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Enhancement of the biodegradability of model wastewater containing recalcitrant or inhibitory chemical compounds by photocatalytic pre-oxidation

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Abstract

m-Dinitrobenzene, diphenylamine and resorcinol, three aromatic compounds found inhibitory or recalcitrant to biological treatments, were chosen as model chemicals for this study on the integration of photocatalytic-biological treatments. The degradation of each of these compounds was achieved by ultraviolet photocatalytic oxidation, leading to the formation of intermediate compounds. The photocatalytic treatment was performed in a TiO_2 slurry reactor containing an aqueous solution of one of the three chemicals. The biodegradability of model wastewater treated photocatalytically was measured in terms of BOD_1/TOC. Intermediate compounds that appeared at early stages of the photocatalytic degradation of m-dinitrobenzene or diphenylamine seemed to be more inhibitory than the parent compounds but this was not the case for resorcinol. A substantial improvement in BOD_1/TOC could be achieved, but it required the mineralization of at least 80% of the organic carbon originally in the water. Microtox® toxicity results confirmed the BOD_1/TOC trends for diphenylamine.

Introduction

Industrial wastewater often contains chemical compounds that are either recalcitrant or inhibitory to microorganisms found in conventional biological treatments. m-Dinitrobenzene, diphenylamine, and resorcinol are among such organics [1]. Various industrial sectors employ these chemicals, but the dye and explosive industries use all of them; wastewater simultaneously containing m-dinitrobenzene, diphenylamine and resorcinol can therefore occur from these industries.

Currently, two strategies are employed for the removal of such recalcitrant organic compounds: phase transfer and oxidation [2, 3]. Among the phase transfer methods are adsorption on granular activated carbon, extraction and air stripping. Phase transfer technologies are becoming unpopular since they only result in the displacement of pollutant molecules from one phase to another. Oxidation Processes are an alternative for the destructive removal of organic compounds from wastewater. At present, ultraviolet light and ozonation treatments are utilized despite the fact that they may only result in a partial destruction of the target contaminants [4].

The coupling of ultraviolet light with an oxidant (O_3, H_2O_2 or O_2 + photocatalyst) is called an Advanced Oxidation Process (AOP) and potentially allows complete mineralization of organic carbon to carbon dioxide. UV-light/O_3 and UV-light/H_2O_2 are currently successfully used for wastewater decontamination [2]. The primary advantage of photocatalysis over other AOPs is that it requires near UV-light as opposed to radiation in the UV-C region. Photocatalysis therefore makes possible the use of solar radiation or of less onerous UV-A lamps for wastewater treatment.

Whereas complete mineralization of almost any compound (exceptions being cyanuric acid, the product of degradation of pesticides containing s-triazine rings such as atrazine [5] and chlorofluorocarbons [6]) can be achieved in slurry reactors with illuminated particles of TiO_2, an important drawback of photo-

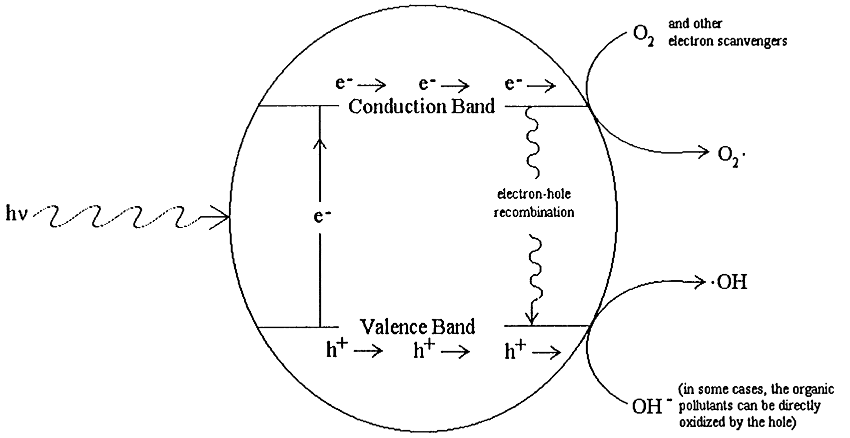

Figure 1. Primary events at the surface of the semiconductor catalyst when irradiated with near UV-light [21].

catalysis is that the operating costs are relatively high compared to those for a biological treatment. Since the oxidation of organics is proportional to electrical energy input, the complete mineralization of pollutants by photocatalysis can be very expensive. However, its use as a pretreatment for the enhancement of the biodegradability of wastewater containing recalcitrant or inhibitory compounds can potentially be justified if the intermediate products resulting from the reaction can be readily used by microorganisms [7-15]. If this is the case, there is, in principle, an optimum time for the photocatalytic treatment at which the recalcitrant or inhibitory chemicals have disappeared but biologically useful intermediate compounds are still present.

The objectives of this study therefore were to confirm the feasibility of photocatalytically degrading m-dinitrobenzene, diphenylamine and resorcinol and to determine if this technology was suitable as a pretreatment for the enhancement of the biodegradability of water containing these compounds.

Mechanisms of Photocatalysis

Photocatalysis involves the use of UV-light to excite a semiconductor catalyst, such as TiO_2, so that it can catalyze redox reactions with chemicals in aqueous solution. The mechanisms for the primary events occurring at the surface of the catalyst have been described elsewhere [4, 16–21] but will be briefly reviewed here.

The irradiation of TiO_2 with photons (hν) of energy equal to or greater than its bandgap results in the promotion of electrons from the valance band (VB) to the conduction band (CB) of the particle. The outcome of this process is a region of positive charge termed a 'hole (h^+)' in the valence band, and a free electron (e^-) in the conduction band (Figure 1).

Once this first excitation reaction has occurred, the hole and the electron can either recombine, leading to the release of heat, or migrate within the lattice and ultimately to the surface of the catalyst where they can participate in redox reactions.

