



PHOTOCATALYTIC DECONTAMINATION OF CHLORANTRANILIPROLE RESIDUES IN WATER USING ZnO NANOPARTICLES

DR. A. RAMESH, Ph.D, D.Sc.,
raamesh_a@yahoo.co.in



OBJECTIVES

- Determination of persistence and photolysis of chlorantraniliprole in water and at different pH conditions
- Liquid phase synthesis of ZnO nanorods
- Decontamination of residues of chlorantraniliprole in water using ZnO nanocatalyst
- LC-ESI-MS/MS confirmation of residues and its metabolites



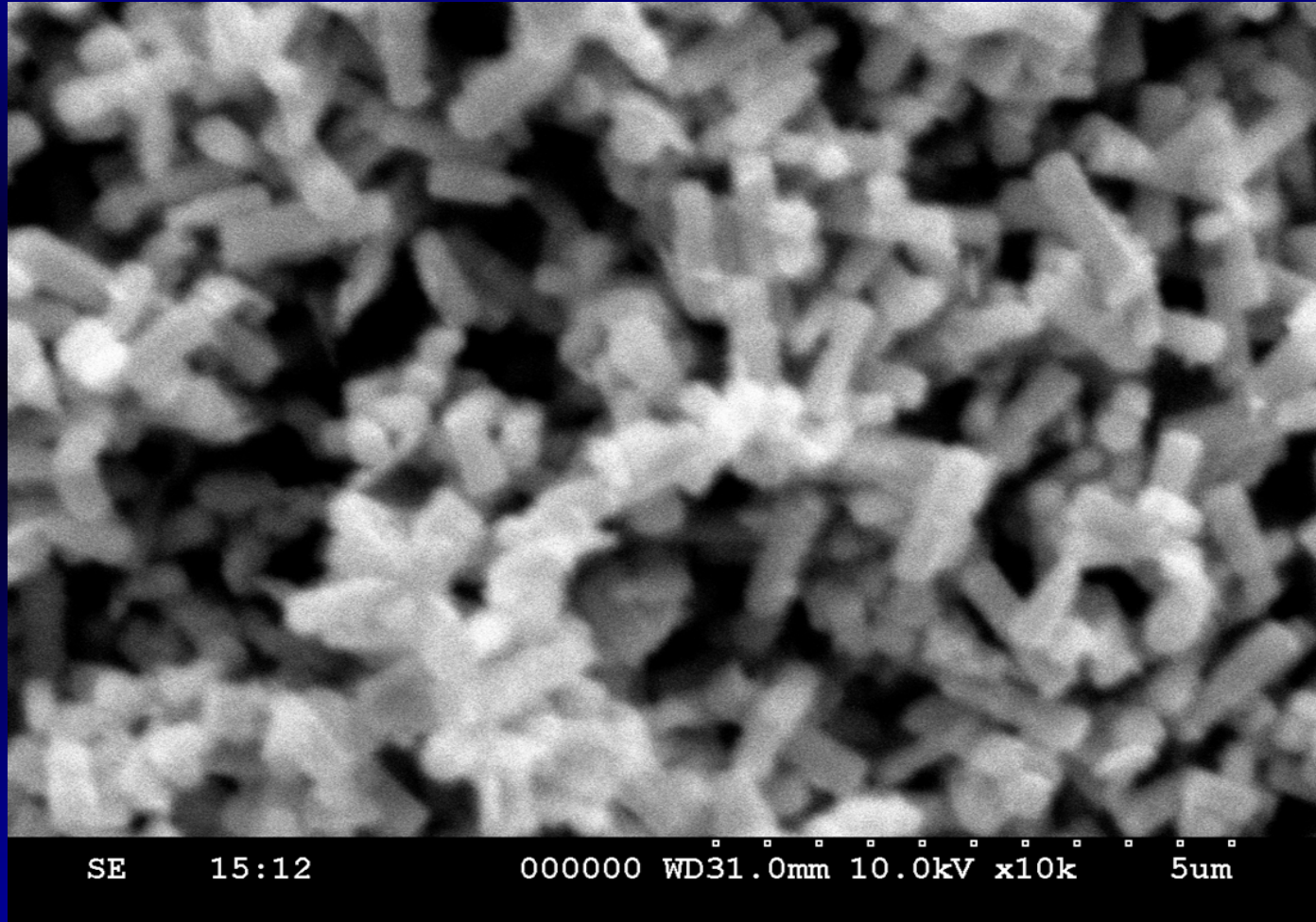
SYNTHESIS OF ZnO NANOPARTICLES

- To 0.05 M Zinc acetate added 0.05 M of triethanolamine drop wise under nitrogen atmosphere
- Sonicated for 2 hours at 80°C
- Resulting light yellow colour precipitate was washed several times with Milli Q water
- Dried at 200° C in air for 2 hours

Ref.: Rongguo Xie et al, Journal of physical chemistry B, 110, 2006, 19147 – 19153.



