



Radiolytic degradation and toxicity changes in γ -irradiated solutions of 2,4-dichlorophenol

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Abstract

Preliminary investigations of a petroleum industry wastes with high concentrations of phenols and chlorophenols have shown that irradiation with electron beam results in the efficient destruction of specific organic compounds. In this study the degradation of 2,4-dichlorophenol (2,4-DCP) was studied using a ⁶⁰Co gamma source. The determination of reaction by-products was carried out with HPLC, ion chromatography with various detectors, GC/MS and total organic carbon analyzer. The toxicity was measured with bioluminescence test Microtox[®]. Studies of products of 2,4-DCP radiolysis at initial concentration level 20–50 mg/l have shown that with increased radiation dose degradation proceeds with a stepwise dehalogenation, through the formation of dihydroxybenzenes followed by the formation of non-aromatic carboxylic acids. The transient formation of dihydroxybenzenes resulted in an increase in toxicity at low doses up to 1 kGy. Even at a dose of 20 kGy, not more than about 20% mineralization was observed. The efficiency and mechanism of 2,4-DCP degradation is affected by the presence of scavengers of hydroxyl radical and hydrated electrons such as nitrate or bicarbonate.

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Keywords: Radiolysis; 2,4-dichlorophenol; Gamma irradiation

1. Introduction

The permanent threat to natural environments, resulting from industrial activity and municipal infrastructures, focuses our continuing attention on the development of efficient technologies for the removal of anthropogenic pollutants from the environment. Although various technologies are being developed, radiation technology in environmental cleanup has already found several advantageous practical applica-

tions (Borrely et al., 1998; Cooper et al., 1998; Pikaev, 2000; Rippon, 1999). An economic analysis has been reported for the ozone/electron beam process for ground water remediation, where the addition of ozone improves the efficiency by the elimination of the reducing species formed simultaneously with the OH[•] free radicals (Gehring and Eschweiler, 1999). The practical usefulness of several routinely utilized technologies such as air stripping, biological degradation, or adsorption on activated carbon has limitations for different organic compounds present, for instance, in effluents from petrochemical industry.

Numerous research groups have recently reported studies on the radiolytic decomposition of organic pollutants such as chlorinated benzaldehydes (Bekbölet

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and Getoff, 1999), trichloroethane and perchloroethylene (Gehring and Matschiner, 1998; Mucka et al., 1999), hydroxybenzoate and hydroxybenzoic ethyl ester (Swoboda and Solar, 1999), EDTA (Krapfenbauer and Getoff, 1999), atrazine (Angelini et al., 2000; Leitner et al., 1999), several pesticides (Dessouki et al., 1999) and polychlorinated biphenyls (Mucka et al., 2000a, b).

Several recently published papers also deal with the practical applications of this technology in pilot installations, e.g., for degradation of PCB in transformer oil (Chaychian et al., 1999), purification of waste water during molasses processing (Gehring and Fiedler, 1998), radiolytic elimination of organochlorine in pulp mill effluent (Taghipour and Evans, 1996) electron beam purification of water from dyes (Pikaev et al., 1997) and treatment of industrial effluents (Duarte et al., 2000; Rela et al., 2000).

Phenolic compounds, and especially chlorophenols, are one of the most common anthropogenic pollutants found in natural waters and wastes, as they are used in the production of biocides, dyes and drugs, and they are formed during paper production, and, the disinfection of tap water by chlorine or chlorine dioxide. Numerous papers have been published on the radiolytic degradation of chlorophenols, mostly with various monochlorophenols (Bettoli et al., 1998; Getoff and Solar, 1986, 1988; Kovacs et al., 1997; Schmid et al., 1997; Zona et al., 1999). Few papers deal with the more highly substituted chlorophenols (Fang et al., 1998; Taghipour and Evans, 1997; Trojanowicz et al., 1997; Zona et al., 1999).

Among the chlorophenols 2,4-dichlorophenol (2,4-DCP) is especially toxic and resistant towards biodegradation (Ikehata and Nicell, 2000). In our initial studies on radiolytic degradation of 2,4-DCP (Drzewicz et al., 1999; Trojanowicz et al., 2000), we have developed an HPLC method for the analysis of irradiated solutions, examined the effect of pH on 2,4-DCP irradiation and the products formed, and, the effect of the presence of several scavengers on the destruction efficiency and the reaction by-products of 2,4-DCP irradiation at different doses.

The goals of this study were to investigate the effects of initial concentration and the effect of dose on the destruction of 2,4-DCP; to examine in more detail the effect of the presence of nitrate at different concentration during irradiation; and, to examine the changes of toxicity in irradiated 2,4-DCP solutions.

