



Degradation of benomyl, picloram, and dicamba in a conical apparatus by zero-valent iron powder

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Abstract

Reduction of some pesticides (benomyl, picloram, and dicamba) was studied in an aerobic batch conical pilot system to investigate the disappearance of these pesticides on contact with iron powder (20 g/l, 325-mesh). Aqueous buffered solutions of the compounds were added to the system followed by zero-valent iron powder (ZVIP), and the decline in the pesticide concentrations was monitored over time. HPLC analyses show a complete disappearance of picloram (1.20 mg/l) after 20 min of reaction. Benomyl (1.00 mg/l) and dicamba (1.25 mg/l) disappear after 25 and 40 min, respectively. The t_{50} values ranged from 3 to 5.5 min, and were about slightly less than the $t_{1/2}$ values reported when the log of the relative HPLC peak area was plotted versus time, where the relative peak area was calculated by dividing the measured peak area by the initial peak area. Pathways for the degradation of the studied pesticides by ZVIP are proposed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Degradation; Iron powder; Pesticides; Reduction

1. Introduction

Pesticides are prevalent groundwater contaminants and are significant components of hazardous waste and landfill sites. The production and the use of pesticides and their apparent hazard to human health have prompted investigations concerning their fate in sub-surface waters, and in treatment facilities. In most of these environments, photolysis, ozonation, and adsorption on activated carbon (De Laat et al., 1995) are not important processes that can be applied at a low cost. However, a novel technology including the use of zero-valent iron (ZVI) becomes one of the encouraging in situ

procedures that was applied since 1993 (Gillham and Burris, 1997).

Picloram is a systemic herbicide used for control of woody plants and a wide range of broad-leaved weeds. Most grasses are resistant to picloram, so it is used in range management programs. Picloram is formulated either as an acid (technical product), a potassium or triisopropanolamine salt, or an isooctyl ester, and is available as either soluble concentrates, pellets, or granular formulations. Picloram is moderately to highly persistent in the soil environment, with reported field half-lives from 20 to 300 days and an estimated average of 90 days. Degradation by microorganisms is mainly aerobic. In a laboratory study, sunlight readily degraded picloram in water, with a half-life of 2.6 days. It is soluble in water, and therefore may be mobile. These properties, combined with its persistence, may indicate a risk of groundwater contamination. Picloram has been detected in the groundwater of 11 states in the USA at

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concentrations ranging from 0.01 to 49 µg/l (Howard, 1991).

Benomyl is a systemic, benzimidazole fungicide that is selectively toxic to microorganisms and to invertebrates, especially earthworms. It is used against a wide range of fungal diseases of field crops, fruits, nuts, ornamentals, mushrooms, and turf. Formulations include wettable powder, dry flowable powder, and dispersible granules. Benomyl is strongly bound to soil and is highly persistent. It completely degrades to carbendazim within several hours in acidic or neutral water. The half-life of carbendazim is 2 months (Howard, 1991).

Dicamba is a benzoic acid herbicide. It can be applied to leaves or to soil. Dicamba controls annual and perennial broadleaf weeds in grain crops and grasslands, and it is used to control brush and bracken in pastures. It will kill broadleaf weeds before and after they sprout. Legumes will be killed by dicamba. It is moderately persistent in soil, the half-life being typically 1 to 4 weeks. Metabolism by soil microorganisms is the major pathway of loss under most soil conditions. In water, microbial degradation is the main route of dicamba disappearance. Photolysis may also occur, aquatic hydrolysis, volatilization, adsorption to sediments, and bioconcentration are not expected to be significant (Howard, 1991).

Research into the use of ZVI metals to remediate groundwater contaminated with mixed wastes (inorganic and organic) has been growing at the US Environmental Protection Agency since 1991. The primary emphasis has been on inorganic constituents such as chromate, arsenic, nitrate and sulfate, and chlorinated organic compounds (e.g., trichloroethylene, *cis*-dichloroethylene, and vinyl chloride). In a recent research report, Rijnaarts (1998) showed results on the reductive degradation of hexachlorocyclohexanes (HCHs) obtained by a full-scale pilot plant. He found that HCHs can be degraded by ZVI without producing benzene as by-product and concluded that iron may be an appropriate reactive material for these types of compounds. Laboratory research conducted by Ghauch et al. since 1999 conclusively demonstrated the effectiveness of ZVIP to remediate water contaminated with pesticides like atrazine and ethyl-parathion (Ghauch et al., 1999), carbaryl (Ghauch et al., 2000; Ghauch, 2000a), and *s*-triazines (Ghauch, 2000b).

