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Photochemical Behavior of the Fungicides Carbendazim and Metalaxyl in Aqueous Solutions Using Advanced Oxidation Processes

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ABSTRACT

To elucidate the photochemical behavior of the fungicides carbendazim and metalaxyl in superficial waters, photolysis studies have been carried out in aqueous solutions using UV- photo catalytic system, Ferric chloride, Ferrous sulphate and zinc oxide alone or in combination with hydrogen peroxide. HPLC has been used for residues determination. Results clearly exhibited that, carbendazim and metalaxyl were almost stable in the dark while UV irradiation decreased their stabilities. $T_{1/2}$ ranged between 2.26 and 8.88 hr. for carbendazim fungicide and from 0.5 to 2.57 hr. for metalaxyl under the conditions of photo-Fenton reactions. The degradation rate of the two tested fungicides were greatly enhanced by Fe(III) than Fe(II). H_2O_2 accelerated the photodegradation of the two fungicides under photo-Fenton reactions. Consequently, treatment of Fe(III)/H_2O_2/UV gave the highest percentage of dissipation (%D) since, after 360 min of irradiation it reached to 85.50% for carbendazim and 99.98% for metalaxyl.

The photodegradation of carbendazim and metalaxyl were greatly enhanced by irradiation under ZnO+H_2O_2/UV compared to ZnO/UV alone. The effect of the system ZnO+ H_2O_2+UV was as equal as that of the photo-Fenton system $FeCl_3$+H_2O_2+UV. The half-life values under ZnO/UV were 9.63 and 4.81 hr. for carbendazim and metalaxyl, but the values of $T_{1/2}$ were decreased under ZnO+H_2O_2/UV to 2.51 and 0.68 hr., respectively. There was a positive relationship between the percentage of fungicides dissipation and the irradiation time for the all running treatments.

Key word: Carbendazim; metalaxyl; half-life; photodegradation; Advanced oxidative process (AOP); Fenton reagents.

INTRODUCTION

Due to the world-wide general application of intensive agricultural practices during the last few decades and to the large-scale development of the agrochemical industry, the variety and quantities of agrochemicals present in continental and marine natural waters has dramatically increased. Pesticides are one of the most important agrochemicals that contaminant the surface and ground water and their contamination was increased many folds in recent years due to their large-scale use in intensive agriculture. The sources of this contamination may be summarized as follows: (i) pesticide treatment as routine agricultural practice; (ii) rinse water polluted with pesticides from containers and spray equipments; (iii) wastewater from agricultural industry (cleaning or post-harvest treatment of fruits and vegetables) and; (iv) plant residues contaminated with pesticides (Devipriya and Yesodharan ,2005).

Advanced oxidation processes (AOPs) are efficient and promising methods to detoxify pesticides, which exhibit chemical stability and resistance to biodegradation (Devipriya and Yesodharan, 2005 and Saien and Khezrianjoo, 2008). The photo-oxidative systems are able to use the UV fraction of sunlight reaching the Earth's surface; however, visible light is not efficiently employed. For this reason, the search for alternative photoactive compounds displaying strong absorption bands in the visible range of the spectrum is still meaningful. (Arques *et al.,* 2009). Solar-driven processes commonly used in detoxification are the photo-Fenton system, which is based on a combination of iron salts with hydrogen peroxide (Perez *et al.,* 2006; Evgenidoua *et al.,* 2007; Lapertot *et al.,* 2007 and Martin *et al.,* 2009) and heterogeneous photocatalysis with ZnO (Evgenidoua *et al.,* 2005; Navarro *et al.,* 2009 and Soler *et al.,* 2009). These methods have been shown to be efficient in the elimination of an important number of pesticides (Devipriya and Yesodharan, 2005; Perez *et al.,* 2006; Evgenidoua *et al.,* 2005, 2007; Lapertot *et al.,* 2007; Saien and Khezrianjoo, 2008; Arques *et al.,* 2009, Cernigoj *et al.,* 2010 and Sojic *et al.,* 2010).

Carbendazim is a systemic benzimidazole fungicide with an extensive and widespread use. Analysis of sewage sludge have shown that carbendazim occur in urban water systems (Plagellat, *et al.,* 2004). It is toxic to aquatic organisms in the ppb range (Cuppen *et al.,* 2000). Under natural environmental conditions, it is very stable (Panades *et al.,* 2000 and Berglof *et al.,* 2002) and it has been frequently detected in surface waters (Fernandez *et al.,* 2001 and Escalada *et al.,* 2006).

Meanwhile, it appears as the active substance of benomyl and thiophanate-methyl fungicides and moreover as the main degradation product of these two compounds (Berglof *et al.*, 2002 and Boudina *et al.*, 2003). This product is toxic for humans, animals and plants (Panades *et al.*, 2000 and Akbarsha *et al.*, 2001). Carbendazim may similarly be found as a pollutant of water resources where it can accumulate. The photo-degradation of carbendazim has been studied under different experimental conditions of irradiating with UV light (Panades *et al.*, 2000 and Mazellier *et al.*, 2002a, b and 2003).