2. Experimental

2.1. Apparatus

The HPLC was a Perkin-Elmer system, consisting of an isocratic pump model LC-250, UV/VIS detector

model LC-95 and integrator LC-100. UV detection at 280 nm, and a reversed phase column, Intersil ODS-2 (4.6 × 250 mm) 5 μm from Chrompack, were used.

The ion-chromatographic determinations of chloride were performed using DX-500 chromatograph from Dionex, equipped with electrochemical anion self-regenerating suppressor model ASRS I, conductivity detector and AG11 guard column with analytical column IonPac AS11.

The irradiation was carried out with a Russian γ -irradiation source "Issledovatel" with ^{60}Co , dose rate 4 kGy/h and mean energy 1.25 MeV or with Gammacell 220 (Canada) with a dose rate of 6.85 kGy/h. Aqueous solutions of 2,4-DCP were irradiated in 100 ml glass conical flasks without deaeration. The pH of the irradiated solutions was adjusted with NaOH or H_2SO_4 solutions.

Total organic carbon (TOC) measurements were carried out using a Shimadzu TOC Analyzer model 5000A. GC/MS measurements were carried out using Varian gas chromatograph model Star 3400 CX coupled to mass spectrometer Saturn-3 equipped with a capillary column DB-1.

2.2. Reagents

Phenol (P), monochlorophenols (CP), and 2,4-DCP were purchased from Aldrich. For the preparation of HPLC eluents solvents for chromatography from Merck were used. Triply distilled water from Milli-Q (Millipore) was used for preparation of eluents and other solutions.

For reversed phase separations, an eluent containing 2 g/l citric acid in a mixture of water, acetonitrile and methanol in the volume ratio 40:30:30 was used. The ion-chromatographic determination of chloride was carried out with gradient elution with the following program: 2.5 min 0.5 mM NaOH, 3.5 min 0.5–0.5 mM NaOH, 12 min 5.0–38.25 mM NaOH. Eluents were degassed using ultrasonic bath.

For preconcentration of the investigated analytes, 500 mg BAKERBOND SPE phenyl microcolumns from Baker (Gross-Gerau, Germany) were used.

2.3. Preconcentration procedure

The SPE columns were rinsed with two 3 ml portions of methanol and water. The pH of the preconcentrated solution was adjusted to 2.0 with HCl and solid sodium chloride was added to a total concentration of 25 g/100 ml. After the sorption from the sample solution, the column was rinsed with 5 ml 10 mM HCl and dried for 5 min purging with a stream of air. Preconcentrated analytes were eluted with 1 ml portion of methanol.

3. Results and discussion

3.1. Effect of dose on the efficiency of 2,4-DCP decomposition

On irradiation of aerated aqueous solutions, two main products of water radiolysis, the hydroxyl radical OH^\bullet and hydrated electrons e_{aq}^- , are formed. The latter are scavenged by oxygen with simultaneous formation of HO_2^\bullet and $\text{O}_2^{\bullet-}$. It was shown previously, for 4-chlorophenol (4-CP), that these radicals do not participate in the radiolysis of 4-CP (Stafford et al., 1994). Therefore, it was expected that the decomposition of 2,4-DCP would mainly be due to reactions with the hydroxyl radicals. A complete decomposition of 2,4-DCP at a concentration level of $50 \mu\text{M}$ (8.15 ppm) has been reported earlier at a radiation dose of 0.5 kGy with about 80% of release of inorganic chloride, while 100% dehalogenation was obtained at 1 kGy (Zona et al., 1999). Others have reported complete dehalogenation during irradiation of 30 ppm 2,3-DCP solutions at a dose as large as 30 kGy (Taghipour and Evans, 1997). In both cases γ -irradiation was used.

Therefore, in these studies the radiolysis of 2,4-DCP was studied at different initial concentrations of the chlorophenol (Fig. 1). At a dose of 1 kGy, in neutral aerated solutions, 20 mg/l of 2,4-DCP was decomposed almost completely, while in solutions of 50 mg/l only 40% was observed by HPLC. Zona et al. (1999) have reported that a 50% decomposition of 8.15 mg/l of the 2,4-DCP was observed at 0.11 kGy. Using ion chromatography, it was shown that in both cases the yield of inorganic chloride is almost half of that expected from the decomposition of the parent compound. These results corroborate those of Drzewicz et al. (1999), where they showed that the chloroorganic compound that required the greatest dose was 4-CP. Likewise, they also reported that the pH of irradiated solution significantly affected the efficiency and the radiolysis products of 2,4-DCP at doses up to 1 kGy. A complete degradation of 2,4-DCP at 50 mg/l can be achieved with doses ≥ 10 kGy.