SEM IMAGE OF ZINC OXIDE NANORODS



Particle size : 0.700 – 1.00 μm length; 100-150 nm Dia.

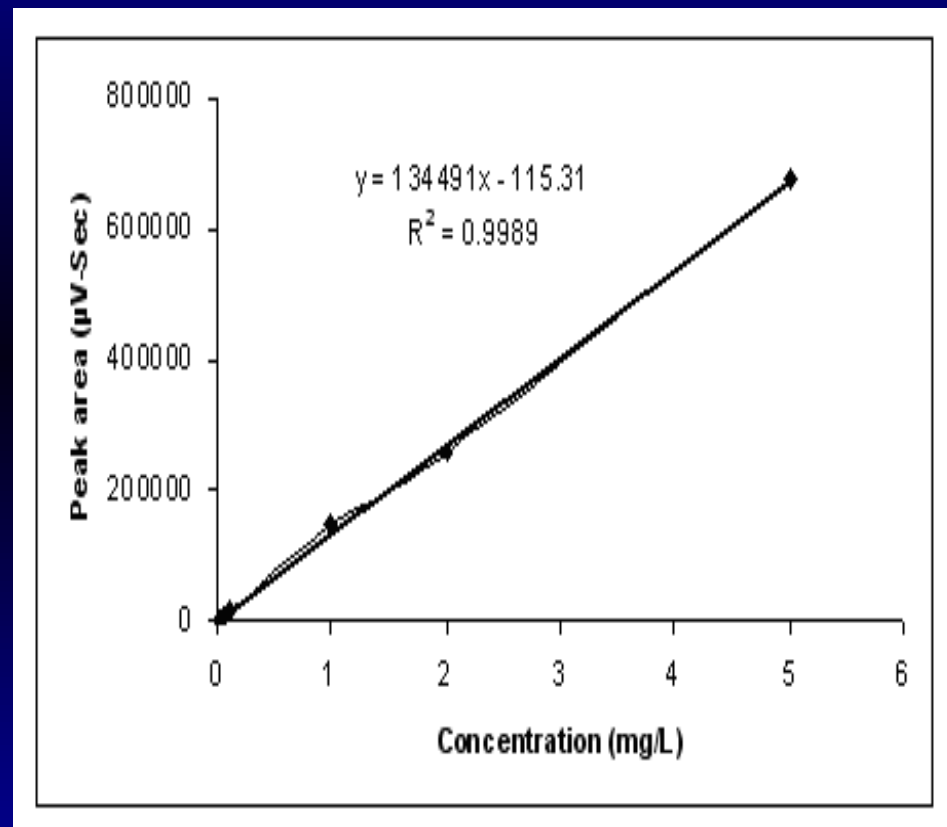


GAS CHROMATOGRAPHIC DETERMINATION OF CHLORANTRANILIPROLE

Instrument	- Shimadzu GC-14B Gas Chromatograph with Electron Capture detector
Column	- DB-5 Megabore (30m length x 0.53 mm I.D., 1.0 μ m film thickness).
Detector	- ^{63}Ni Electron Capture Detector
Temperature conditions	
Oven	- 300°C
Injector	- 300°C
Detector	- 300°C
Gas flow rate	
Nitrogen	- 100 KPa
Makeup	- 50 KPa
Current	- 1 nA
Retention time (approximate)	- 9.3 minutes

CALIBRATION - CHLORANTRANILIPROLE

Concentration (mg/L)	Peak area (μ V-sec)
5	675780
2	254014
1	147011
0.1	12109
0.05	6596
0.01	1247



LOD – 0.01 mg/L BASED ON SIGNAL TO NOISE RATIO 3:1



EXTRACTION/DERIVATIZATION PROCEDURE

- Five mL of water sample was partitioned with 40 mL of hexane : ethyl acetate (50:50) mixture
- The organic layer was separated and evaporated to dryness and reconstituted the residues using acetonitrile with 0.15% ammonium hydroxide
- The content were placed in a heating block and held at 70°C for 2 hours.
- Partitioned with 2 x 50 mL portions of ethyl acetate
- Evaporated to dryness and reconstituted the residues with acetone