Metalaxyl is a systemic acylanilide fungicide. It is effective against Oomycetes, especially *Peronosporales* such as *Phytophthora* spp., *Pseudoperonospora* spp., *Peronospora* spp., *Sclerospora* spp., *Bremia* spp., *Pythium* spp., and other species causing downy mildews, late blight, damping off as well as root, stem and fruit rots in many crops. It is stable against hydrolysis under normal environmental conditions (Sukul, 2006 and Spessoto *et al.*, 2006). It is also photolytically stable in water and soil when exposed to natural sunlight. Its tolerance to a wide range of pH, light, and temperature leads to its continued use in agriculture (Sukul and Spiteller, 2000). Metalaxyl is considered as a model compound of an organic waste photodegradable substance in water (Topalov *et al.* 1999).

The aim of the present work was to study the effect of different advanced oxidation processes (AOPs), photocatalytic oxidation; Fenton's chemistry (belonging to the class of advanced oxidation processes) and hydrogen peroxide (belonging to the class of chemical oxidation technologies) under UV light irradiation on the degradation of carbendazim and metalaxyl in water solutions to find out the fastest and cheapest degradation system.

MATERIALS AND METHODS

Chemicals:

Carbendazim fungicide ($C_9H_9N_3O_2$) methyl benzimidazol-2-yl carbamate, [CAS No.:10605-21-7, MW=191.19] and Metalaxyl ($C_{15}H_{21}NO_4$) methyl *N*-(methoxyacetyl)-*N*-(2,6-xylyl)-DL-alaninate[CAS No: 57837-19-1, MW= 279.3], analytical standard grade 98% and 96% respectively, were supplied by Syngenta Co. The chemical structures of these fungicides are shown in Fig. 1.

Ferric chloride ($FeCl_3.6H_2O$), Ferrous sulphate ($FeSO_4 .7H_2O$), hydrogen peroxide (H_2O_2 30% w/v), zinc oxide (ZnO) and sulphuric acid for pH adjustment were reagents grade. All the used solvents were of A.R. grade

Experimental set-up.

For Fenton reagent, the solution was prepared by adding desired amount of carbendazim or metalaxyl (5 mg/L) to water, and then the mixture was carefully agitated in standard flask. Freshly prepared Fe^{2+}/H_2O_2, Fe^{3+}/H_2O_2 as ferrous sulphate and ferric chloride were then added alone at 20 mg /L or in combination with H_2O_2 at 0.05%. The initial pH of the solution was adjusted to 2.8, the optimum pH for photo-Fenton treatment using sulphuric acid (Perez *et al.*, 2006 and Pignatello *et al.*, 2006).

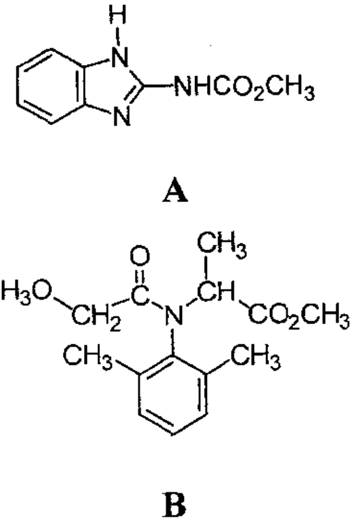


Fig. 1: Chemical structure of carbendazim A and metalaxyl B.

For ZnO catalyst, fungicides at concentration of 5 mg/L with the appropriate amount of ZnO catalyst (300 mg/L) was shacked carefully before illumination and left for 30 min in the dark in order to achieve the maximum adsorption of the pesticide onto semiconductors surface, then the pH was adjusted to 7, the optimum pH for ZnO catalyst (Evgenidou *et al.*, 2005). The solutions of all the treatments (Dark, UV light, H_2O_2+UV, Fe_2Cl_3+UV, $Fe_2Cl_3+H_2O_2$+UV, $FeSO_4$+UV, $FeSO_4+H_2O_2$+UV, ZnO+UV and ZnO+H_2O_2+ UV) were transferred from the standard flask to a quartz glass cell and exposed to irradiation of the UV mercury lamp (model VL-4.LC '8W' with a wavelength range of 254-365nm, the distance between the lamp and fungicides solution was 15 cm). Samples were taken at different time intervals (10, 30, 60, 120, 240 and 360 min) for HPLC analysis.

Quantitative estimation of fungicides by HPLC:

The samples were analyzed by HPLC system Perkin Elmer HP 200 L, column C18 reversed A Tracor 985 HPLC and Tracor 951 LC pump. Carbendazim was measured at 285 nm, the used solvent was methanol+H_2O (4 + 1 by volume) and 10 drops/L ammonium hydroxide. Flow rate was 0-5 ml/min. Metalaxyl was estimated at 205 nm. For the first 15 min the mobile phase (1 ml min^{-1}) was 10% acetonitrile in water and pH was adjusted to 4.0 with 0.15M H_3PO_4. For the next 5 min., the acetonitrile was increased to 90%. The recovery percentage of carbendazim and metalaxyl was ranged between 95% and 88%, respectively.