The surface of TiO_2 is readily hydroxylated when in contact with moisture, meaning that both dissociated (OH^- and H^+) and molecular (H_2O) water are bound to it. Therefore, holes can be trapped by adsorbed hydroxide ions and molecular water to produce hydroxyl radicals ($\cdot OH$). The counterpart of these oxidation reactions has to be reductive reactions through which electrons are scavenged by oxidants such as oxygen, which results in the production of superoxide ion radicals ($O_2^{-\cdot}$). These radicals then undergo various reactions that may also result in the production of hydroxyl radicals [5, 6, 22–24]. Although hydroxyl radicals are believed to be primarily responsible for the oxidation of the organic pollutant molecules, there have been some reports of direct oxidation by valence band holes, before their trapping by OH^- and H_2O [19, 20, 25]. Moreover, the destruction of certain organic pollutants, including nitrogen-containing compounds, through a reductive pathway has been reported [25–31]. In the specific case of the photocatalytic degradation of aromatic compounds, it was observed that the degradation intermediates often initially were mono or polyhydroxylated species. Attack by hydroxyl radicals is, in these cases, the primary mode of oxidation.

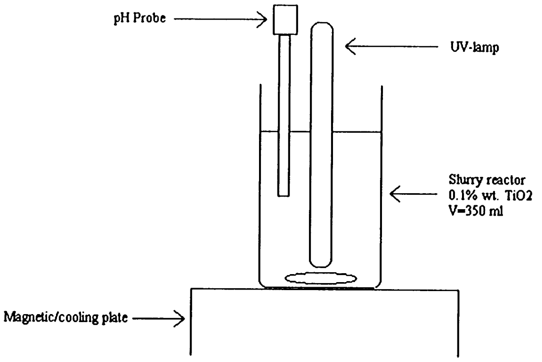

Figure 2. Photocatalytic reactor.

During this hydroxylation process, the substituents on the nucleus may or may not be split. The intermediate products obtained in this manner are often unstable, and their initial hydroxylation is usually followed by a rapid ring cleavage, resulting in aliphatic compounds that may contain one or several of the following functionalities: alcohol, aldehyde, ketone, amide and acid [6]. At low pollutant concentrations, these aliphatic intermediates contain an equal or smaller number of carbon atoms than the initial organics. Progressively, these aliphatic compounds are degraded. Ultimately, all the organic carbon initially present in the wastewater is converted to CO_2. As for any radical driven mechanism, the chemistry of heterogeneous photocatalysis is rather complex. Thus, the determination of specific photocatalytic degradation pathways requires careful observation since it depends on operating conditions such as pH, temperature, light intensity, presence of competing organic or inorganic compounds, mass transfer limitations and oxygen concentration.

Experimental Section

Materials

Photocatalytic treatment

Reagent grade m-dinitrobenzene, diphenylamine and resorcinol were obtained from Sigma Chemical Co., St-Louis, Missouri. De-ionized water was used to prepare solutions of these compounds. The photocatalyst was Degussa P25 TiO_2 (75% anatase, average primary particle size of 30 nm, approximately 55 m^2/g).

BOD tests

One capsule of Polyseed® bacteria (United-States EPA accepted BOD inoculum) re-hydrated in 500 ml of BOD water prepared according to the Standard Methods for the Examination of Water and Wastewater [32] was the seeding material. The Polyseed® was obtained from Fisher Scientific, Toronto, Ontario. In addition to the organic compounds resulting from the photocatalytic pretreatment of m-dinitrobenzene, diphenylamine or resorcinol, sodium acetate (99%) obtained from BDH (Toronto, Ontario) was used as a supplementary source of carbon at a concentration of 5 mg/l.

Photoreactor

Figure 1 shows the reactor used for the photocatalytic degradation of the recalcitrant or inhibitory compounds studied. It is a 500 ml Pyrex Berzelius beaker in which 0.1% by weight of TiO_2 was added to 350 ml of model wastewater. A 9 W actinic fluorescent lamp (Phillips PL-S9W/10) was used for the emission of photons with wavelengths in the UV-A region (primarily at about 365 nm). An intensity of 15 000 $\mu W/cm^2$ was measured at the UV-lamp surface. A cooling/magnetic plate was used to maintain a constant temperature of about 25 °C and to provide stirring. The pH was monitored with an Orion pH probe, model 250A. Reactions were started at a pH of 4.5 to 5.

Sample Analysis

Samples were retrieved from the photocatalytic reactor at various times during the course of an experiment and centrifuged at 6000 rpm for 10 min to separate the aqueous solution from the TiO_2. The composition was then analyzed using reverse phase C_{18} HPLC with UV detection at a wavelength of 275 nm. The eluent composition was 50:5:45 methanol: acetonitrile: water. The methanol and acetonitrile were of HPLC grade and the water was de-ionized with a Millipore Q System. At the end of a photocatalytic reaction, the Total Organic Carbon (TOC) content of the treated model wastewater was determined with an Astro 2001 UV-persulphate TOC analyzer. Ammonia was measured spectrophotometrically using a HACH (Toronto, Ontario) spectrophotometer and HACH procedure and chemical reagents for low range ammonia. Nitrite and nitrate were analyzed with a Dionex ion chromatograph equipped with an IONPAC AS4A-SC column and a Dionex CDMII conductivity detector. The elu-