An investigation of the degree of mineralization of irradiated 2,4-DCP solutions by measurements of TOC was carried out. These results suggested that even at a dose of 20 kGy, complete mineralization was not achieved (approximately 20% was not mineralized), Fig. 2. These results are similar to data reported recently for measurements of DOC for several different chlorophenols (Zona et al., 1999). The degree of mineralization, of irradiated solutions, can be reduced by the addition of strong scavengers of the hydroxyl radicals, such as nitrite ion (Fig. 2).

The major reaction by-products from the radiolysis of 2,4-DCP after dehalogenation were determined mostly with high-performance ion chromatography with con-

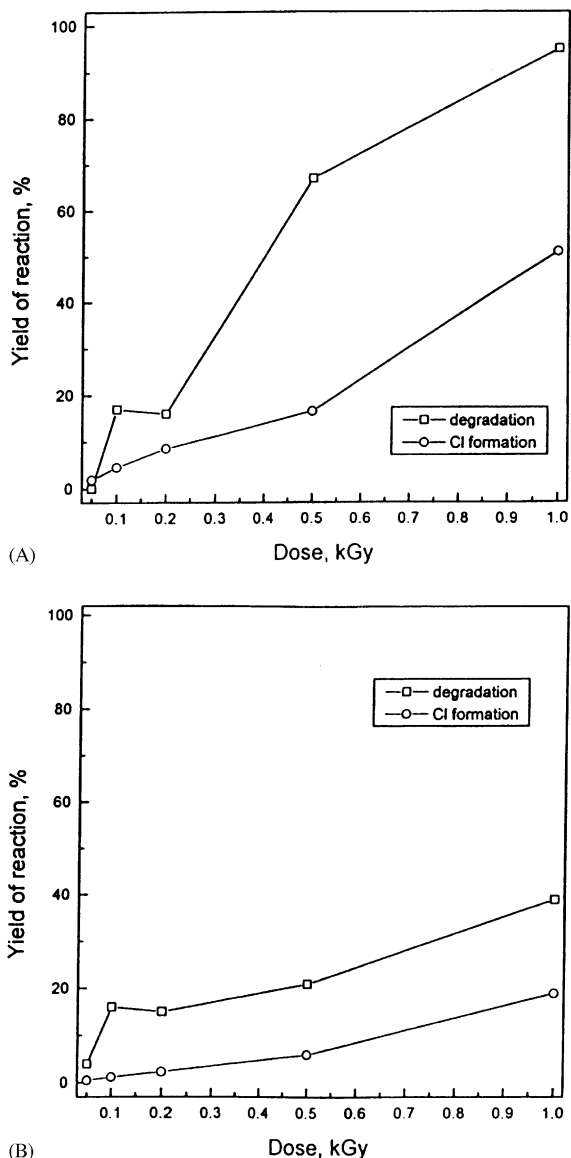


Fig. 1. Effect of dose on the yield of 2,4-DCP decomposition and inorganic chloride formation for the irradiation of 20 ppm (A) and 50 ppm (B) aerated solutions of initial pH 7.0.

ductivity detection. This method allows the determination of inorganic anions as well as anions of simple carboxylic acids as shown in Fig. 3 for a synthetic mixture. In earlier studies of the radiolysis of monochlorophenols, it was shown that although the yield of degradation depended essentially on the position of chlorine atom relative to OH in the molecule (Schmid et al., 1997), the degradation in steady-state radiolysis initially formed various hydroxybenzenes (phenol, catechol, resorcinol, hydroquinone, hydroxyquinone) (Getoff

and Solar, 1986) and that leads to the formation of simple carboxylic acids (formic, oxalic, maleic, muconic) (Getoff and Solar, 1988). Both in the radiolytic degradation of 4-CP in aerated solutions (Getoff, 1997) and in photocatalytic degradation of chloroorganic compounds involving TiO_2 (Dabrowski, 2000), the formation of oxoanions of chlorine was suggested based on the oxidation of chloride ion by hydroxyl radical. In

chromatographic measurements carried out in this work, it was shown that the main products of radiolytic degradation of 2,4-DCP at doses ≥ 10 kGy were formate and acetate ions (Fig. 4). Such species as oxalate, muconate or chlorine oxoanions were not observed at the level of detection by ion chromatography.

In the earlier work (Zona et al., 1999) it was reported that dose rate had no effect on the radiolytic yield of 2,4-DCP, therefore this factor was not investigated in this work.