Data Calculation:

The calculation of half-life was performed using the first-order rate equation:

$$C_t = C_0 e^{-kt}$$

Where C_t represents the concentration at time t; C_0 represents the initial concentration and k is the constant rate. When the concentration is reduced to 50% of its initial amount, half-life ($T_{1/2}$) can be determined by the following equation:

$$T_{1/2} = \left[\frac{\ln(\frac{Co}{Co/2})}{K}\right] = \frac{0.693}{K}$$

Where k is the degradation constant (Monkiedje and Spiteller, 2005).

The degradation efficiency or conversion (X) of carbendazim and metalaxyl with respect to its initial concentration at any time can be obtained by the following equation:

$$X = \frac{Co - C}{Co}$$

Where Co is the initial concentration of organic compound and C the concentration at a given time.

RESULTS AND DISCUSSION

The photodegradation of carbendazim and metalaxyl by UV-irradiation at low wavelength (254 nm) in aqueous solutions using advanced oxidation processes (AOP) by addition of photo-fenton and photo-catalytic reagent were studied by monitoring their loss by HPLC with UV detection.

Degradation of fungicides under dark, UV and hydrogen peroxide/UV light:

The kinetic data derived from first-order function and the half-life of carbendazim and metalaxyl were represented in Tables (1 and 2). The degradation of the fungicides at concentration level of 5 mg/L was observed to estimate thier degradation rate under dark, UV light and hydrogen peroxide/UV conditions. In the present study, the absorption spectra of carbendazim and metalaxyl were studied at different times of irradiation (10, 30, 60, 120, 240 and 360 min). The data included the Percentages of dissipation Table (1 and 2) while, the degradation efficiency or conversion of the tested fungicides were presented in (Fig. 2a and b).

The aqueous solution of carbendazim was stable in the dark and nearly no degradation was observed. These result was agreed with the study undertaken by Abu-Qare and Duncan, 2002; Mazellier *et al.*, 2002a and Boudina *et al.*, 2003. The stability of carbendazim was decreased under UV irradiation and the degradation efficiency was 0.186 after 360 min of irradiation (Fig. 2a). In other words, pesticide eliminations could be achieved by using UV irradiation, this was the same result of Shawaqfeh *et al.*, 2010, they found that 50% of Vydine was eliminated under UV (254 nm). The presented data in Table (1) revealed that, the photodegradation and accordingly the percentage of dissipation under H_2O_2/UV system was higher than that under UV light alone at the same exposure time, since it reached to 41.87% for H_2O_2/UV and 18.56 % for UV alone after 360 min of irradiation. Our finding was agreed with Mazellier *et al.*, 2002a,b and 2003; Chelme-Ayala *et al.*, 2010, who reported that, in the system hydrogen peroxide/UV, the transformation of carbendazim and other pesticides was very efficient because of the generation of hydroxyl radicals in the solution. The observed photoproducts were explained as the result of two main degradation pathways: (1) benzene group oxidation, giving rise to hydroxylated benzimidazoles, and (2) change of the 2-$NHCO_2Me$ group to 2-$NHCO_2CO_2H$, and 2-$NHCO_2CHO$ (Mazellier *et al.*, 2002a,b and Boudina *et al.*, 2003). With respect to the significant degradation of carbendazim which was followed by the UV absorbance at appropriate maximum wavelengths, attributed to the benzene ring, and with respect to the reported works on mineralization of other pesticides (Malato *et al.*, 2002; Saien and Khezrianjoo, 2008), the appropriate mineralization reaction can be given here with the most oxidized state as:

$$C_9H_9N_3O_2 + 14O_2 \longrightarrow 3HNO_3 + 9CO_2 + 3H_2O.$$

Slight degradation of metalaxyl was achieved under dark system, the percentage of dissipation was 1.14% after 360 min of irradiation. This degradation might be due to the hydrolysis of this pesticide (Katsumata *et al.*, 2005). Furthermore, approximately 31.24% and 69.34 % of metalaxyl were remediated under UV light and UV/H_2O_2 system after 360 min, respectively (Table 2). The degradation efficiency was increased using the UV/H_2O_2 compared with dark system, the values were 0.312 and 0.011, respectively (Fig. 2b). Metalaxyl underwent a parallel/consecutive photodegradtion to give *N*-2,6-xylyl-D,L-alaninate (I) and *N*-(methoxyacetyl)-2,6-dimethylaniline (II). Compound (I) was easily converted to 2,6-dimethylaniline (III) as earlier, while compound (II) was more stable to photolysis. (Filippo *et al.*, 1996). The photocatalytic degradation of this fungicide yields its complete mineralization after hydroxylation of the aromatic ring, oxidation of the methyne group and the simultaneous cleavage of the β-bond from nitrogen to the ester moiety and decarboxylation reactions completed the degradation pathway (Topalov *et al.*, 1999).