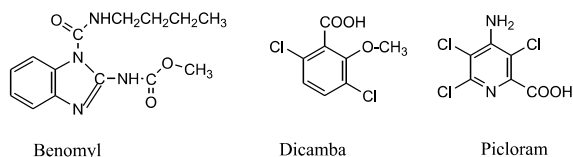


Fig. 1. Structure of pesticides.

This paper presents, results obtained with a conical laboratory constructed apparatus for the treatment of water contaminated with picloram, dicamba and benomyl pesticides (Fig. 1) at room temperature ($22 \pm 1^\circ\text{C}$). The estimated reductive degradation pathways are presented for each of picloram, dicamba, and benomyl. The effects of pH and dissolved oxygen (DO) are not studied. A comparison between the t_{50} values and the half-lives $t_{1/2}$ of all the pesticides studied is also reported.

2. Experimental

2.1. Instrument

HPLC analyses of pesticides were performed by a Diode Array Controller (Waters TM 996), equipped with a diode array detector, and supplemented with a programmable multiwavelength UV/VIS detector. 20 µl samples taken from the pilot were injected automatically via a C18 non-polar column (Supelco, Discovery 250 × 4.6 mm, porosity = 5 µm). The mobile phase (flow rate = 1.5 ml/min) was a mixture of acetonitrile/water (20:80, v/v) for benomyl and dicamba, and (5:95, v/v) for picloram.

2.1.1. Conical pilot

A laboratory constructed apparatus (Fig. 2) was developed to study the degradation of picloram, dicamba and benomyl using ZVIP. Iron was treated with HCl (1 M), washed with distilled water, and then manually introduced into the equipment. The apparatus is equipped with a propeller located at middle height, allowing the aspiration of ZVIP through a 5 mm diameter tube, from the bottom to the top surface, for ZVIP to be propagated in the whole reactive zone. Once settled, the ZVIP is aspirated again continuously. The pilot equipment was built to be used in batch, semi-batch, or in continuous mode.

2.1.2. Reagents

Iron powder (purity > 99%, 325-mesh nitrogen flushed) was purchased from Acros (Geel, Belgium), and KH_2PO_4 and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ from Prolabo (France). Picloram, dicamba and benomyl were obtained from Riedel-de-Haën (Germany) at the highest purity available. Acetonitrile was of spectroscopic grade and purchased from Acros. Deionised water was used throughout the experiments.

2.2. Experimental

All experiments were carried out at room temperature ($22 \pm 1^\circ\text{C}$) in phosphate buffered solutions (0.025 M; pH = 6.6). The ZVIP was pretreated with 200 ml 1 M HCl for 10 min, then washed with distilled water (400

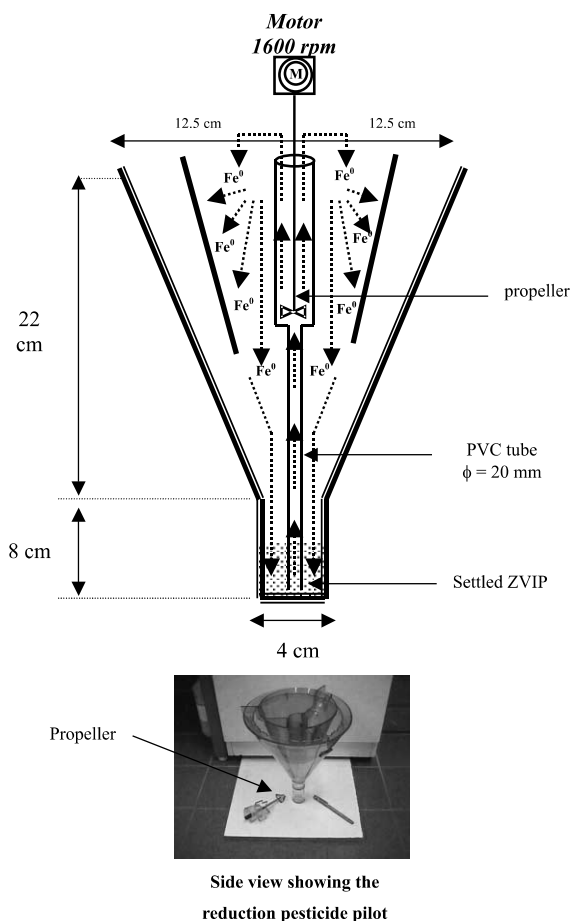


Fig. 2. Schematic representation of the conical pilot. Capacity: 3.75 l, material: clear PVC, weight: 1 kg.