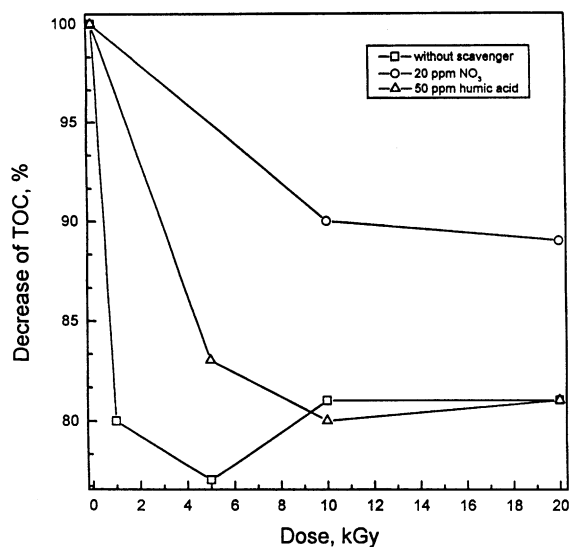


Fig. 2. Effect of dose on the changes of total organic carbon in irradiated 20 ppm aerated solutions of 2,4-DCP without scavengers and with 20 ppm nitrate and 50 ppm humic acid.

3.2. Effect of nitrate on 2,4-DCP degradation

In earlier studies (Drzewicz et al., 1999; Trojanowicz et al., 2000) and in the work of others (Bettoli et al., 1998) some effects of the presence of scavengers have been shown for the radiolytic degradation of chlorophenols. Some of them (nitrate, carbonate) are commonly present in natural and wastewaters. Therefore, the effect on the radiolytic degradation of organic pollutants seemed to be desirable. The reactivity of the hydroxyl radicals with carbonate CO_3^{2-} is almost two orders of magnitude larger than with bicarbonate HCO_3^- (Buxton et al., 1988), hence radiolytic processes, in the presence of carbonate, should be carried out in neutral rather than alkaline solution. Similar scavenging effect towards the hydroxyl radical was also exhibited by humic substances present in natural waters (Arai et al., 1986); therefore, their presence in the irradiated solution may affect both the yield and the products of the radiolytic decomposition of 2,4-DCP. Nitrate ions are effective scavengers of hydrated electrons, and the nitrite

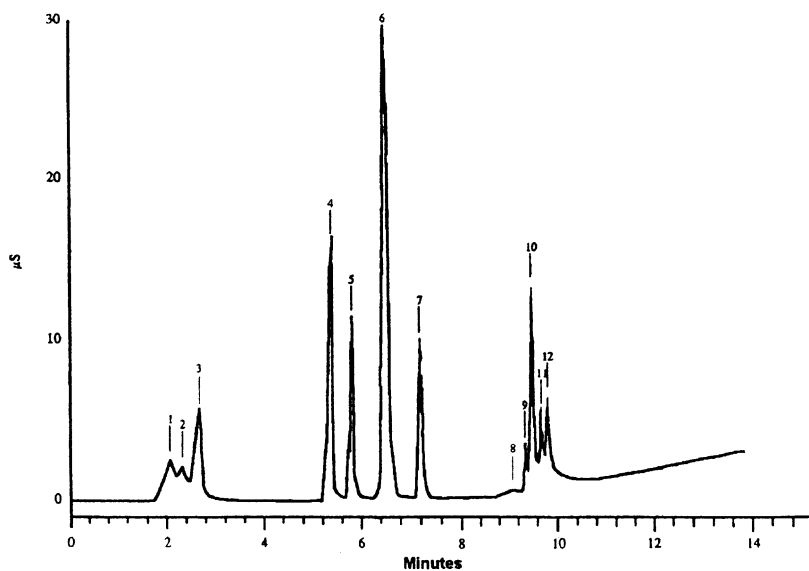


Fig. 3. Ion-chromatogram obtained in the system with conductivity detection in optimized conditions for a mixture of anions containing 15 ppm of each solute. Peak identification: (1) acetate; (2) propionate; (3) formate; (4) chloride; (5) nitrite; (6) trifluoroacetate; (7) nitrate; (8) bicarbonate (traces); (9) maleate; (10) sulfate; (11) oxalate; and (12) muconate.

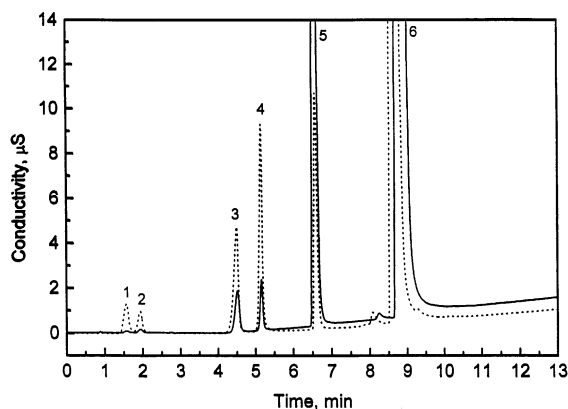


Fig. 4. Ion chromatograms recorded for 20 ppm 2,4-DCP solutions containing 50 ppm nitrate with 0.5 kGy (.....) and 10 kGy (—) doses. Peak assignment: (1) formate; (2) acetate; (3) chloride; (4) nitrite; (5) nitrate; and (6) sulfate.

