) appearance regardless whether the process is catalytic or not.

Aromatic intermediates formed during the catalytic oxidation are similar to those obtained in the noncatalytic process. The relative concentration of aromatic intermediates, obtained as the ratio of a peak area to the total area,

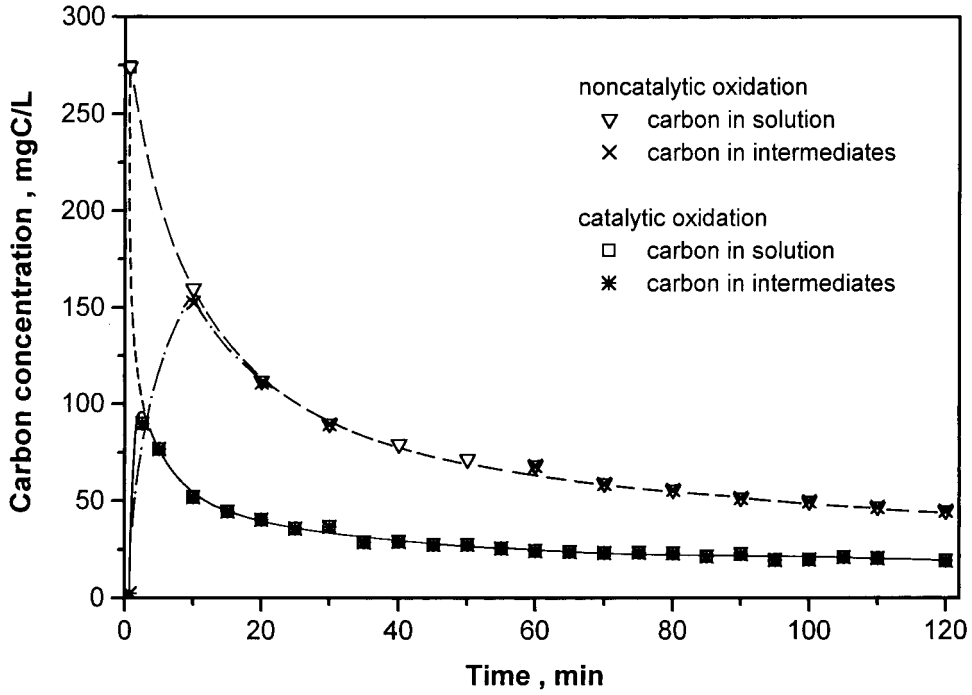

FIGURE 4. Total organic carbon in solution and in intermediates in noncatalytic and catalytic experiments as a function of time at 230 °C and 10 bar of oxygen partial pressure.

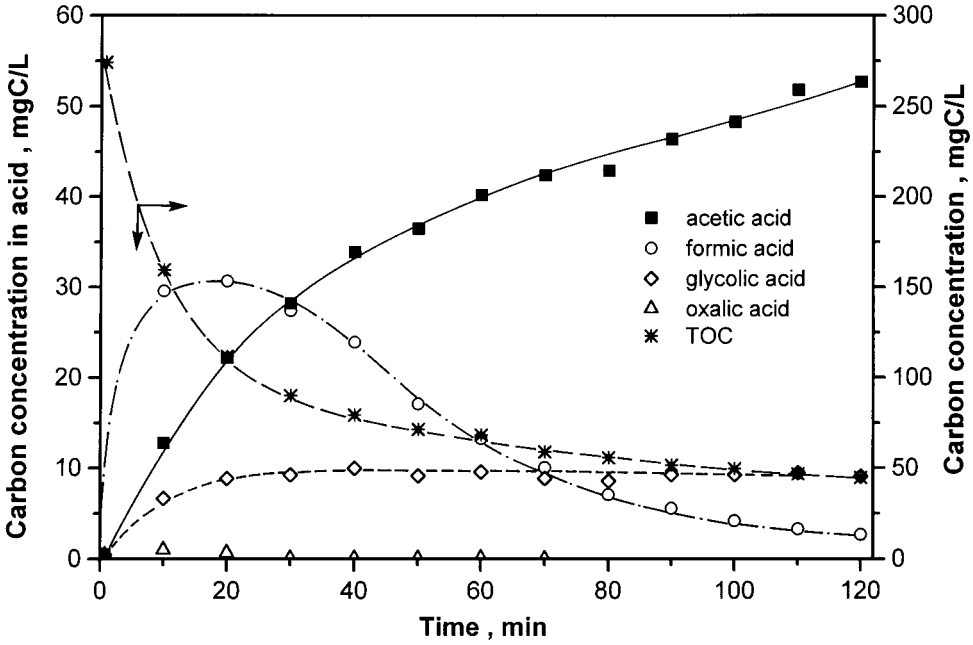

FIGURE 5. Distribution of organic acids in the noncatalytic experiment carried out at 230 °C and 10 bar of oxygen partial pressure.