ml) four times to remove residual HCl and Fe²⁺. Pesticide stocks solutions were prepared in aqueous phosphate buffered solution as follows: picloram (20 mg/l), benomyl (4 mg/l) and dicamba (6 mg/l). Working solutions were prepared by an appropriate dilution giving 1.00 mg/l for benomyl, 1.20 mg/l for picloram and 1.25 mg/l for dicamba. 75 g of acid-washed ZVIP were manually added to the pilot containing 3.75 l of pesticide solution. At intervals, 20 μ l were taken with a syringe from the reactive media to carry out HPLC analyses during the reductive process.

3. Results and discussion

To understand the global reductive device, we proceeded to study the degradation of each pesticide by using HPLC to separate by-products and to monitor the disappearance of the starting compounds and the appearance of the new and final by-products. All tests were

carried out in a non-deoxygenated solution at 8 mg/l of DO. Effect of DO is not studied here, but the consequence of the DO on the degradation rate of pesticides should be non-negligible. This phenomenon was studied by Siantar et al. (1996) who found that increasing the amount of DO from 0 to 41.6 mg/l (saturation concentration of O₂ in water at 22°C) decreases linearly the pseudo first-order rate reduction of 1,2-dibromo-3-chloropropane to propane from 0.28 ± 0.03 to 0.07 ± 0.02 min. They concluded that this observation may indicate that the DBCP competes with O₂ for iron surface active sites and/or that the O₂ deactivates the surface by forming non-reactive iron oxide coatings. In the O₂ concentration range relevant for deionised water (under the conditions of the current experiment, 8 mg/l), the decrease in pesticide transformation rate should match with that obtained for 1,2-dibromo-3-chloropropane by a maximum of 17%.

3.1. Benomyl

Fig. 3 shows chromatograms of benomyl (1.00 mg/l) before and after treatment with ZVIP. As can be seen, after 25 min of contact with ZVIP, a complete disappearance of benomyl was observed. Under aerobic conditions (8 mg/l DO), benomyl was reduced by ZVIP within few minutes of half-life $t_{1/2}$. On the other hand, the appearance of some by-products was detected after 5 min of contact with ZVIP. The by-product at retention time $Rt = 7.54$ min presents a UV absorption spectrum with a maximum at 223.8 nm. However, the by-product at $Rt = 3.34$ min shows a shift to longer wavelength (299.3 nm) for the second peak of the parent product which is situated at 285.1 nm. These by-products disappeared completely after 25 min and are converted to a final product having $Rt = 1.04$ min and a maximum of absorbency at 270.9 nm. This fact can be explained by a major transformation in the structure of benomyl pesticide and then, the molecular weight of the final product is to be very lowest than the parent compound. It could be a reductive dealkylation of the amino alkylated group followed by the nitrogen ring opening, shown in Fig. 4 and the formation of *o*-phenylenediamine as final by-product. This phenomenon was observed by Sweeny (1981) who treated hexachlorocyclopentadiene by ZVIP. Reduction led to the production of non-chlorinated branched chain alkanes, evidence of dechlorination and ring opening. The concentration in the reactive zone of the pilot showed what appeared to be an exponential decline in concentration to about undetectable amount at the last part of the experiment (40 min). The log of relative HPLC peak area versus time, where relative peak area was calculated by dividing the measured peak area by the initial peak area, is included in Fig. 5 with a first-order decay model. The half-life obtained ($t_{1/2}$) from the model was 4.32 min, with a coefficient of