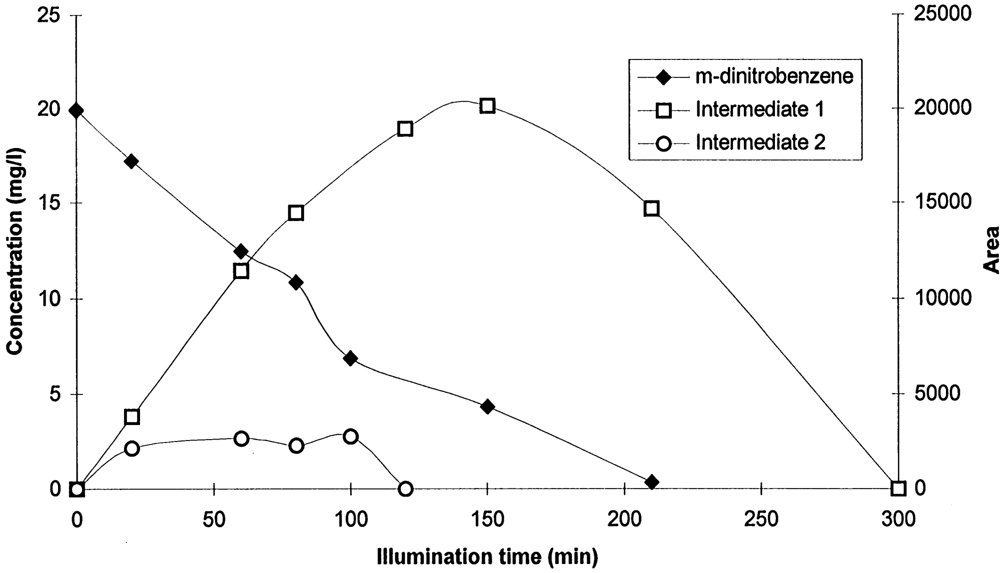

Figure 3. Photocatalytic degradation of m-dinitrobenzene initially at 20 mg/l.

ent was composed of 50:50 1.8 mm $NaCO_3$:1.7 mm $NaHCO_3$.

Assessment of the Biodegradability or of the Toxicity of the Samples

The efficacy of the photocatalytic treatment on the biodegradability was evaluated by measuring the one day Biochemical Oxygen Demand (BOD_1) and normalizing it with the amount of organic carbon that the microorganisms were fed with. For the BOD tests, 125 ml of treated or untreated model wastewater were mixed with 124 ml of BOD water, 50 ml of Polyseed® solution and 1 ml of a concentrated solution of sodium acetate (1500 mg/l). Dissolved oxygen concentrations were measured with an Orion DO meter, Model 810. In some cases, the relative toxicity was also measured by performing Microtox® tests (AZUR Environmental, Carlsbad, California). This technique involves the use of a bacteria, *Photobacterium phosphoreum*, which emits light. The Microtox® system measures the light output of the bacteria after they have been challenged by a sample of unknown toxicity and compares it to a control that does not contain toxic substances. A light output lower than the control indicates a toxic effect of the sample.

Results and Discussion

Photocatalytic Treatment

Initial experiments confirmed that it is possible to degrade m-dinitrobenzene, diphenylamine and resorcinol by photocatalysis. Figure 3 shows that the concentration of a solution of m-dinitrobenzene decreased from 20 to 0 mg/l in about 200 min when treated photocatalytically in the reactor illustrated in Figure 2. In addition, two unidentified intermediate organic compounds were detected in the HPLC analysis.

After the disappearance of the m-dinitrobenzene, one of the two intermediate products of degradation could still be detected, as seen on Figure 3. After 300 min of treatment, no chemicals were detectable by HPLC-UV analysis. However, TOC analyses in later experiments showed that organic compounds were still present, although not detectable by the HPLC-UV method.

After a treatment of 400 min, no organic compounds could be detected by TOC analysis, demonstrating that the full mineralization of m-dinitrobenzene is achievable by photocatalysis.

Photocatalysis was found to be the only mechanism responsible for the degradation of m-dinitrobenzene since no changes in its concentration were observed when it was treated for a period of 6 hours with UV-light only, with TiO_2 only, and with stirring only. Thus,

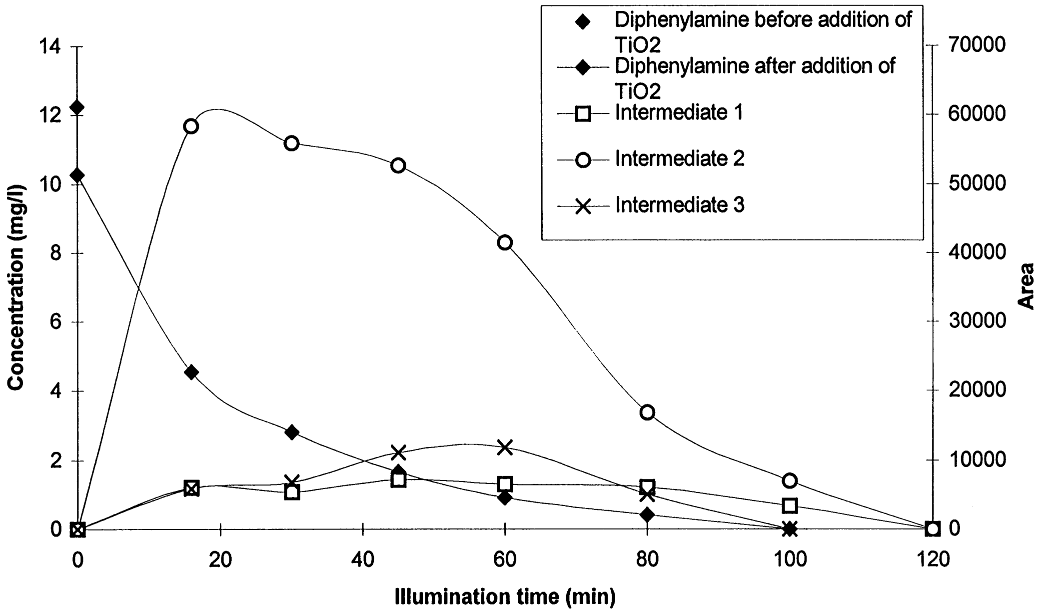

Figure 4. Photocatalytic degradation of diphenylamine initially at 12.3 mg/l.