In the presence of UV/H_2O_2, a first-order rate equation was calculated and the observed half-life were 12.83 and 3.98 hr. for carbendazim and metalaxyl, respectively and these times were shorter than those found in the absence of H_2O_2 since the values were 23.10 and 16.5 hr., respectively (Table 1 and 2).

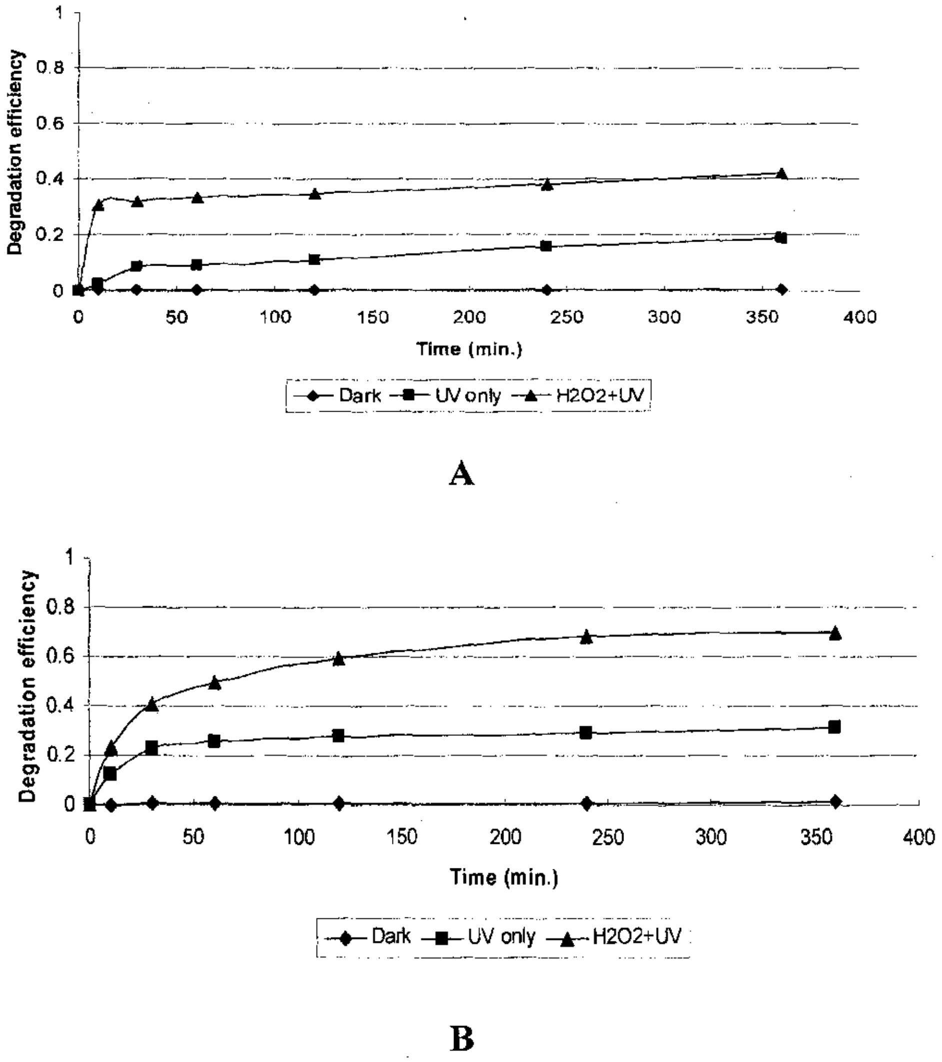


Fig. 2: The degradation efficiency of carbendazim (A) and metalaxyl (B) at different irradiation time intervals under dark, UV and H_2O_2/UV systems.

Table 1: Percentage of dissipation (%D), regression equation, correlation coefficient (R^2) and half-life values of carbendazim in aqueous solutions using (AOP) conditions at different time intervals (min.).

Treatments	Percentage of dissipation (%D)						Regression eq.	R^2	$T_{1/2}$ (hr.)
	10	30	60	120	240	360			
Dark	0.32	0.32	0.33	0.33	0.35	0.36	y = 4.9883 -0.0005x	0.2359	802 (d)*
UV only	2.63	8.51	9.19	11.22	15.81	18.56	y = 4.7915 -0.0022x	0.8391	23.10
H_2O_2 + UV	30.77	31.9	33.56	34.75	38.21	41.87	y = 3.863 -0.0032x	0.3841	12.83
Fe_2Cl_3 + UV	12.45	19.94	32.80	53.60	64.40	68.40	y = 4.2522 -0.009x	0.8249	3.60
Fe_2Cl_3+H_2O_2 + UV	15.32	30.12	52.67	68.40	78.00	85.50	y = 3.880 -0.0106x	0.7643	2.26
$FeSO_4$ + UV	2.99	8.20	14.40	19.20	35.40	36.87	y = 4.7754-0.0052x	0.9186	8.88
$FeSO_4$+H_2O_2 + UV	9.64	16.26	28.78	44.59	53.60	54.77	y = 4.3635-0.0072x	0.7969	5.25
ZnO + UV	3.80	10.45	15.49	24.90	32.98	35.40	y = 4.6805-0.0048x	0.8639	9.63
ZnO + H_2O_2 + UV	20.82	34.40	48.00	62.28	74.20	83.50	y = 3.8402-0.0098x	0.7911	2.51

Table 2: Percentage of dissipation (%D), regression equation, correlation coefficient (R^2) and half-life values of metalaxyl in aqueous solutions using (AOP) conditions at different time intervals (min.).