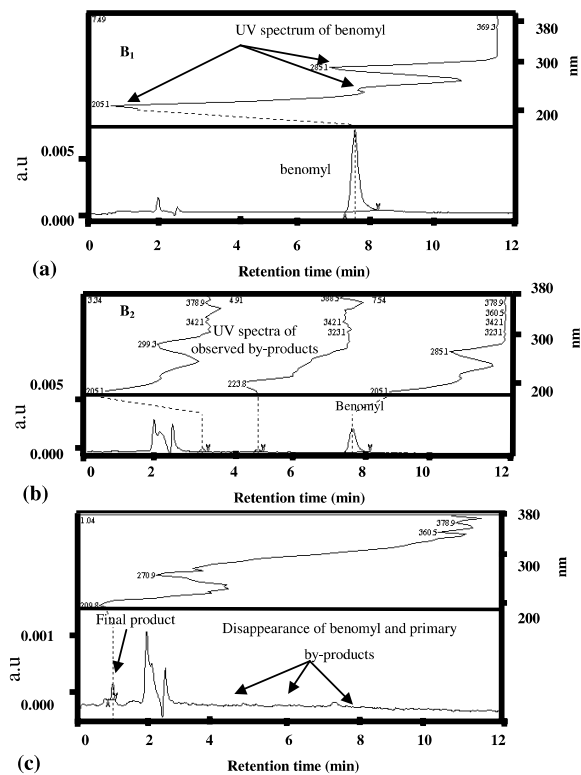


Fig. 3. (a) B₁-HPLC chromatogram and UV absorption spectrum of benomyl $R_t = 7.4$ min. Maximum absorption peaks are at 205.2 and 285.1 nm, and a shoulder at 242.6 nm; (b) B₂-HPLC chromatogram and UV absorption spectra of by-products at 5 min of treatment with ZVIP (20 g/l) at room temperature ($22 \pm 1^\circ\text{C}$); (c) B₃-HPLC chromatogram and UV absorption spectrum of the final by-product at 25 min of contact with ZVIP $R_t = 1$ min. Maximum absorption peaks are at 209.8 and 270.9 nm.

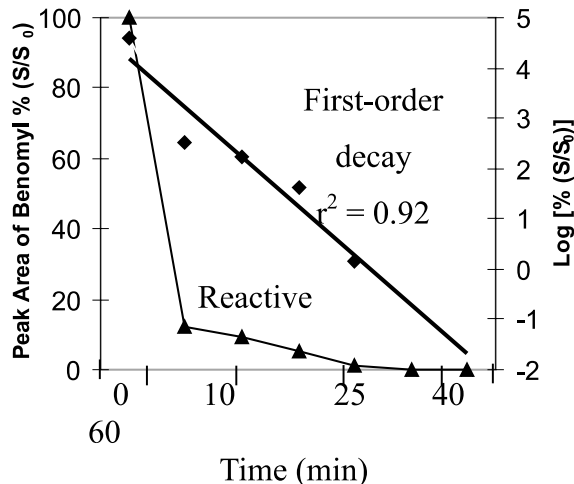


Fig. 5. Disappearance of benomyl (1.00 mg/l). System: 20 g/l of ZVIP, buffered pH 6.6 phosphate 0.025 M and 22°C . The line on the (reactive) benomyl data is an arbitrary polynomial fit.

variation (r^2) of 0.92. As a second index of reaction rate, the time required for a 50% reduction in the initial concentration ($t_{50} = 3$ min) is lower than the half-life (Table 1). The same result was observed by Gillham and O'Hannesin (1994) on solutions containing halogenated aliphatic compounds. These authors suggested the following: “for compounds that degraded slowly, with an apparent decline in the rate constant at late time, the half-lives obtained by least-squares fit of the first-order model are higher than the actual values at early time and lower than the actual values at late time”. Based on the generally high r^2 value, but the late-time trends in the data for those compounds that degrade slowly, it is proposed that the reaction is indeed pseudo first-order with respect to the parent compound, but that the rate

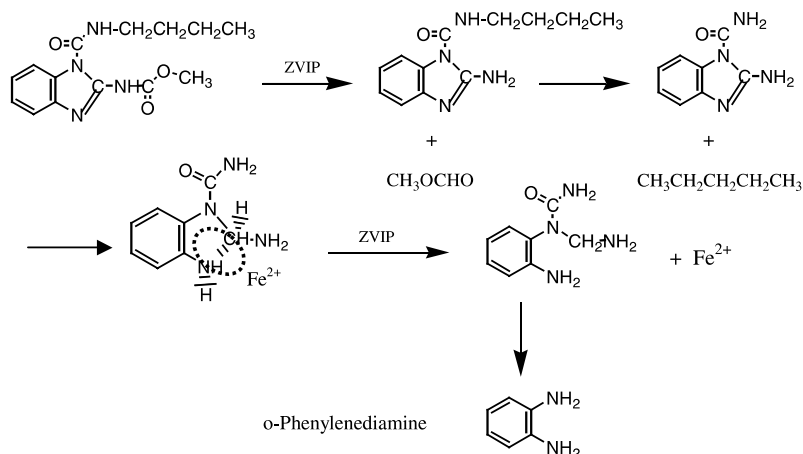


Fig. 4. Degradation mechanism of benomyl.