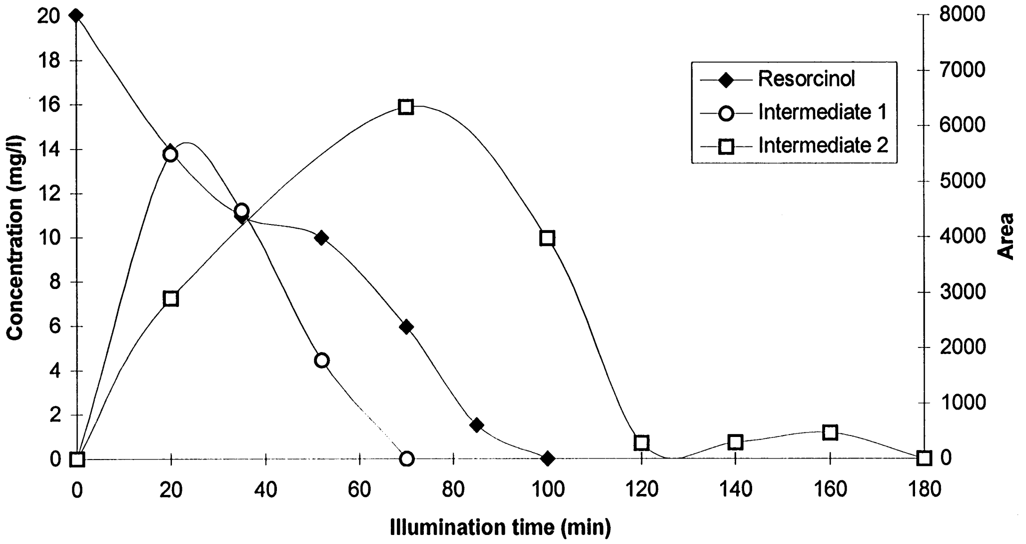

Figure 5. Photocatalytic degradation of resorcinol initially at 20 mg/l.

photolysis (direct attack of the compound by photons) did not play a role in its degradation.

Figure 4 shows that the concentration of a solution of diphenylamine decreased from 12.3 to 0 mg/l in about 100 min when subjected to a photocatalytic treatment. When TiO_2 was added to the original solution of diphenylamine, the concentration in the bulk of the aqueous solution dropped to about 10 mg/l, suggesting that diphenylamine strongly adsorbs onto the catalyst's surface. Since it is believed that most of the oxidation processes in photocatalysis are attributable to the attack of organic pollutants by hydroxyl radicals formed in the vicinity of the catalyst's surface [17, 22, 33], it is beneficial that the target compound be adsorbed to TiO_2.

Table 1. Toxic or inhibitory effect of the chemical compounds on the Polyseed® inoculum

	Concentration (mg/l)	BOD_5 (mg/l)	BOD_5/TOC
m-Dinitrobenzene	30.0	0	0
	15.0	0	0
Diphenylamine	30.0	0	0
	15.0	0	0
Resorcinol	30.0	0	0
	27.5	4.48	0.249
	15.0	5.15	0.525
	9.2	4.40	0.731

At least four intermediate compounds could be detected by HPLC-UV during the photocatalytic treatment of diphenylamine, the three most predominant are presented on Figure 4. These unidentified organic chemicals arise early in the photocatalytic process and require a treatment of about 20 min more than diphenylamine in order to be broken down to non-detectable compounds. As discussed later, the full mineralization of diphenylamine and its intermediate products of degradation was found achievable, but required more than six times the time required for the degradation of diphenylamine only.

Figure 5, confirms that resorcinol too can be degraded by photocatalysis. Its concentration decreased from 20 to 0 mg/l in about 100 min. At least two but probably three intermediate compounds could be detected by HPLC-UV. The two predominant ones are shown on Figure 5. Both intermediate compounds disappeared almost concomitantly with resorcinol. In addition, TOC analysis revealed that only small amounts of organic products other than resorcinol were present in solution at all times during the photocatalytic reaction, including after the complete disappearance of resorcinol. The TOC analysis also showed that the full mineralization of resorcinol is possible.

Effect of the Photocatalytic Treatment on Biodegradability

Effect of m-Dinitrobenzene, Diphenylamine and Resorcinol on Polyseed® Microorganisms

The first step for this study was to verify the recalcitrant and/or inhibitory nature of m-dinitrobenzene, diphenylamine and resorcinol. Measurements of BOD_5/TOC at different concentrations of pollutant compounds were conducted to indicate whether they are recalcitrant to biological attack or not [7, 11]. The results of these experiments are presented in Table 1. The Polyseed® microorganisms could not use m-dinitrobenzene nor diphenylamine, confirming their recalcitrant and/or inhibitory character at the concentrations studied. As the concentrations of resorcinol increased, the values for BOD_5/TOC decreased, indicating an inhibitory effect of that compound on the microorganisms.

Moreover, to verify if a source of carbon known to be easily utilized by Polyseed® microorganisms could be used in the presence of m-dinitrobenzene, diphenylamine and resorcinol, BOD_1/TOC tests were performed with 5 mg/l of sodium acetate ($NaC_2H_3O_2$) and various amounts of the three pollutant compounds. The results of these experiments are presented in Table 2.

Less sodium acetate was consumed by Polyseed® microorganisms when m-dinitrobenzene was present in the media, as indicated by the BOD_1 values that, for a constant amount of sodium acetate, were lower when m-dinitrobenzene was added. This suggests a toxic or inhibitory effect of m-dinitrobenzene on the microorganisms. Although diphenylamine was not used as a source of carbon by microorganisms, it did not appear to have a pronounced toxic effect on microorganisms, as shown by the BOD_1 values which are only slightly lower than the pure sodium acetate control, and which decrease very subtly with increasing concentrations of diphenylamine. Finally, it appears that small amounts of resorcinol could be oxidized by the microorganisms (as seen from the results of Table 1, and since BOD_1 is greater when both a small amount of resorcinol and sodium acetate are present than when sodium acetate is the only source of carbon). However, it had an inhibitory effect on microorganisms when present at concentrations greater than about 8 mg/l.

Effect of Photocatalysis on Biodegradability

BOD_1/TOC was measured to assess the effect of a photocatalytic treatment on the biodegradability of model wastewater containing either m-dinitrobenzene,

Table 2. Response of Polyseed® microorganisms to the presence of m-dinitrobenzene, diphenylamine or resorcinol. TOC includes 1.464 mg/l from sodium acetate.