METHOD OF CALCULATION

$$\text{Chlorantraniliprole content (ppm)} = \frac{A \times B \times C}{D \times E} \times F \times 1.0387$$

Where,

- | | | |
|--------|---|-------------------------------------|
| A | - | Peak area in sample (μV-sec) |
| B | - | Final volume of the sample (ml) |
| C | - | Concentration of the standard (ppm) |
| D | - | Peak area in standard (μV-sec) |
| E | - | Volume of the sample (ml) |
| F | - | Dilution Factor |
| 1.0387 | - | Conversion factor |



RECOVERY OF CHLORANTRANILIPROLE IN WATER AT DIFFERENT pH LEVELS

SUBSTRATES	RECOVERY (%)
Acidic water	95
Neutral water	93
Basic water	91
Milli Q water	96

LIMIT OF QUANTIFICATION 0.03 mg/L BASED ON SIGNAL TO NOISE RATIO 10:1



PERSISTENCE AND DECONTAMINATION OF CHLORANTRANILIPROLE RESIDUES IN WATER

- Fortified concentrations - 1.0 and 2.0 mg/L
- Water pH - 4.0, 7.0 and 9.0
- Sampling occasions - 0, 1, 3, 5, 7, 10, 15, 20, 30 and 50 days after fortification.

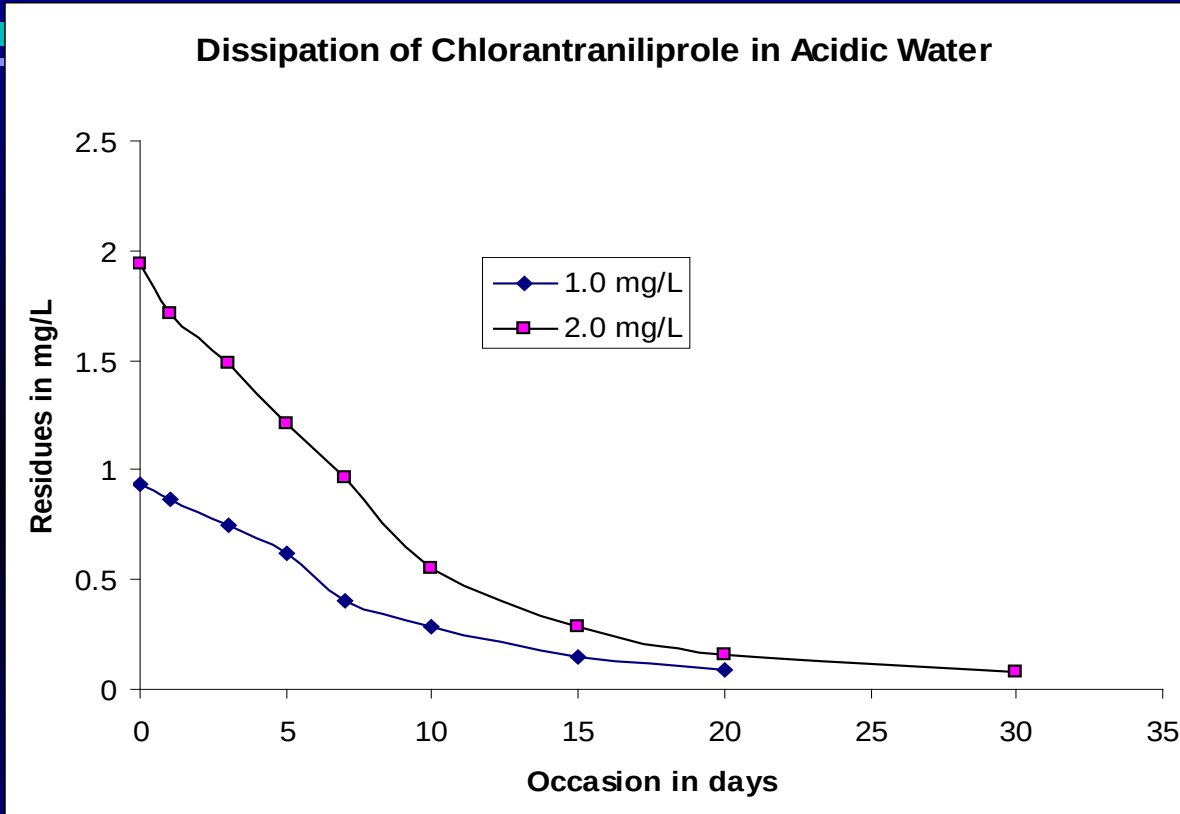
Photocatalysis with ZnO nanorods

- Optimum catalyst amount - 0.04 g/L
- Sampling occasions - 0, 3, 6, 9, 15 and 20 hours after fortification