Table 1

Table of compounds studied showing the calculated half-lives ($t_{1/2}$), and the regression coefficients (r^2) determined from fitting the first order decay equation to the experimental data and times for 50% loss (t_{50})

Pesticides	Initial concentration (mg/l)	$t_{1/2}^a$ (min)	r^2	t_{50}^b (min)
Benomyl	1.00	4.32	0.92	3.1
Picloram	1.20	4.20	0.99	4.0
Dicamba	1.25	5.57	0.97	4.8

^a Calculated half-lives.

^b Times for 50% loss.

constant declines at the late time as a consequence of secondary effects. They may include the accumulation of reaction products, a slight increasing of the pH, or other unidentified changes in the reaction conditions.

3.2. Dicamba

The benzoic acid compound investigated in this work has two chlorine atoms on its ring. The first transformation should be the elimination of the chlorine atoms after contact with ZVIP. The HPLC monitoring during the reductive treatment (Fig. 6) shows a complete disappearance of dicamba after 40 min. Dicamba, which has $R_t = 4.79$ min, presents a UV absorption spectrum with a maximum at 205.1 nm, a shoulder at 226 nm and a secondary peak at 275.7 nm. Only the 205.1 nm peak is not affected by the reductive treatment. However, the

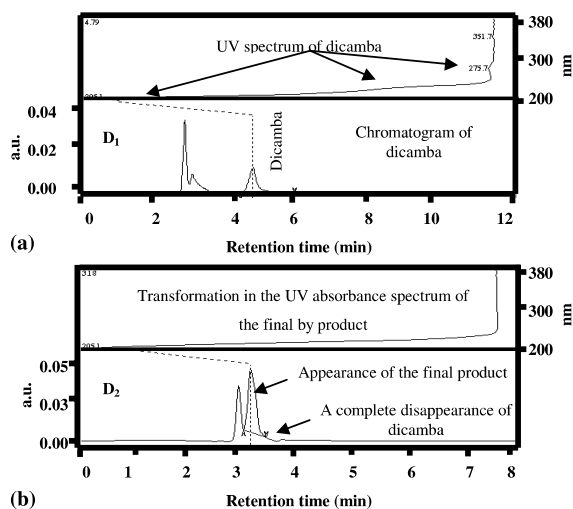


Fig. 6. (a) D_1 -HPLC chromatogram and UV absorption spectrum of dicamba (1.25 mg/l) $R_t = 4.79$ min. The UV spectrum shows two peaks at 205.2 and 275.7 nm and a shoulder at 226 nm; (b) D_2 -HPLC chromatogram and UV absorption spectrum of the final product after 40 min of treatment with ZVIP (20 g/l) at room temperature ($22 \pm 1^\circ\text{C}$).

shoulder at 226 nm and the secondary peak at 275.7 nm disappeared completely in the UV absorption spectrum of the by-product obtained after 40 min of reaction ($R_t = 3.18$ min). On the other hand, the rate of degradation of dicamba seems to be similar to benomyl. From the examination of the graph (Fig. 7), dicamba reflects a declining rate constant at late time (after 12 min of contact with ZVIP). This appeared as a slowly declining but persistent “tail” in the concentration versus time graph. Then again, the time required for a 50% reduction in the initial concentration ($t_{50} = 4.8$ min) (Table 1) is lower than the half-life of dicamba obtained by fitting $\log(S/S_0)$ versus time (min) ($t_{1/2} = 5.57$ min).