	Concentration of pollutant (mg/l)	Organic carbon from the pollutant (mg/l)	Total Organic Carbon (mg/l)	BOD_1 (mg/l)	BOD_1/TOC
m-Dinitrobenzene	16.667	7.145	8.609	1.07	0.124
and 5 mg/l of sodium acetate	4.167	1.786	3.250	1.02	0.314
	0.000	0.000	1.464	1.50	1.025
Diphenylamine	12.696	10.813	12.277	1.35	0.110
and 5 mg/l of sodium acetate	9.113	7.762	9.226	1.62	0.176
	2.598	2.213	3.677	1.74	0.473
	1.991	1.696	3.160	1.73	0.547
	0.000	0.000	1.464	1.81	1.236
Resorcinol	31.250	20.453	21.917	1.18	0.054
and 5 mg/l of sodium acetate	20.833	13.635	15.099	1.24	0.082
	8.333	5.454	6.918	2.19	0.317
	0.000	0.000	1.464	1.50	1.025

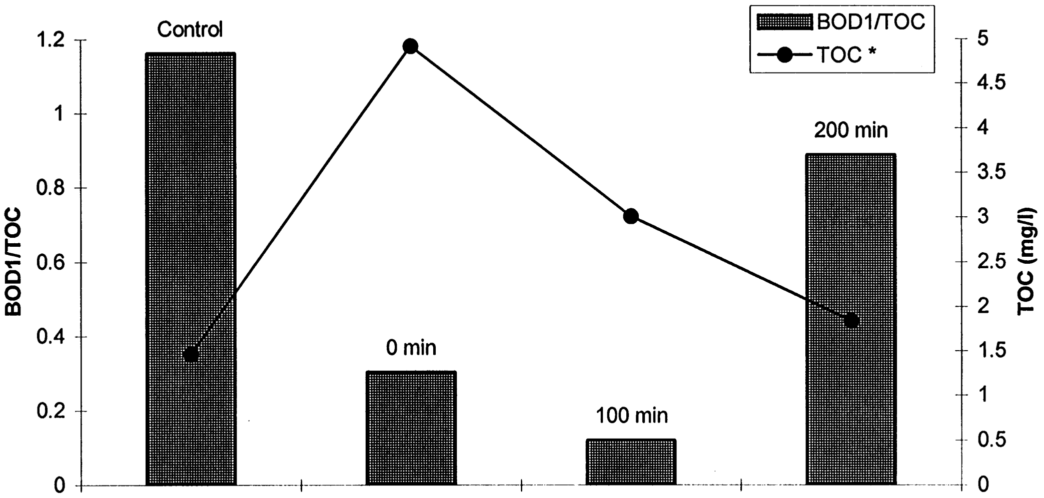

Figure 6. BOD1/TOC for m-dinitrobenzene initially at 20 mg/l treated photocatalytically. Length of pretreatment is shown in minutes. The control contained only sodium acetate and was not pretreated. * TOC values include a small amount of sodium acetate. This amount is the same in all four cases shown here.

diphenylamine or resorcinol. A small constant amount of sodium acetate (no more than 40% of the TOC of the initial model wastewater) was utilized for these experiments as a readily usable additional source of carbon for the Polyseed® bacteria. Figure 6 shows the values of BOD_1/TOC obtained for 20 mg/l solutions of m-dinitrobenzene treated by photocatalysis for various periods of time.

After 100 min of photocatalytic treatment, about 5 mg/l of m-dinitrobenzene remained in solution and both intermediate compounds identified by HPLC were present. Intermediate compounds therefore appear to be responsible for an increase in inhibition. The low value of BOD_1 after 100 min of treatment compared to the sodium acetate control, or even to the initial solution of m-dinitrobenzene, shows that the early intermediate compounds resulting from the degradation of m-dinitrobenzene are even more toxic or inhibitory to the Polyseed® microorganisms than the parent organic chemical.

Almost no m-dinitrobenzene could be detected after 200 min of treatment but intermediate number

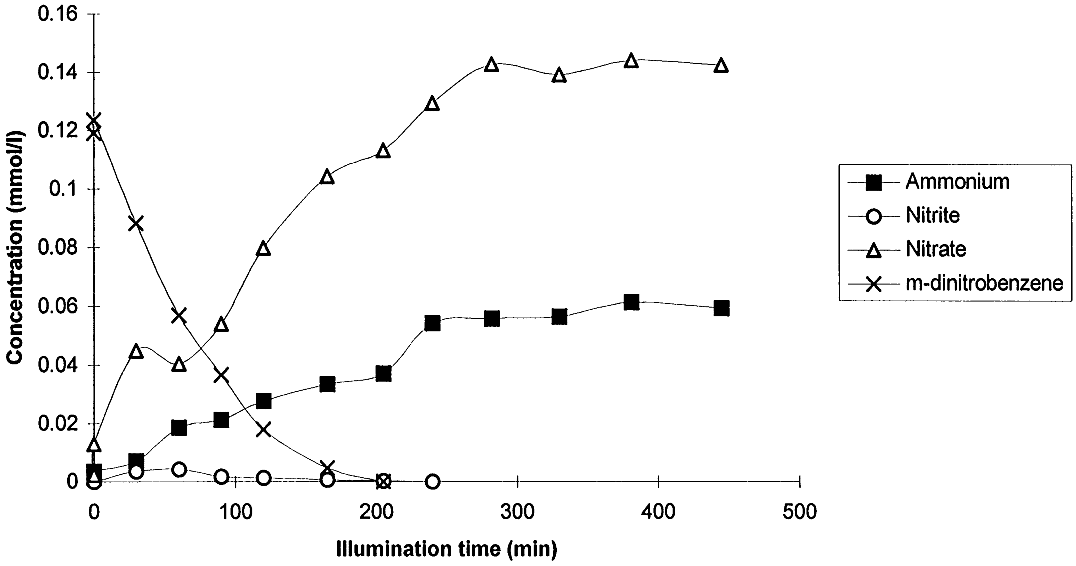

Figure 7. Production of inorganic nitrogen from the photocatalytic treatment of m-dinitrobenzene initially at 20 mg/l.