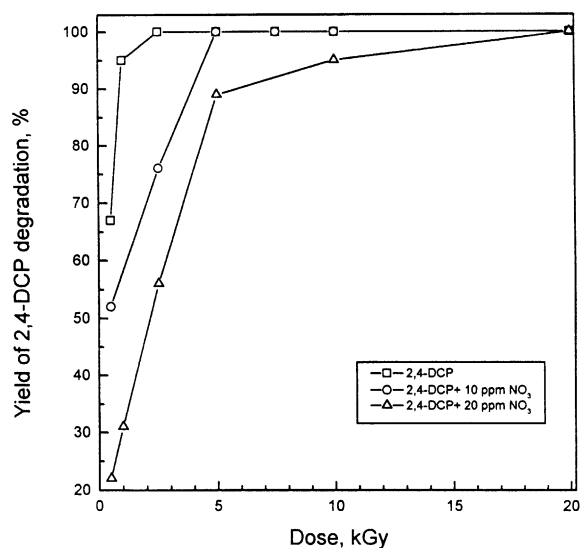


Fig. 5. Effect of the presence of nitrate at different concentration for the effectiveness of radiolytic decomposition of 2,4-DCP in 20 ppm aerated solutions of pH 7.0.

ions that are formed scavenge hydroxyl radicals very effectively (Coddington et al., 1999; Merenyi et al., 1999).

The effect of the nitrate ion on the radiolysis of 2,4-DCP at a concentration of 20 mg/l is shown in Fig. 5. The presence of 20 mg/l nitrate ion in irradiated solutions of 2,4-DCP increases the necessary dose for the decomposition of the target compound to 10 kGy.

In studies of the radiolysis of nitrate ion it was found that the yield of nitrite ions decreases rapidly with increasing radiation dose due to back oxidation of

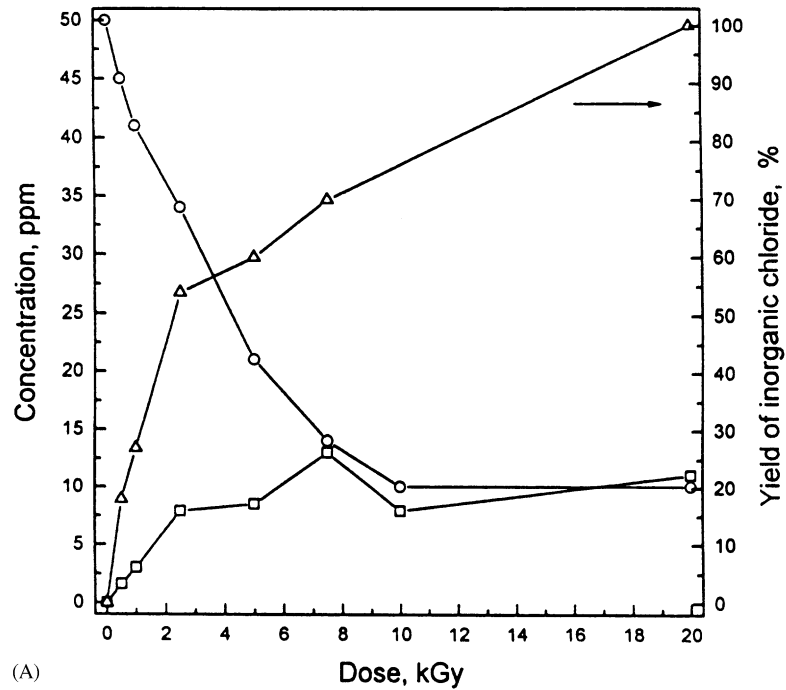
nitrite by hydroxyl radicals (Proksch et al., 1989). In another work, the irradiation of 4-CP solutions carried out in the presence of 50 mg/l nitrate, even trace nitrite ion was not detected (Bettoli et al., 1999). This was not confirmed in this study. During the irradiation of solutions containing nitrate with doses above 1 kGy the formation of toxic nitrite has been observed at concentration levels exceeding permissible levels in waters and did not decrease with an increase of dose (Fig. 6A). Ion-chromatographic measurements have also shown the formation of ammonia in solutions containing 50 mg/l nitrate at doses above 1 kGy (Fig. 6B). GC/MS measurements in the same irradiated solutions did not show the formation of any organic species containing nitrogen.