To trace a scheme presenting the degradation mechanism of dicamba (Fig. 8), we have suggested a hypothesis similar to the reduction of polyhalogenated alkanes (Siantar et al., 1996) that results in production of both alkanes and alkenes. Vogel et al. (1987) described that the reduction of halogenated aliphatic compounds depends on the formation of the alkyl radical that is a process governed by carbon–halogen bond energies. In general, smaller carbon–halogen bond energies conducive to faster reduction and the heat of formation of the alkyl radical is one measure of the

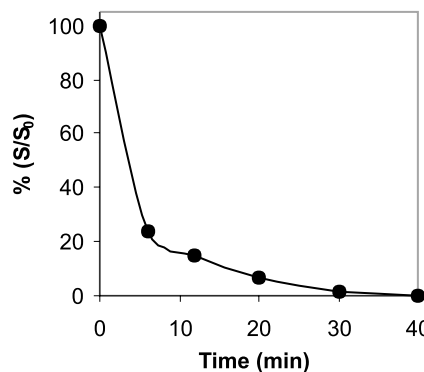


Fig. 7. Disappearance of dicamba (1.25 mg/l). System: 20 g/l iron, buffered pH 6.6, and 22°C .

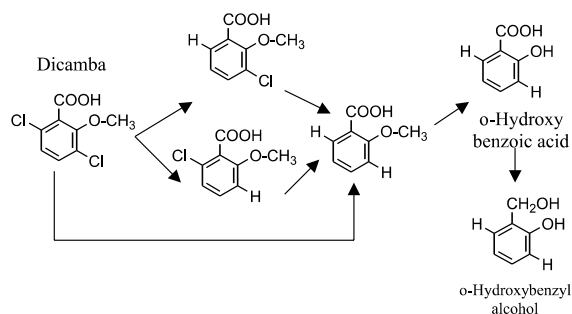


Fig. 8. Degradation mechanism of dicamba.

carbon–halogen bond strength and is inversely proportional to the rate of reduction (Vogel et al., 1987). For dicamba, the C–Cl bond strength depends on the presence of other groups on the molecular ring. For example, the presence of the methoxy group (O–CH₃) influences the elimination rate of the chlorine atoms situated on the adjacent and on the second carbon of the benzoic acid ring. As well, carboxylic group (COOH) may also minimize the strength of the C–Cl bond due to its electronegative properties, so the rate of dechlorination should be higher than molecules that do not contain attractive group on their ring. The elimination of the chlorine atoms occurs successively (beginning from the

chlorine atom situated on the adjacent carbon of the carboxylic function) or simultaneously followed by the formation of the hydroxy-benzoic acid as a by-product that will be transformed to the corresponding alcohol (hydroxybenzoyl alcohol). The degradation mechanism of dicamba is shown in Fig. 8.

3.3. Picloram

After 10 min of contact of picloram with ZVIP, a complete transformation of its structure was observed (Fig. 9). This statement is explained by the disappearance of the 223.8 nm peak of its UV absorption spec-