Treatments	Percentage of dissipation (%D)						Regression eq.	R^2	$T_{1/2}$ (hr.)
	10	30	60	120	240	360			
Dark	0.22	0.480	0.66	0.79	0.82	1.14	y = 4.9854-0.0001x	0.775	231.0
UV only	12.12	23.07	25.23	27.26	28.67	31.24	y = 4.2881-0.0029x	0.505	16.5
H_2O_2 + UV	23.11	40.68	49.47	58.97	68.60	69.34	y = 3.6666-0.0075x	0.643	3.98
Fe_2Cl_3 + UV	36.08	57.79	69.10	72.87	83.05	88.93	y = 3.1058-0.0087x	0.577	2.26
Fe_2Cl_3+H_2O_2 + UV	38.62	58.32	81.22	91.71	99.64	99.98	y = 2.8655-0.0104x	0.572	0.50
$FeSO_4$ + UV	8.68	37.66	55.59	67.85	75.95	81.66	y = 3.8297-0.01x	0.694	2.57
$FeSO_4$+H_2O_2 + UV	27.93	47.12	67.43	80.91	88.11	92.92	y = 3.3169-0.0103x	0.655	1.67
ZnO + UV	11.01	30.3	44.9	52.98	57.8	62.18	y = 3.9979-0.0072x	0.666	4.81
ZnO + H_2O_2 + UV	60.34	78.53	84.52	92.65	99.46	99.85	y = 2.3078-0.0084x	0.421	0.68

The Advanced oxidation process (AOP) is based on the formation of HO• radicals by means of the photolysis of hydrogen peroxide and the subsequent propagation reactions, (Eq. 1) (Marc *et al.*, 2004).

$$H_2O_2 + h\nu \longrightarrow 2HO^{\bullet} \qquad (1)$$

Degradation of fungicides under Photo-Fenton system:

The Fenton method requires H_2O_2, Fe^{2+} salts and acidic pH. Under these conditions highly reactive and unselective oxidants, OH radicals, are produced. With UV–vis light, the formed Fe^{3+} complexes are photolysed, which enables regeneration of Fe^{2+} (catalyst): the process is called photo-Fenton (Lapertot *et al.*, 2007).

It was quite clear from Table 1 and 2 that carbendazim and metalaxyl were degraded in short time with photo-Fenton reaction, since the $T_{1/2}$ ranged between 2.26 and 8.88 hr. for carbendazim fungicide and from 0.5 to 2.57 hr. for metalaxyl. Perusal of these results clearly exhibited that, the degradation rate of the tested fungicides were greatly enhanced by Fe(III) than Fe(II), H_2O_2 also accelerated the photodegradation of the two fungicides with photo-Fenton reaction. This result was in harmony with the result of Evgenidoua *et al.*, 2007 and Shawaqfeh *et al.*, 2010. Consequently, treatments could be arranged according to the speeding up of the photodegradation of the fungicide carbendazim in decreasing order as follows: Fe(III)/ H_2O_2 / UV > Fe (III) / UV > Fe (II) /H_2O_2 / UV > Fe(II)/UV at the different times of irradiation, The percentages of dissipation (%D) of these systems were reached to 85.50, 68.40, 54.77 and 36.87%, respectively after 360 min (Table 1). The values of %D of metalaxyl were higher than those of carbendazim and the treatments followed the same order up to 60 min., while after 120min the order of the treatments was as follow: Fe(III) / H_2O_2 / UV > Fe (II) / H_2O_2 / UV > Fe(III) / UV > Fe(II) / UV with values of %D 99.98, 92.92, 88.93 and 81.66%, respectively at 360 min from irradiation (Table 2). There was a positive relationship between the percentage of fungicides dissipation and the irradiation time within the same order of photo-Fenton reagents (Fig. 3a and b). Photo-Fenton had been demonstrated to be more effective than TiO_2 (catalytic agent) (Parra *et al.*, 2000; Bressan *et al.*, 2005 ; Da Hora *et al.*, 2005; Farre *et al.*, 2005; Malato *et al.*, 2005 and Perez *et al.*, 2006).