3.3. Toxicity changes in irradiated 2,4-DCP solutions

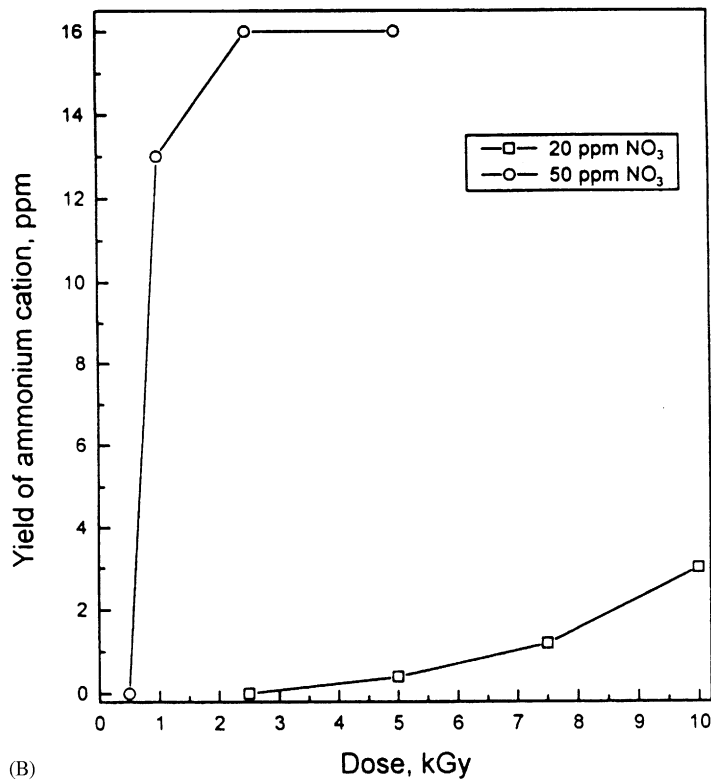
The principal aim of the radiation treatment of polluted waters or effluents from various sources is not necessary for the complete mineralization of the organic pollutants present. For many reasons it may be sufficient to reduce the toxicity caused by the presence of pollutants.

For evaluation of the toxicity numerous different tests are used, based on the interaction of the sample containing pollutants, with various organisms. A number of such tests have been employed for the evaluation of toxicity of samples containing chlorophenols (Beaton et al., 1999; Cassells et al., 2000; Ikehata and Nicell, 2000; Phillips et al., 2000). The most commonly accepted toxicity test, which is commercially available, is bacterial bioluminescent test Microtox[®] (Chang et al., 1981). Bacterial tests are particularly useful for quick testing due to their ease of use, relatively low cost, and statistical advantage in using a large number of bacteria instead of the small number of organisms associated with other bioassay. For the Microtox test, based on bioluminescent marine bacterium *Vibrio fischeri*, a high correlation with the responses of more complex organisms has been demonstrated. For radiation-based technologies it has been recently used for the evaluation of toxicity of irradiated industrial effluents (Borrely et al., 2000).

In this study, the Microtox test was employed to evaluate toxicity changes in irradiated solutions of 2,4-DCP with and without the presence of scavengers of hydroxyl radicals. As it can be seen from data tabulated for about 1300 chemicals (Kaiser and Palabrica, 1991), of which some are listed in Table 1, 2,4-DCP exhibits a medium level of toxicity in the chlorophenols. The data shown in Table 1 indicate an increase in toxicity with an increase in the number of chlorine atoms in the chlorophenols, as well as a difference in toxicity between isomers. Data obtained after the irradiation of pure 20–50 mg/l solutions of 2,4-DCP (Fig. 7) indicated a



(A)



(B)

Fig. 6. Effect of the presence of nitrite in irradiated 20 ppm solution of 2,4-DCP on formation of nitrite (A) and ammonium (B) during irradiation at different doses. (A) measurements in the presence of 50 ppm nitrate: (△) inorganic chloride concentration; (○) nitrate; and (□) nitrite.

Table 1
Toxicity of selected compounds determined with Microtox
(Kaiser and Palabrica, 1991)

Compound	Toxicity EC ₅₀ (ppm)
Pentachlorophenol	0.08–1.0
2,3,4,6-tetrachlorophenol	1.27
2,3,5,6-TeCP	2.21
2,3,4-trichlorophenol	1.25
2,3,5-TCP	1.46
2,3,6-TCP	13–21
2,4,5-TCP	1.27
2,4,6-TCP	7.7–12
3,4,5-TCP	0.36
2,4-dichlorophenol	1.2–6.1
2,5-DCP	10.5
2,3-DCP	5.27
2,6-DCP	13.2
3,4-DCP	0.6–1.6
3,5-DCP	2.8–8.2
2-chlorophenol	21–34
4-CP	1.1–8.3
Phenol	21–42
Hydroquinone	0.04–0.08
Hydrazine	0.01
Ammonia (free)	2.0