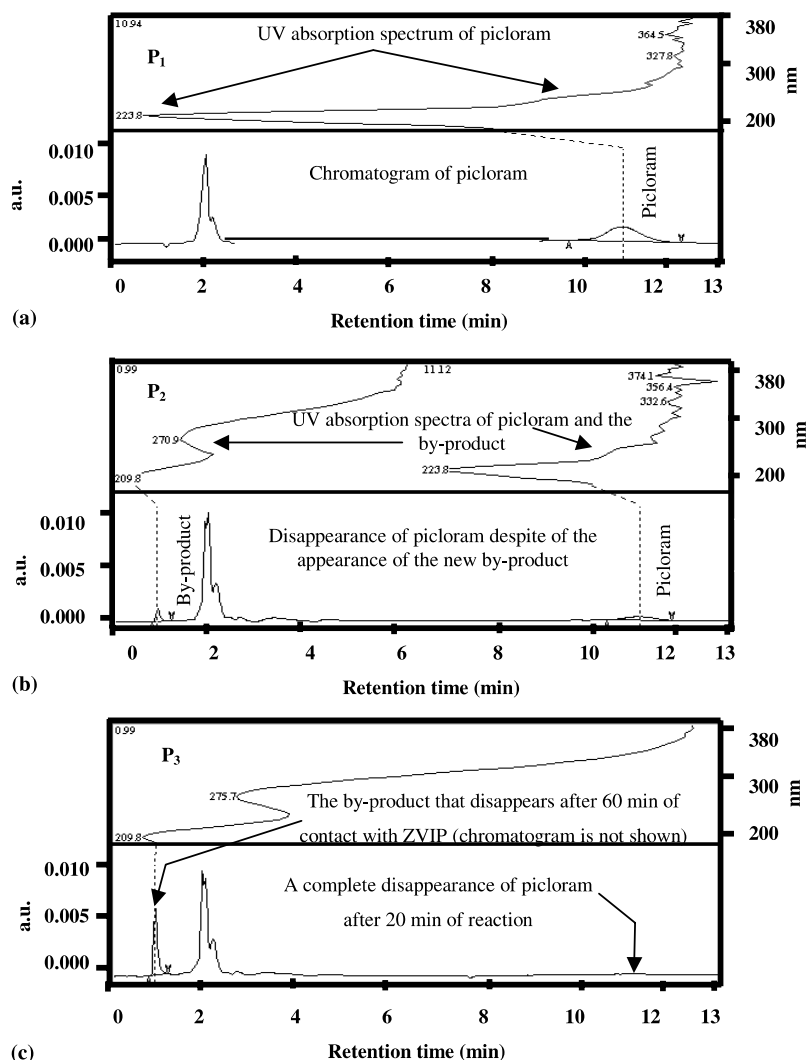


Fig. 9. (a) P₁-HPLC chromatogram and UV absorption spectrum of picloram (1.20 mg/l), $R_t = 10.9$ min, maximum absorption peak is at 223.8 nm and a shoulder at 252 nm; (b) P₂-HPLC chromatogram and UV absorption spectra of by-products at 10 min of treatment with ZVIP (20 g/l) at room temperature ($22 \pm 1^\circ\text{C}$); (c) P₃-HPLC chromatogram and UV absorption spectrum of the intermediate by-product ($R_t = 1$ min) after 20 min of reaction. Maximum absorption peaks are at 209.8 and 275.7 nm.

trum and the appearance of a by-product at $Rt = 1$ min presenting two maximum absorption peaks at 209.8 nm and 270.9 nm. However, as the reaction continues, the absorption peak at 270.9 nm shifts to longer wavelength (275.7 nm), nevertheless the 209.8 nm peak persists. This observation is true until 30 min of reaction because the by-product decreases to undetectable amount after 60 min, shown in Fig. 10. This observation is probably due to the elimination of chlorine atoms and appearance of by-product (4-aminopyridine-2-carboxylic acid) at $Rt = 1$ min, followed by the transformation of the COOH group to CH₂OH group (4-amino-2-pyridylcarbinol) under the enhanced reductive ZVIP treatment (disappearance of the by-product). The presence of three chlorine atoms on the pyridine ring results in a more rapid dechlorination of the compound. This result matches with results obtained by Gillham and O'Hannesin (1994) who concluded that within each group of halogenated aliphatic compounds (methanes, ethanes and ethenes), the rate of degradation increases with an increase in the degree of chlorination. Under the reducing conditions of tests, the more highly oxidized compounds would be most susceptible to degradation. A similar result was observed for picloram on the t_{50} and the $t_{1/2}$ values than for benomyl and dicamba. Table 1

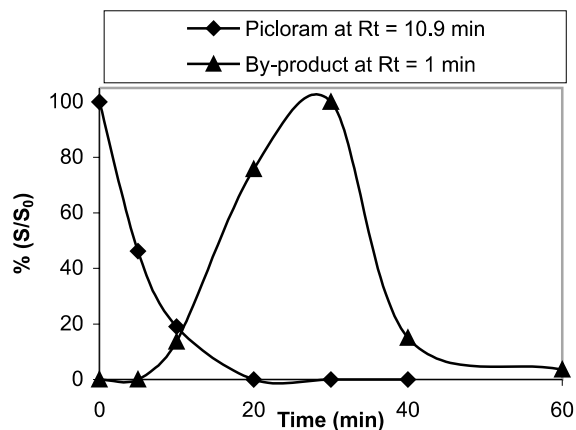


Fig. 10. Graph showing the accumulation and subsequent degradation of the by-product during the degradation of picloram (1.2 mg/l and 20 g/l of ZVIP). Buffered solution pH 6.6 in 0.025 M phosphate.

shows that t_{50} closes to 4.00 min, however the $t_{1/2}$ of picloram closes to 4.20 min when $\log(S/S_0)$ is plotted versus time (graph not shown). The dechlorination of picloram can occur at different carbon of the pyridine