showed that, in the noncatalytic treatment after 120 min at 230 °C, 24.3% of aromatics is found as naphthol, 7.0% as 1,3-isobenzofurandione, 7.1% as 2-hydroxymethylbenzoic acid, 2.4% as benzenesulfonic acid, 4.9% as 1,2-benzenedicarboxylic acid, and 3.6% as 4-hydroxybenzenesulfonic acid. The catalytic process at the same conditions yielded 37.9% of naphthol, 11.3% of 1,3-isobenzofurandione, 11.9% of 2-hydroxymethylbenzoic acid, 4.3% of benzenesulfonic acid, 5.4% of 1,2-benzenedicarboxylic acid, and 3.5% of 4-hydroxybenzenesulfonic acid. In the catalytic oxidation experiment carried out at 200 °C, about 7 wt % of the initial carbon was found on the catalyst surface in a form of water-insoluble polymeric products. The NMR $\{^1H\}^{13}C$ CPMAS examination of the products indicated that they were most probably formed by a substitution reaction between the 1,2-naphthoquinone and the aldehyde group of cinnamic acid as well as by polymerization of 1,2-naphthoquinone. Analogously to the phenol catalytic destruction (*12*), it can be speculated that the catalytic oxidation of Orange II also undergoes a heterogeneous−homogeneous free-radical mechanism. Active oxygen species, such as peroxyl radicals, responsible for oxidation are generated on the catalyst surface in addition to thermal reactions in the liquid phase. Thermally formed radicals are converted rapidly into the corresponding peroxyl radicals in the presence of oxygen (*17*). A simplified decay mechanism of oxidized dye radicals has been reported by Vinodgopal et al. (*18*).

Intermediates similar to ours were also found during ozonation of 1-phenylazo-2-naphthol (*19*) and Orange II (*10*) in photoassisted catalytic degradation on TiO_2 (*18*) as well

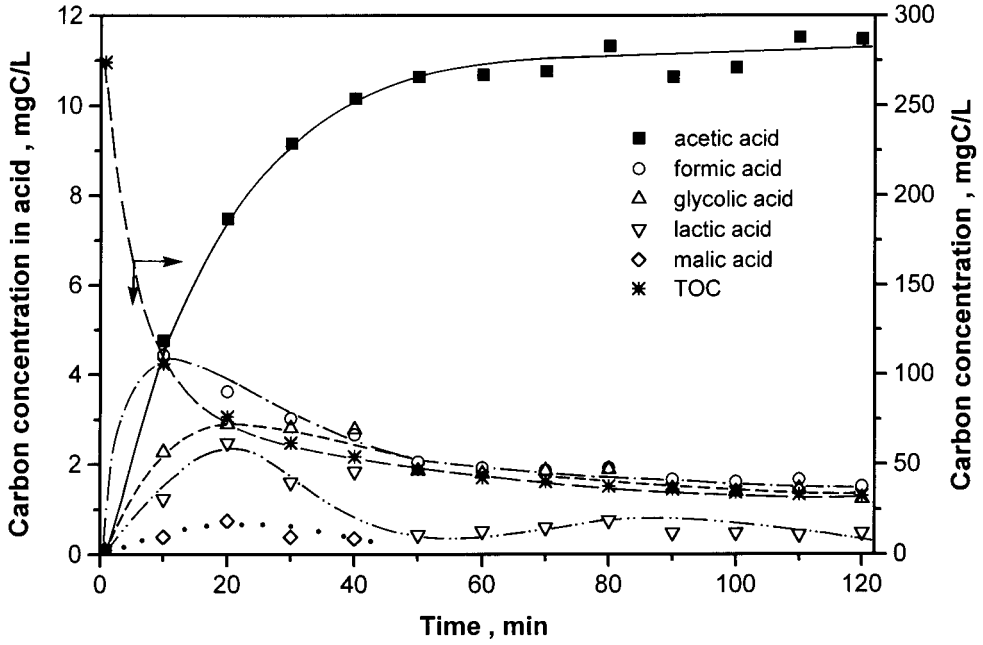

FIGURE 6. Distribution of organic acids in the catalytic experiment carried out at 190 °C and 10 bar of oxygen partial pressure.