1 was still present in the media. The TOC level at that time was only 0.90 mg/l, which represents 10.5% of the carbon initially in solution. The BOD_1/TOC after 200 min of treatment has improved considerably compared to before the photocatalytic treatment but since very little organic carbon is left in the media at that time, this improvement is probably simply attributable to the disappearance of most of the organic carbon, regardless of its nature. Moreover, since m-dinitrobenzene is relatively resistant to photocatalytic oxidation, the intermediate compounds resulting from its degradation are oxidized themselves at a somewhat higher rate such that when m-dinitrobenzene has been completely degraded, almost no other source of carbon is still present in the aqueous media. Thus, photocatalysis is effective at degrading m-dinitrobenzene but there only are very low amounts of organic carbon that remain in the media after its complete disappearance. This residual carbon has a very small inhibitory or beneficial impact on microorganisms. Due to this fact, photocatalysis does not appear to be useful for increasing biodegradability of m-dinitrobenzene, although it can result in a reduction of inhibition.

The nature of the inorganic ions produced from the degradation of m-dinitrobenzene may have an impact on the biological treatment and on wastewater quality. Figure 7 presents a time evolution of inorganic nitrogen compounds produced from the degradation of m-dinitrobenzene in the photocatalytic treatment.

The first observation that is obtained from Figure 7 is that the mass balance on nitrogen can be closed relatively well. Of the 0.238 mmol/l of organic nitrogen that were present initially, none was recovered as nitrite, 61% was present as nitrate and 29% was present in ammonium ions after 400 min of treatment. An interesting point to note is that it only is after about 380 min of photocatalytic treatment that most of the initial organic nitrogen is found in an inorganic form. Since all m-dinitrobenzene has long disappeared at that time, a significant amount of nitrogen was contained in organic compounds other than m-dinitrobenzene between 200 and 380 min. This is also true before the complete disappearance of m-dinitrobenzene since all the initial nitrogen cannot be accounted for in m-dinitrobenzene, nitrite, nitrate and ammonium ions between times 30 min and 200 min. Such a lag in the release of inorganic nitrogen after the disappearance of the parent compound has been reported elsewhere [34]. This suggests that at least part of the m-dinitrobenzene is degraded by attack of oxidizing species directly on the ring. Other interesting aspects of these results are that nitrite seemed to be rapidly oxidized to nitrate once released in the aqueous media. Since nitrite may inhibit microbial growth, its rapid oxidization to nitrate in the photocatalytic environment is advantageous. Ammonium ions were not easily oxidized in the photocatalytic treatment, which has been observed previously [27, 35]. Finally, it is interesting to note that ammonium ions are formed from a compound that initially contains two nitro groups. Only the reduction of these nitro groups can explain this last observation; reduction rather than oxidation is therefore partly responsible for the photocatalytic degradation of m-dinitrobenzene. Previous studies have shown that reduction has a significant role in the mineralization of nitrogen-containing compounds [25-31]. On the other hand, it was also shown that highly hydroxylated products often result from the photocatalytic degradation of organic nitrogen-containing compounds [26, 36, 37]. The detection of stable intermediates that were more hydroxylated than the parent compounds showed the importance of oxidation by $OH^{\cdot}$ in the process of mineralization. Therefore, the results shown here are in accordance with previous findings which showed that both oxidation and reduction contribute to the degradation of organic-nitrogen containing compounds.

The BOD_1/TOC of treated solutions of diphenylamine initially at 10.7 mg/l are presented on Figure 8. After 50 min of treatment, only about 0.43 mg/l of diphenylamine remained in solution and all three intermediates detected by HPLC-UV were present. At that stage of the reaction, the model wastewater's biodegradability was lower than before any treatment. If the photocatalytic degradation is pursued for an additional 50 min, diphenylamine is no longer in the media but all three intermediates are still detectable. At that stage of the process, the biodegradability of the model wastewater slightly increased compared to its initial value. If treated for a total time of 120 min, no chemical compound could be detected by HPLC-UV. The TOC at that time was 1.41 mg/l, which represents 15.4% of the carbon initially in solution. The biodegradability in terms of BOD_1/TOC increased by 110% at that stage of the treatment. This indicates that the organic carbon remaining in solution after 120 min of treatment is less toxic or recalcitrant than diphenylamine. However, the biodegradability for the sodium acetate control was 1.6 times higher than for the model wastewater treated for 120 min. This indicates that the organic carbon that remained in solution after 120 min of treatment was not as readily usable than sodium acetate, still had an inhibitory effect on the microorganisms, or was in a more oxidized state than sodium acetate, thus requiring less O_2 to be mineralized by microorganisms. The results shown on Figure 8 can therefore not confirm the complete removal of the inhibitory nature of the solution, or of its improved biodegradability by photocatalytic treatment. However, a reduced toxicity of the treated solution compared to the initial model wastewater is observed.

The nature of the inorganic nitrogen compounds released by the photocatalytic degradation of 11.1 mg/l of diphenylamine was also assessed. It was found that of the initial 0.0656 mmol/l of organic nitrogen that were present, none was in the form of nitrite, 14% was recovered as nitrate and 86% was present in ammonium ions after 690 min of treatment. Figure 9 presents these results.

Ammonium ions are the predominant form under which nitrogen appears from the photocatalytic treatment of diphenylamine. This result has been previously observed during the photocatalytic degradation of other organic compounds containing secondary amines [27]. This suggests further reduction rather than oxidation of the amine function of diphenylamine (or its nitrogen containing intermediates). The lag period between the disappearance of diphenylamine and the full recovery of the initial nitrogen in an inorganic form was extremely long, taking approximately 630 min. Before that time, some nitrogen had to be included in organic molecules other than diphenylamine. This residual organic carbon therefore took 630 min before being completely mineralized, confirming previous work which showed that residual organic carbon is resistant to photocatalytic oxidation [25].

The biodegradability of solutions of diphenylamine initially at a concentration of 15 mg/l and treated for various periods of time were also assessed by Microtox® toxicity tests. The results of these experiments are presented on Figure 10. This method uses luminescent bacteria to estimate the EC_{50} of samples of water, where EC_{50} is the concentration of wastewater at which the light output from the bacteria is reduced by 50%. Concentration is expressed in% volume of the sample, which means that the closer the result is to 100, the less toxic the sample is.