Fe^{2+} salt is rapidly converted to Fe^{3+} if there is excess H_2O_2 (during the first seconds after adding H_2O_2), but the •OH produced by Fenton reaction (Eq. 2) are not enough for significant oxidation of organics. When Fe^{3+} salt is used, it is reduced to Fe^{2+}, mainly by solar irradiation and by H_2O_2 (Eqs. 3 and 4). The primary step is a ligand-to-metal charge transfer reaction. Later intermediate complexes dissociate as shown in Reaction 5. The ligand can be any Lewis base (L) able to form a complex with ferric iron (OH^-, H_2O, HO_2^-, Cl^-, $R\text{-}COO^-$, R-OH, $R\text{-}NH_2$, *etc.*). Depending on the reacting ligand, the product may be a hydroxyl radical such as in Eqs. 6 and 7 or another radical derived from the ligand. (Zepp *et al.*, 1992).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \qquad \textbf{(2)}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe(OOH)^{2+} + H^{+} \qquad \textbf{(3)}$$

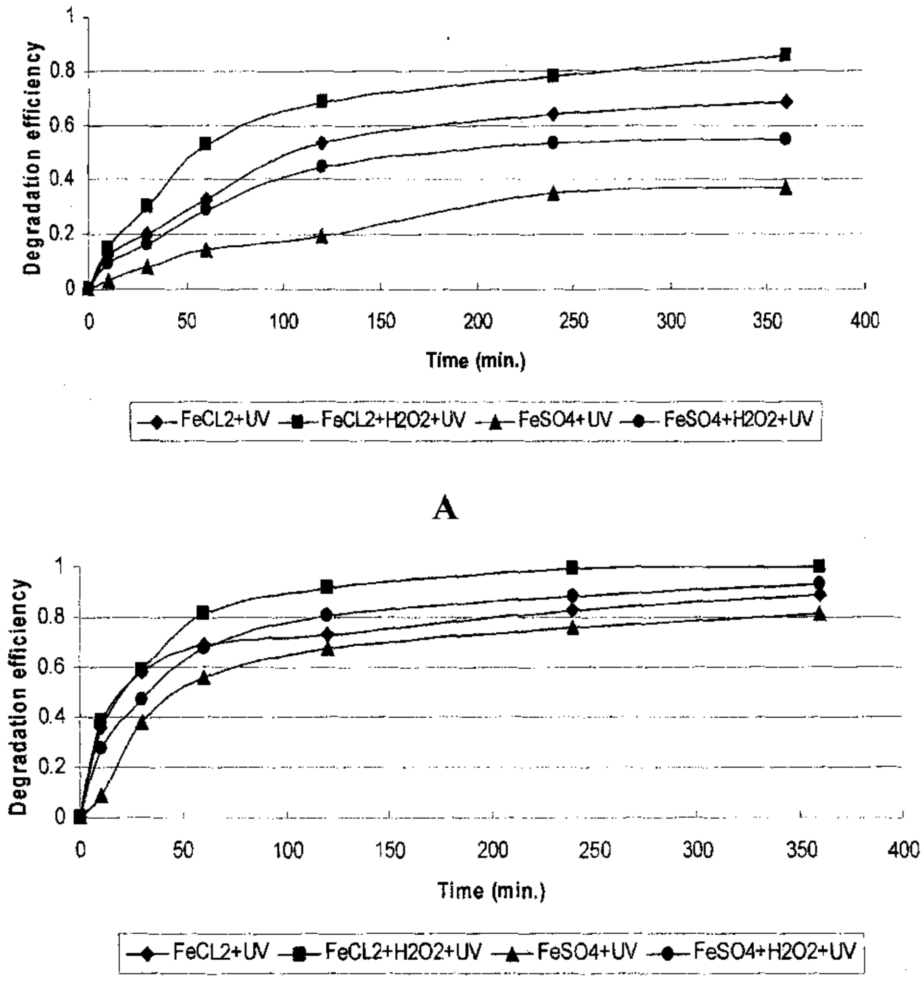
$$Fe(OOH)^{2+} \rightarrow Fe^{2+} + OH_2^{\bullet} \qquad \textbf{(4)}$$

$$[Fe^{3+}L] + h\nu \rightarrow [Fe^{3+}L]^{*} \rightarrow Fe^{2+} + L^{\bullet} \qquad \textbf{(5)}$$

$$[Fe(H_2O)]^{3+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} + H^{+} \qquad \textbf{(6)}$$

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \qquad (7)$$

As the system behaves independently of the initial oxidation state of iron, ferrous iron cannot usually be distinguished from ferric iron by the reaction mechanism. However, in practice, differences in degradation rates may be observed (Mazellier *et al.*, 2002b).



A

B

Fig. 3: The degradation efficiency of carbendazim (A) and metalaxyl (B) at different irradiation time intervals under Photo-Fenton systems.

Efficiency of the photocatalyst ZnO

The changes in carbendazim and metalaxyl concentrations or in other words degradation efficiency at different times during the photocatalytic degradation systems of (ZnO/UV) and (ZnO+H_2O_2/UV) were shown in Fig. 4 a and b. Evgenidou *et al.*, 2005 showed that hydrogen peroxide enhanced the degradation efficiency of the ZnO catalyst and this is due to the dual role of hydrogen peroxide which can act as an electron acceptor promoting the charge separation and it is also able to produce additional •OH radicals. The present results are compatible with them since, the two tested fungicides were more degradable under ZnO+H_2O_2/UV system than the other one and metalaxyl had higher values of degradation efficiency than the carbendazim. Also, the positive relationship between the degradation efficiency of the fungicides and the irradiation time was observed.