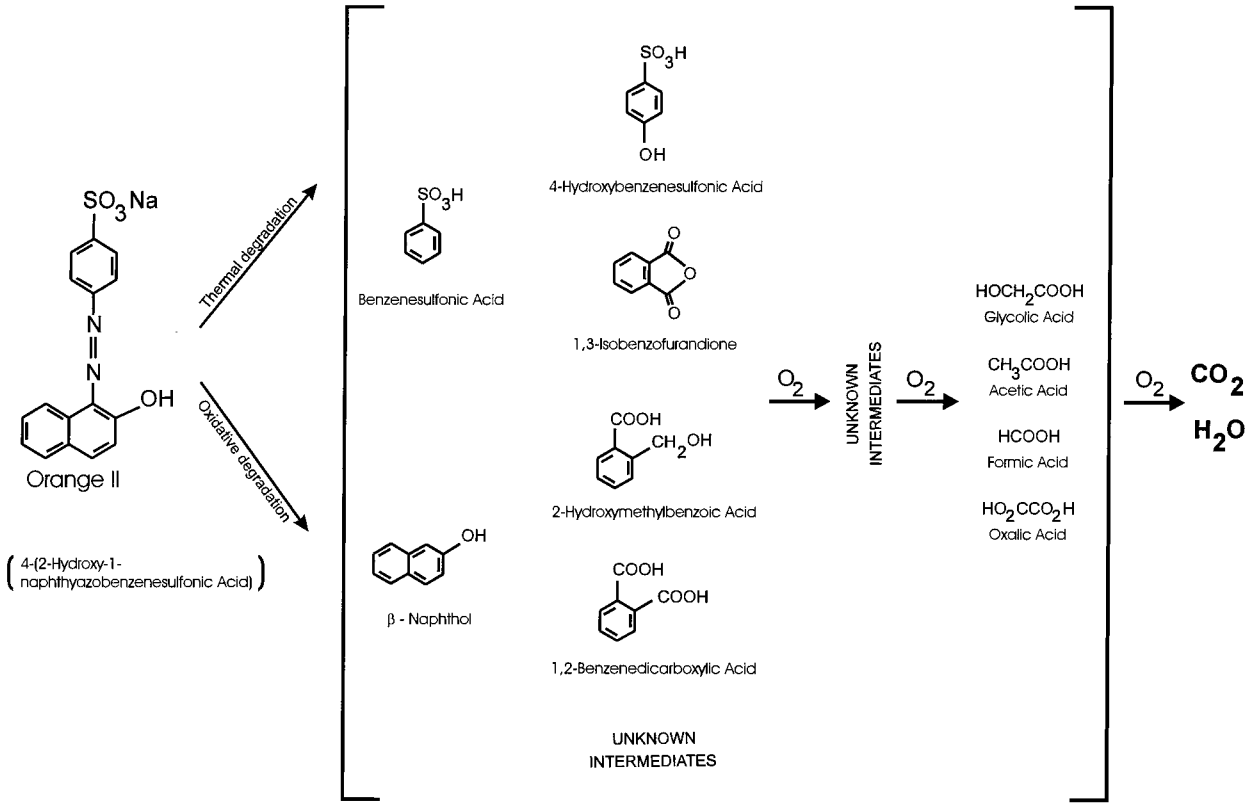

FIGURE 7. Simplified reaction pathway of Orange II oxidation in aqueous solution.

as in hydroxyl radical mediated degradation of azo dyes (*20*). These findings allow us to further speculate about the possible oxidation route. Mono- and dihydroxylated derivatives indicate that active oxygen species are involved in the reaction. The active oxygen species react with the azo linkage-bearing carbon of a hydroxy or an amine substituted ring. The resulting active oxygen adduct breaks down to produce a substituted phenyldiazene and a naphthoxy radical. Both of them are unstable and will react further with active oxygen species resulting in the aromatic ring degradation. The simplified reaction pathway of Orange II oxidation is schematically presented in Figure 7. Since benzene was not found as an intermediate product, our findings have not confirmed the route for benzene formation from phenyldiazene proposed by Spadaro et al. (*20*). The aromatic ring degradation leads obviously to the formation of acids that are the last intermediate products. The speculation discussed above is also supported by the appearance of hydroxylated aromatic intermediates reported by Devlin and Harris (*21*) and the progressive loss of dye chromophoric group observed in our investigation. Nitrogen from the dye chromophoric group is mostly released as a gas formed during