The trend shown by this figure for reduction of toxicity versus time of treatment is similar to the trend in increase of biodegradability shown by the BOD_1/TOC tests: the toxicity initially increases, presumably because of the more toxic nature of the newly formed intermediate compounds, then it starts to decrease slightly as the concentration of intermediates detectable by HPLC-UV significantly decreases. Finally toxicity decreases drastically at 120 min when no compounds can be detected by HPLC-UV, but while there still is residual organic carbon in the media. The reduction in toxicity measured with

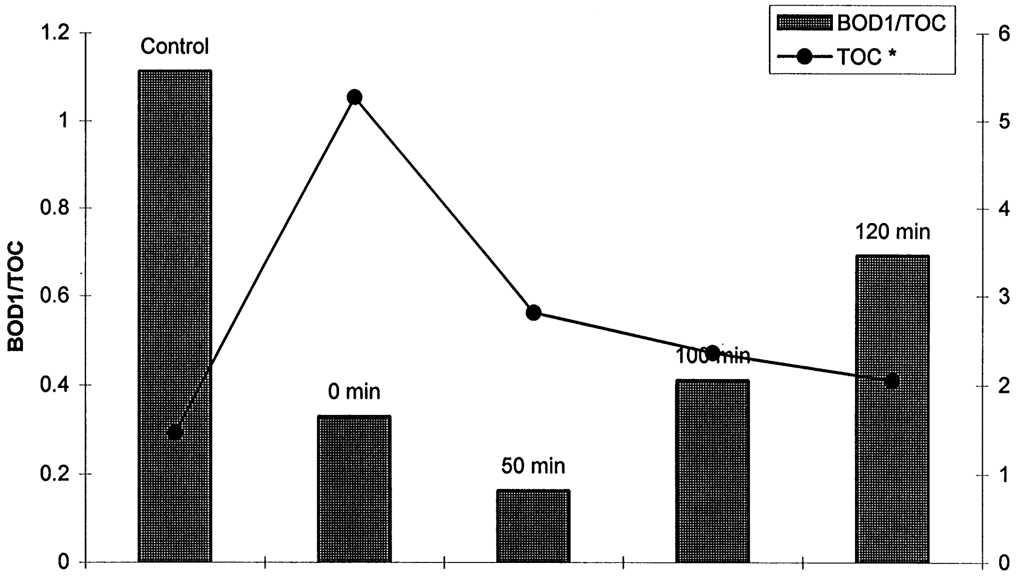

Figure 8. BOD1/TOC for diphenylamine initially at 10.7 mg/l treated photocatalytically. Length of pretreatment is shown in minutes. The control contained only sodium acetate and was not pretreated. * TOC values include a small amount of sodium acetate. This amount is the same in all five cases shown here.

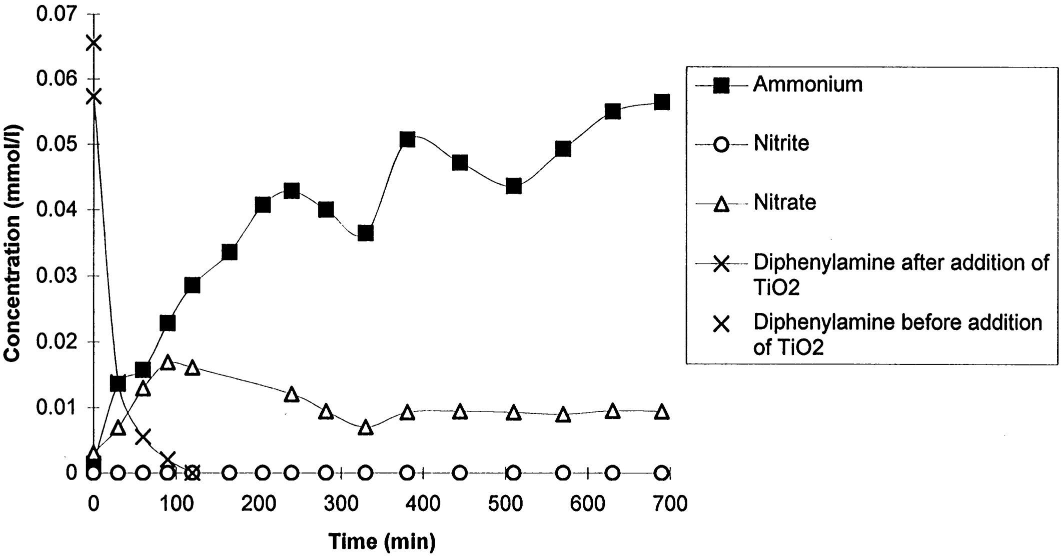

Figure 9. Production of inorganic nitrogen from the photocatalytic treatment of diphenylamine initially at 11.1 mg/l.

Microtox® is much more dramatic than the improvement in biodegradability measured by BOD_1/TOC. This can be attributed to the much higher sensitivity of the pure culture used to perform Microtox® analysis compared to the mixed culture utilized for the BOD_1 tests. As reported by King et al. [38], Microtox® tests are likely not the best suited methods to assess the biodegradability of wastewater in biological treatments such as activated sludge due to their high sensitivity to certain compounds. Results from BOD_1/TOC tests are of greater significance since the response of a mixed culture to a multicompound wastewater is more representative of the situation of a biological treatment such as an activated sludge.

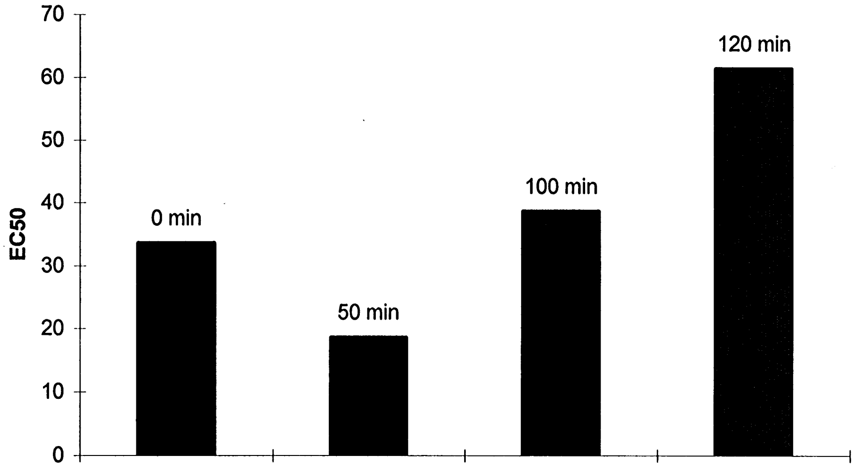

Figure 10. Assessment of toxicity with Microtox for samples of diphenylamine initially at 10.7 mg/l treated by photocatalysis for various periods of time.