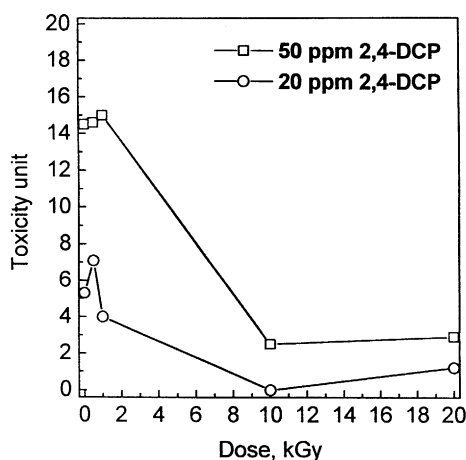


Fig. 7. Effect of dose on the toxicity measured in irradiated 20 ppm (○) and 50 ppm (□) aerated 2,4-DCP solutions.

significant reduction in toxicity at 10 kGy. At doses of 20 kGy the toxicity is not reduced further, and for 20 mg/l solutions it caused an increase.

Another observation was a slight increase in toxicity at doses below 1 kGy compared to the initial toxicity of the solutions prior to irradiation. A similar effect was reported, without explanation, for the radiolytic decomposition of monochlorophenols (the 2,4-DCP was negligible) (Zona et al., 1999). This effect is much more pronounced in the presence of nitrate ion (Fig. 8A), and also in the presence of a large excess of chloride ion in irradiated 2,4-DCP solutions (Fig. 8B). The presence of 20–50 mg/l nitrate ion significantly inhibited the reduction in toxicity of irradiated solutions and even at 20 kGy dose some residual toxicity remained. Such an effect was not observed for solutions of humic acid (Fig. 8B), while the presence of excess of chloride caused an increase in toxicity of the products as the dose increased from 10 to 20 kGy (Fig. 8B). This may be the result of secondary chlorination of the products of 2,4-DCP radiolysis.

An increase in toxicity at low doses may be attributed to the formation of hydroquinone. Its presence among the products has been identified in radiolytic decomposition of 4-CP (Getoff and Solar, 1986; Stafford et al., 1994). Because of insufficient resolution of dihydroxybenzenes in the reversed-phase HPLC method, for a more reliable HPLC determination of the hydroquinone amperometric biosensor made of graphite paste with immobilized tyrosinase was applied (Szewczyńska and Trojanowicz, 2000). This allowed a more selective detection of hydroquinone (Fig. 9). Measurements carried out in the presence of 50 mg/l nitrate ion indicated a high level of hydroquinone at low doses, and an increase of hydroquinone concentration between 5 and 10 kGy (Fig. 10). In the presence of a large concentration of nitrate ion or for laboratory waste sample spiked with 20 mg/l 2,4-DCP (where GC/MS measurement showed the presence of cyclohexanone and 2-chlorocyclohexanone as the main organic components) doses of 20 kGy were not sufficient for the satisfactory reduction in toxicity of the irradiated solutions. It seemed that an improvement in the degradation might be carried out in the presence of ozone, due to the additional conversion of the hydrated electron to hydroxyl radical. The advantages of such combined process have been already demonstrated for instance for radiolytic degradation of pentachlorophenol (Fang et al., 1998), and also for 4-CP, where irradiation of solutions saturated with a mixture of oxygen and ozone resulted in more than a 5-fold increase of yield of chloride release than in aerated solutions (Getoff and Solar, 1988).

4. Conclusions

For the proper evaluation of the applicability of a radiation method for the degradation of organic