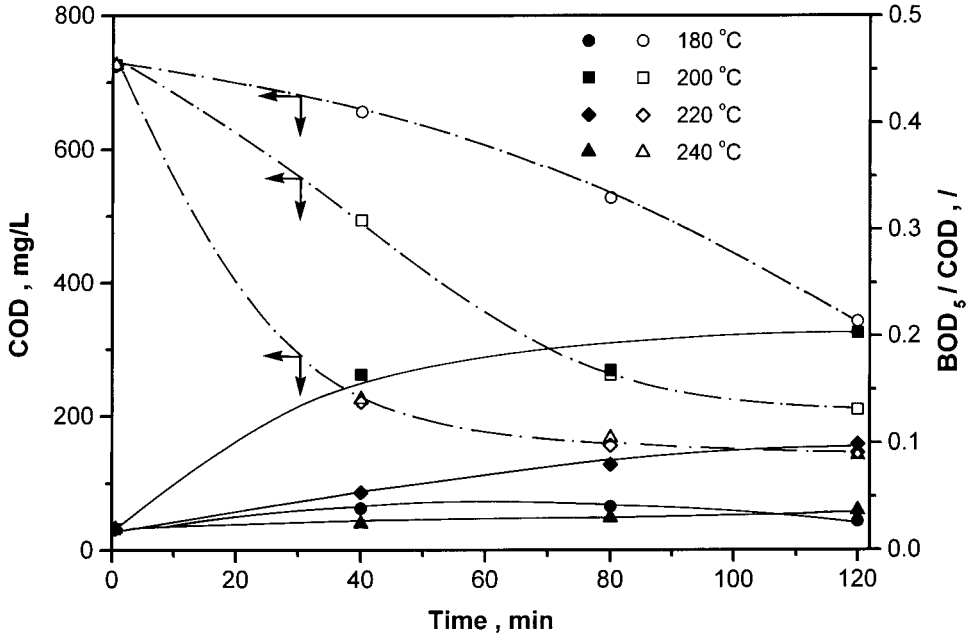

FIGURE 8. COD and BOD_5/COD values of effluent samples treated by noncatalytic oxidation as a function of time. (Each point represents an average of six measurements.)

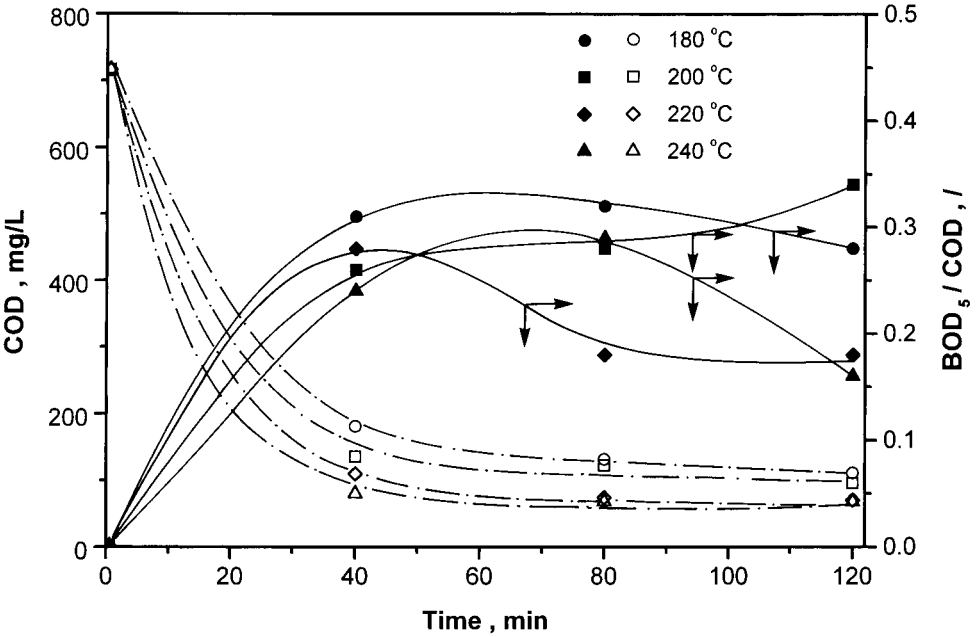

FIGURE 9. COD and BOD_5/COD values of effluent samples treated by catalytic oxidation as a function of time. (Each point represents an average of six measurements.)