Tables 1 and 2 showed that, in the presence of ZnO and ZnO/H_2O_2 under UV light, 35.40 and 83.50% removal of the carbendazim could be achieved in 360 min. While almost the same percentages 44.90 and 84.52% could be reached in the case of fungicide metalaxyl after 60 minutes only under the same conditions.

The first-order rate equation and the half-life ($T_{1/2}$) for carbendazim and metalaxyl were also presented in Tables 1 and 2. $T_{1/2}$ for carbendazim was 9.63 hours under ZnO/UV system and it was decreased to 2.51hr. under ZnO+H_2O_2/UV system, whilst for metalaxyl it was 4.81 hr. and 0.68 hr. under the two systems, respectively.

The effect of the system ZnO + H_2O_2+UV was equal to the photo-Fenton system $FeCl_3$+H_2O_2+UV, where the percentages of carbendazim dissipation after 360 min of irradiation were 85.5 and 83.5%, respectively and 99.98 and 99.85% for metalaxyl, respectively.

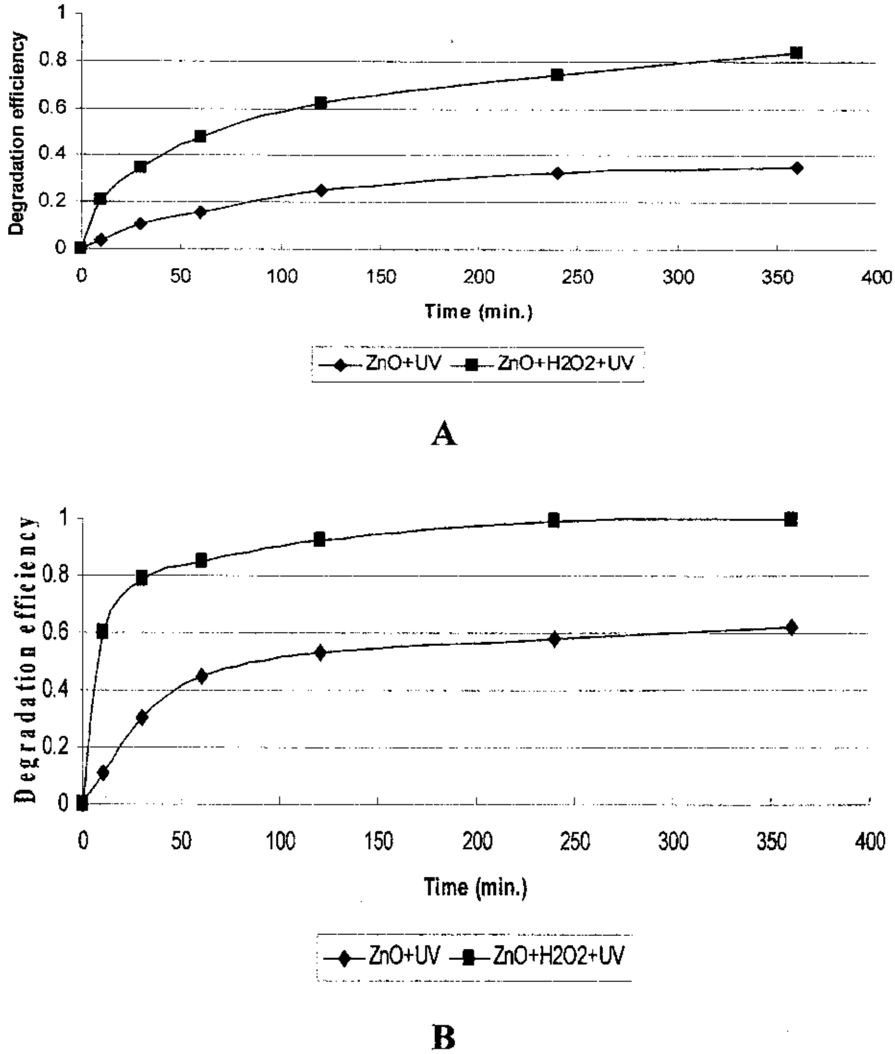


Fig. 4: The degradation efficiency of carbendazim (A) and metalaxyl (B) at different irradiation time intervals under Zinc oxide systems.