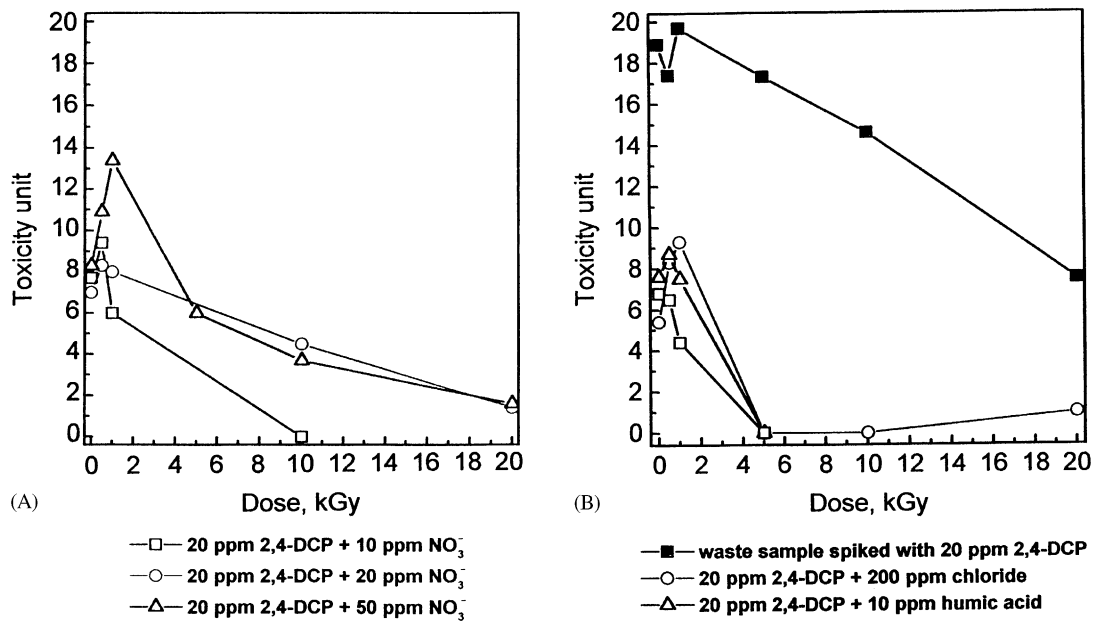


Fig. 8. Effect of dose on the toxicity measured in irradiated 20 ppm aerated 2,4-DCP solutions. (A) irradiation in the presence of nitrate: 10 ppm (□); 20 ppm (○); and 50 ppm (△). (B) irradiation in the presence of 200 ppm chloride (○); 10 ppm humic acids (△); 50 ppm humic acid (□); and waste sample spiked with 20 ppm 2,4-DCP (■).

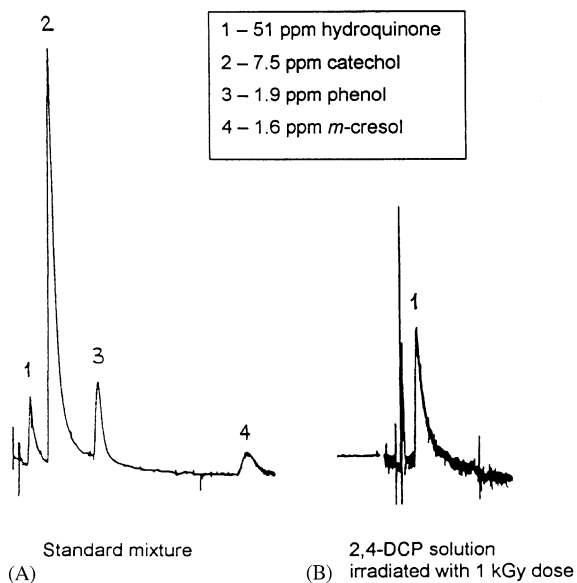


Fig. 9. Chromatograms recorded for reversed-phase chromatography with amperometric detection using tyrosinase-based biosensor for: (A) standard mixture containing 51 ppm hydroquinone (1); 7.5 ppm catechol (2); 1.9 ppm phenol (1) and 1.6 ppm *m*-cresol; and (B) for 20 ppm 2,4-DCP solution irradiated with 1 kGy dose.

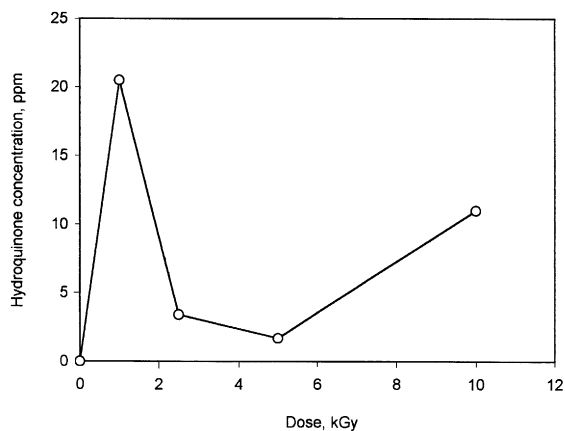


Fig. 10. Effect of dose on formation of hydroquinone in 20 ppm irradiated solutions of 2,4-DCP. Data obtained by reversed-phase chromatography with amperometric enzymatic detection.

pollutants in waste streams, for environmental protection, it is insufficient to optimize the conditions of radiolysis of the target compound and to establish a molecular mechanism of this process. It is also of great practical importance to determine the effect of the presence of other species present in irradiated sample

solutions and also to evaluate the toxicity of the products. The significant role of these factors has been demonstrated in this work for radiolytic degradation of 2,4-DCP.

Acknowledgements

The authors thank Professor K. Bobrowski of the Institute of Nuclear Chemistry and Technology for making possible the use of ion chromatography equipment. The authors thank the Polish State Committee of Scientific Research (KBN) for supporting Polish–Brazilian collaboration on this project.

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