the thermal degradation. Small quantities are also transformed into ammonia, which is usually a typical nitrogen product obtained during the wet oxidation of nitrogen-containing organic compounds. Nitrite and nitrate were not detected. Because the quantities of ammonia were found much lower than expected on the basis of complete nitrogen transformation into ammonia, the loss of the dye chromophoric group is first of all due to the loss of nitrogen and radical formation in the thermal degradation process. It should be added that ionic reactions involving electrophilic attack on the azo linkage are also possible (*19*). In this case, some rearrangements may occur (*22*).

Biodegradability. From the ecological point of view, it is necessary to assess the biodegradability of all waste streams leaving industrial processes; aerobic biodegradability is often accomplished by measuring the BOD, COD, and TOC values of a stream. Figure 8 shows the COD and BOD_5/COD values as a function of time for the experiments performed without the catalyst at four different temperatures. In Figure 9, these results are depicted for the experiments with the catalyst. In both cases, the BOD_5/COD ratio generally increases with the oxidation time, except in the catalytic experiments of 220 and 240 °C. The increase is caused by both the BOD increase and the COD reduction. One of the main reasons for the rapid initial increase in the BOD_5/COD value is the more pronounced formation of hydroxy and carboxy functional groups and denitrogenation during the initial steps of the oxidation process. The most significant increase in the BOD_5/COD ratio is exhibited in the oxidation at 200 °C and not in the experiments performed at higher temperatures as one

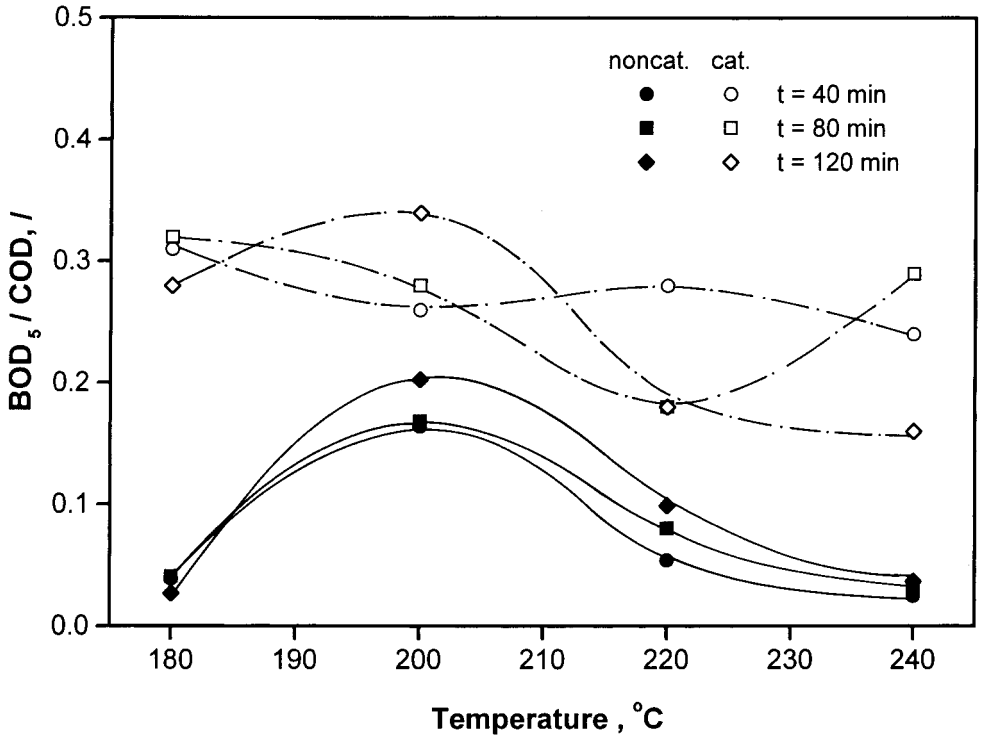

FIGURE 10. BOD_5/COD values of effluents from noncatalytic and catalytic oxidation as a function of temperature at different treatment times. (Each point represents an average of six measurements.)

might expect. There are two possible explanations. Higher BOD_5/COD ratio at lower temperature might be a consequence of the presence of aromatics, which are a better food source for the microorganisms. Molecules such as acetic acid offer less metabolic energy to aerobic cells. On the other hand, acetic acid is also known to act as an inhibitor when present in high concentrations.