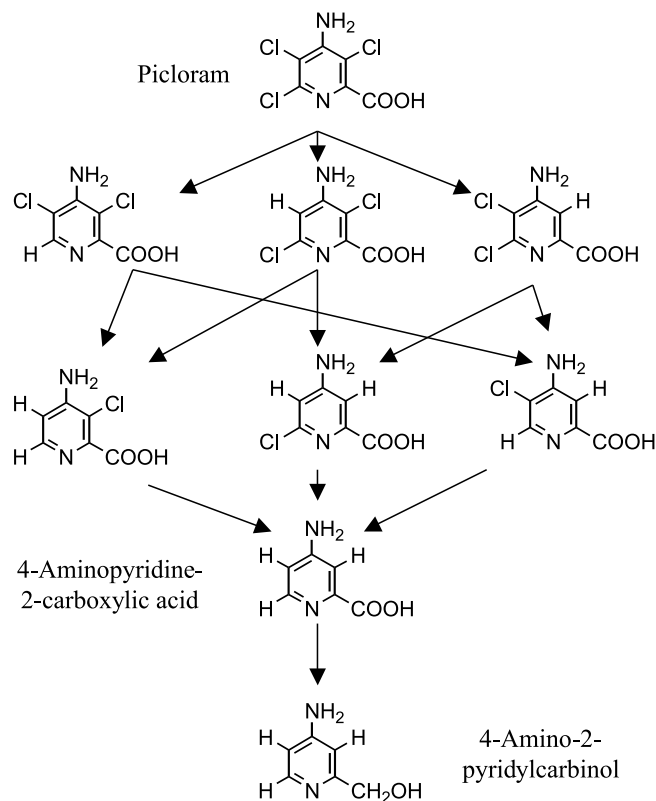


Fig. 11. Degradation mechanism of picloram.

ring. The breakdown of the C–Cl bond neighboring to the nitrogen atom should arise before the other C–Cl bonds because of the electrophile property of the nitrogen atom in an acidic media. However, we are not interested here if the elimination of the first chlorine atom occurs on one carbon before another, but we can conclude that the dechlorination takes place in the presence of ZVIP in the media. A degradation map showing the dechlorination of picloram is presented in Fig. 11.

4. Conclusions

We have demonstrated the ability of ZVIP to degrade pesticides in buffered water (pH 6.6) at room temperature (22°C). By analogy to the mechanism of aqueous ZVI reductive treatment of halogenated solvents (Matheson and Tratnyek, 1994), the disappearance of benomyl, dicamba and picloram is pseudo first-order rate. The degradation of picloram occurs more easily than dicamba perhaps due to its higher degree of chlorination. The t_{50} values of all pesticides are lower than their $t_{1/2}$ values when $\log(S/S_0)$ is plotted versus time. Acquired results are analogous to those obtained recently by Ghauch et al. (2000) and Ghauch (2000b), where the time required for a 50% reduction in the initial pesticide concentration is less than 5 min.

The use of a conical apparatus has shown its effectiveness compared to the last cylindro-conical system developed by Ghauch (2000b) for pesticides treatment. For example, a problem like iron settling was not observed, the increase in the rotating of the propeller from 900 to 1600 rpm has more facilitated the propagation of the ZVIP in the pilot, and then makes easy the mass transport of the target molecules to the surface layer of ZVIP from the bulk of the solution. This fact might be also an extra factor of cleaning the surface area of the metal.

Finally, the use of ZVI continues to grow and to receive considerable attention. The in situ technology (Permeable Reactive Barriers or Treatment Walls, (US EPA, 1997)) for groundwater remediation from organic and inorganic pollutants has been proven to work (Starr and Cherry, 1994; Gillham and Burris, 1997; Vogel, 1998). Indeed, clearer explanation on how to determine long-term effects of the iron activity on ground water remediation is needed. There are many preventive factors for example, bioclogging, redox limitations, and concentrations or combinations of contaminants such as nitrates (Siantar et al., 1996), pesticides (Ghauch et al., 1999, 2000; Ghauch 2000b), dyes (Cao et al., 1999), chlorinated solvents (Sweeny, 1981; Roberts et al., 1996), and chromate (Powell et al., 1995) that should be investigated for the in situ ZVIP technology.

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