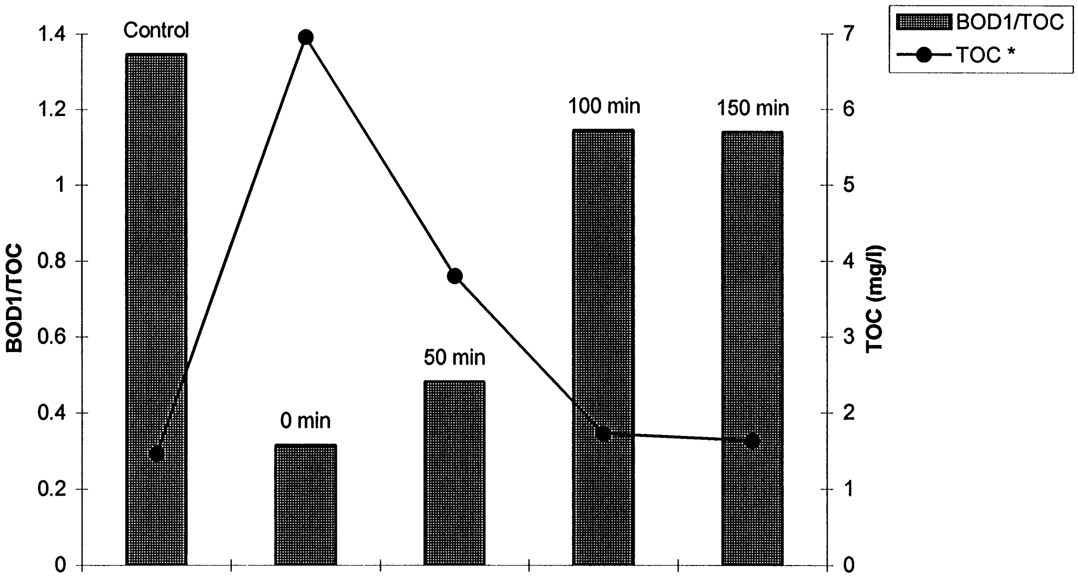

Figure 11. BOD/TOC for resorcinol initially at 20 mg/l treated photocatalytically. Length of pretreatment is shown in minutes. The control contained only sodium acetate and was not pretreated. * TOC values include a small amount of sodium acetate. This amount is the same in all five cases shown here.

Presented in Figure 11 are the results of a photocatalytic treatment on the biodegradability of solutions of resorcinol initially at 20 mg/l. After only 50 min of treatment, the biodegradability of the model wastewater has increased by 52%, and BOD_1 is comparable to the sodium acetate control. After 100 min of treatment, the model wastewater's biodegradability is as high as 85% of the control's biodegradability, which represents an increase of 260% compared to its initial value when no treatment was applied. At that stage of the process, the resorcinol concentration had been just reduced below the detection limit of 0.25 mg/l. Only 0.65 mg/l of organic carbon was still in solution at that time, which represents 5.0% of the organic carbon initially in solution. Similarly than for m-dinitrobenzene, the intermediate compounds resulting from the degradation of resorcinol are oxidized themselves at a rate such that when resorcinol has been completely degraded, almost no other source of carbon is still present in the aqueous media. Again, the detrimental or beneficial effect on the microorganisms of such small amounts of organic carbon is difficult to measure; the observed improvement in biodegradability may therefore simply be attributable to the disappearance of resorcinol.

Conclusions

This study has confirmed that the degradation of m-dinitrobenzene, diphenylamine and resorcinol is possible by photocatalysis. The full mineralization of all three compounds has also been observed.

Inorganic nitrogen in the form of both ammonium ions and nitrate is produced during the degradation of m-dinitrobenzene and diphenylamine. The production of significant amounts of ammonium ions suggests that reduction has an important role in the degradation of these two nitrogen-containing organics.

The photocatalytic treatment of model wastewater containing m-dinitrobenzene or diphenylamine initially produced an increase of toxicity. Further treatment lead to reduced levels of toxicity compared to the initial solutions. In the case of model wastewater containing resorcinol, no initial increase in toxicity was observed but rather, the level of toxicity was reduced shortly after the beginning of the photocatalytic treatment. For solutions of m-dinitrobenzene or resorcinol, the increase in BOD_1/TOC with time of treatment was mostly attributable to the mineralization of almost all the organic carbon. Thus, although reduced levels of inhibition of solutions of m-dinitrobenzene and resorcinol were obtained by photocatalysis, the treatment did not improve the biodegradability of these solutions. Significant amounts of organic carbon remained in solution after the complete removal of diphenylamine (approximately 15% of the original content). Thus, the improved value of BOD_1/TOC obtained after the removal of diphenylamine by photocatalysis could indicate either a reduced toxicity or an improved biodegradability of the solution. However, since the values of BOD_1/TOC of solutions of diphenylamine treated photocatalytically did not reach levels comparable to those of sodium acetate controls, it is possible that the treated solutions still had some inhibitory effect on the microorganisms. These lower values of BOD_1/TOC obtained for treated solutions of diphenylamine compared to sodium acetate controls could also be explained by the fact that the organic compounds resulting from the photocatalytic treatment were not as readily biodegradable as sodium acetate, or were in a more oxidized form than sodium acetate, thus producing a lower biological oxygen demand.

The results presented in this study support the conclusion [7] that the effects of oxidative pretreatment can not be predicted a priori without much detailed mechanistic and kinetic studies on both the pretreatment and biotreatment processes.

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