Figure 10 represents the BOD_5/COD ratio vs temperature dependence for samples taken out from the reactor at different residence times. As can be seen, the maximum obtained with noncatalyzed oxidations disappears when the catalyst is present. One may expect that, by increasing the oxidation temperature, more amenable intermediates would be formed. However, we found with Orange II oxidation that increasing the reaction temperature, despite faster COD reduction, did not increase the aerobic biodegradability of the effluent. During the wet oxidation many intermediates were formed, and their distribution plays a decisive role in biodegradable properties of the Orange II solutions treated by oxygen. Relatively low aerobic biodegradation may be mostly attributed to the presence of intermediates that are less susceptible to microbial degradation or that act as inhibitors for the type of microorganisms we used. It may also result from a synergistic effect caused by different species. Since organic carbon is eventually found accumulated mostly in highly oxidized short-chain acids (acetic, oxalic, formic, glycolic, lactic, and malic acids), we assumed that they have a dominant impact on the aerobic biodegradability of treated effluents. The concentration−time dependence of acids identified during the noncatalytic experiments showed that at lower temperatures formic acid is found dominant while at higher temperatures acetic acid (Figure 5) represents a major contribution. On the other hand, in the catalytic experiments acetic acid was found in large quantities regardless of the temperature used (Figure 6). Taking into account the most pronounced formation of acetic acid, one may expect that aerobic biodegradability would increase with oxidation temperature and time, since we found that the BOD_5/COD ratio for acetic acid to be 0.55. However, one should be aware that the biodegradability of a mixture cannot be predicted only by knowing the BOD_5/COD for individual intermediates. This is demonstrated by assessing the following BOD_5/COD ratios for detected acids: 0.16 for formic, 0.55 for acetic, 0.33 for oxalic, 0.67 for glycolic, 0.26 for lactic, and 0.74 for malic. Using these results, in addition to the data on the structure/biodegradability relations from the literature, one is still not in position to further speculate on the aerobic biodegradability of treated samples mainly due to the possible synergistic effects.

A significant increase in the BOD_5/COD ratio (Figure 8) is exhibited in an experiment without the catalyst at 200 °C; the ratio increases in the whole range of residence time investigated. On the other hand, much better aerobic biodegradability properties of the treated solution were obtained (BOD_5/COD $\approx$ 0.3) after 40 min at 180 °C when the catalyst was employed (Figure 9). Although the readily biodegradable effluents were not reached (BOD_5/COD > 0.5), one can conclude by inspecting Figure 10 that the catalytic oxidation yields effluents more amenable to biological treatment. On the other hand, the results in Figure 10 imply that the intermediate products formed at higher temperature are less amenable to aerobic biological degradation. It is believed, however, that the decreased values of the BOD_5/COD ratio at higher temperatures are mainly the result of low metabolic values of formed acids.

Nonbiodegradability of the effluents from ozonation treatment of aqueous Orange II solutions has also been reported (*9*−*11*). They have all found a maximum either in BOD_5 or BOD_5/COD vs time behavior. In a 3-h ozonation treatment of aqueous Orange II solutions with the initial concentration of 1.44×10^{-3} mol/L, Takahashi et al. (*9*) found that the highest value of BOD_5/COD equals 0.2. In the experiments of Liakou and Lyberatos (*10*), the extreme value was 0.17 when the initial concentration of 0.5 g/L was used. Matsui et al. (*11*) observed a maximum value in BOD. They found the value of BOD_6/TOC ratio to be 0.53 when initial organic carbon in Orange II solution was 144 ppm. This value corresponds to approximately 0.2 of the BOD_5/COD

value. As one can see, the catalytic as well as the noncatalytic oxidations have yielded similar aerobic biodegradability improvements as ozonation.

Acknowledgments

The authors wish to thank the EU/GD-XII (Grant ERB CIPD CT94 0111) and the Slovenian Ministry of Science and Technology (Grant J2-6179) for their financial support.

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Received for review July 22, 1997. Revised manuscript received January 12, 1998. Accepted January 30, 1998.

ES970643N