Irradiation system due to a general ZnO photocatalytic mechanism are proposed as follows: Under the irradiation of energy greater than the band gap and valence band electrons are promoted to the conduction band leaving a hole behind (Eq. 8). The high oxidative potential of the hole (h_{VB}^+) in the catalyst permits the direct oxidation of organic matter to reactive intermediates (Eq. 9). Very reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq. 10) or by the reaction of the hole with OH^- (Eq. 11). The hydroxyl radical is an extremely strong one and a non-selective oxidant that leads to degradation of organic chemicals (Khodja *et al.*, 2001; Daneshvar *et al.*, 2004, 2007 and Behnajady *et al.*, 2006). Electron in the conduction band (e_{CB}^-) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. 12). This radical, in the presence of organic compound, may form organic peroxides (Eq. 13) or hydrogen peroxide (Eq. 14). Electrons in the conduction band are also responsible for the production of hydroxyl radicals, which have been indicated as the primary cause of organic matter mineralization (Eq. 15) (Daneshvar *et al.*, 2004 and Konstantinou and Albanis, 2004).

$$ZnO + h\nu \rightarrow ZnO(e_{CB}^- + h_{VB}^+) \quad (8)$$

$$h_{VB}^+ + \text{pesticides} \rightarrow \text{oxidation of the pesticide} \quad (9)$$

$$h_{VB}^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH \quad (10)$$

$$h_{VB}^+ + OH^- \rightarrow {}^{\bullet}OH \quad (11)$$

$$e_{CB}^- + O2 \rightarrow {}^{\bullet}O^-_2 \quad (12)$$

$$ {}^{\bullet}O^-_2 + \text{pesticide} \rightarrow \text{pesticide} - OO^{\bullet} \quad (13)$$

$$ {}^{\bullet}O^-_2 + HO_2^{\bullet} + H^+ \rightarrow H_2O_2 + O_2 \quad (14)$$

$$\bullet OH + \text{pesticide} \rightarrow \text{degradation of the pesticide} \quad (15)$$

The fact that mankind has to face the problem of water pollution as an important threat. So, this study may be used as a step for pesticides elimination from the water and accordingly it can be used to purify wastewater to achieve the desired degree of quality. Moreover, this study may be used as a key step in understanding the interaction between pesticides and foliar fertilization.

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الملخص العربى

التحطم الكيمو- ضوئى للمبيدات الفطرية (كاربندازيم وميتالاكسايل) فى البيئة المائية باستخدام عمليات الأكسدة المتقدمة

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تمت دراسة التحطم الكيمو- ضوئى للمبيدات الفطرية كاربندازيم وميتالاكسايل وذلك بغرض محاولة معرفة سلوكهما وازالتهما من البيئة المائية الملوثة بهذه المبيدات وذلك بإستخدام عمليات الاكسدة المتقدمة والمتمثلة فى إستخدام كلوريد الحديديك (الأيون الثلاثى Fe^{3+}) - كبريتات الحديدوز (الأيون الثنائى Fe^{2+}) بالإضافة إلى أكسيد الزنك كلاً على حده أو مع فوق أكسيد الهيدروجين وذلك تحت ظروف التعرض لأشعة فوق البنفسجية. وقد تم تقدير متبقيات هذه المبيدات الناتجة من التحطم الضوئى بإستخدام التحليل الكروماتوجرافى السائل وكذلك تم تقدير ثوابت عملية التحطم. وقد أظهرت النتائج أن كلا من الكاربندازيم والميتالاكسيل ثابتين في البيئة المائية ولم يتعرضا للتحطم فى الظلام (فى عدم وجود الضوء) ولكن مع هذا إنخفض هذا الثبات عند التعرض للاشعة فوق البنفسجية. وتراوحت فترة نصف العمر ما بين ٢,٢٦ - ٨,٨٨ ساعة لمبيد الكاربندازيم و ٠,٥ - ٢,٥٧ ساعة لمبيد الميتالاكسيل وذلك بتاثير المعاملات المختلفة للفوتوفينتون. وقد كان الأيون الثلاثي للحديد تحت ظروف الفوتوفينتون أكثر تأثيرا على عملية التحطم من الأيون الثنائى. وقد أدى وجود فوق اكسيد الهيدروجين إلى زيادة عملية التحطم والإسراع منها لكلا المبيدين وذلك فى جميع معاملات الفوتوفينتون. وعلى ذلك نجد أن معاملة $Fe(III)/H_2O_2/UV$ أعطت اعلي نسبة تحطم للمبيدين حيث وصلت إلى ٨٥,٥ للكاربندازيم و٩٩,٩٨% للميتالاكسيل وذلك بعد ٣٦٠ دقيقة من التعرض للأشعة فوق البنفسجية. وزادت عملية التحطم الضوئى للكاربندازيم والميتالاكسيل بشكل واضح نتيجة المعاملة $ZnO+H_2O_2/UV$ بالمقارنة بالمعاملة بدون استخدام فوق أكسيد الهيدروجين حيث وجد أن فترة نصف العمر لمبيدى الكاربندازيم والميتالاكسيل هى ٩,٦٣ و ٤,٨١ ساعة على التوالى وذلك فى حالة معاملة ZnO /UV وانخفضت هذه القيم لتصل إلى ٢,٥١ و ٠,٦٨ ساعة فى معاملة $ZnO+H_2O_2/UV$. كذلك وجدت علاقة طردية بين معدل التحطم ووقت التعرض للاشعة فوق البنفسجية وذلك فى جميع المعاملات المستخدمة.