DISSIPATION OF CHLORANTRANILIPROLE IN ACIDIC WATER WITHOUT CATALYST

Sampling occasion (Days)	Residues (mg/L)	
	Acidic water (pH 4)	
	1.0 mg/L	2.0 mg/L
0	0.939	1.941
1	0.867	1.713
3	0.751	1.491
5	0.622	1.214
7	0.405	0.961
10	0.283	0.552
15	0.147	0.287
20	0.093	0.156
30	<LOQ	0.078
50	<LOQ	<LOQ

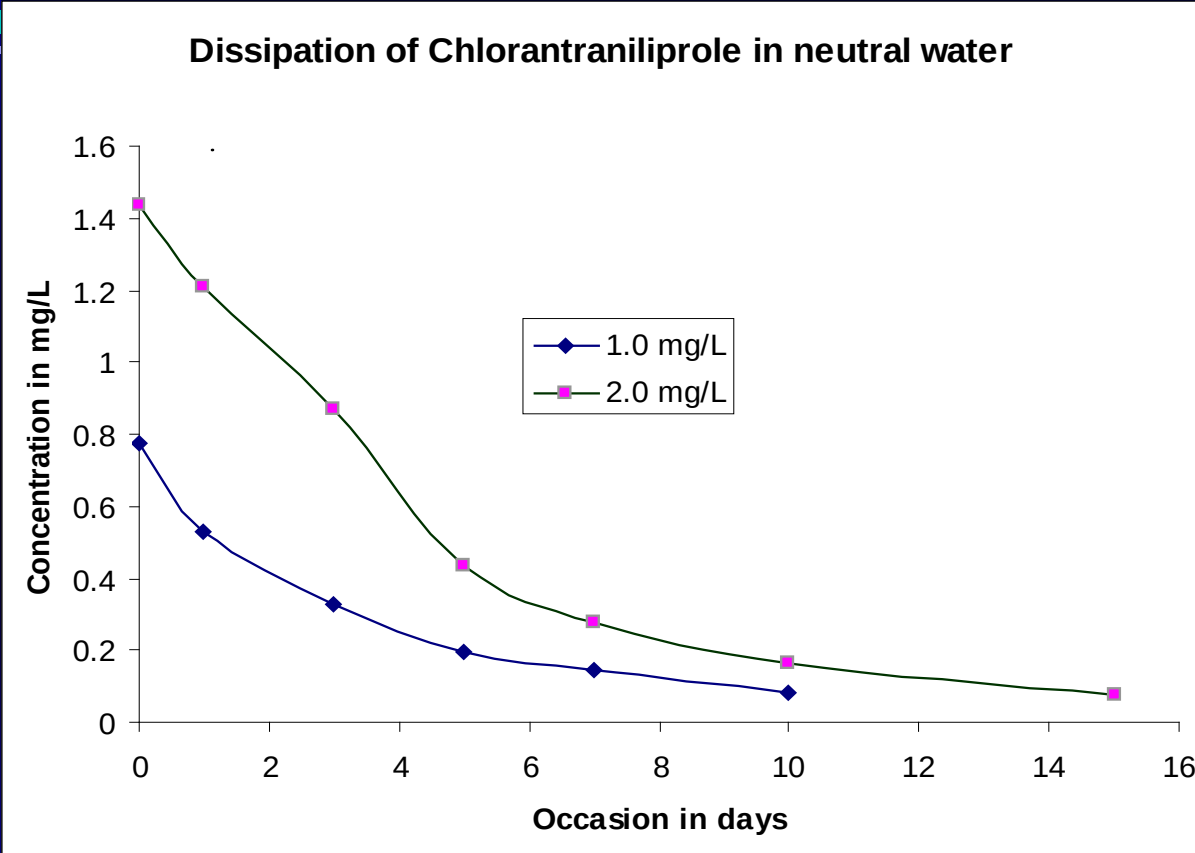


DT ₅₀ in days		DT ₉₀ in days	
1.0 mg/L	2.0 mg/L	1.0 mg/L	2.0 mg/L
5.68	6.04	18.87	20.08



DISSIPATION OF CHLORANTRANILIPROLE IN NEUTRAL WATER WITHOUT CATALYST

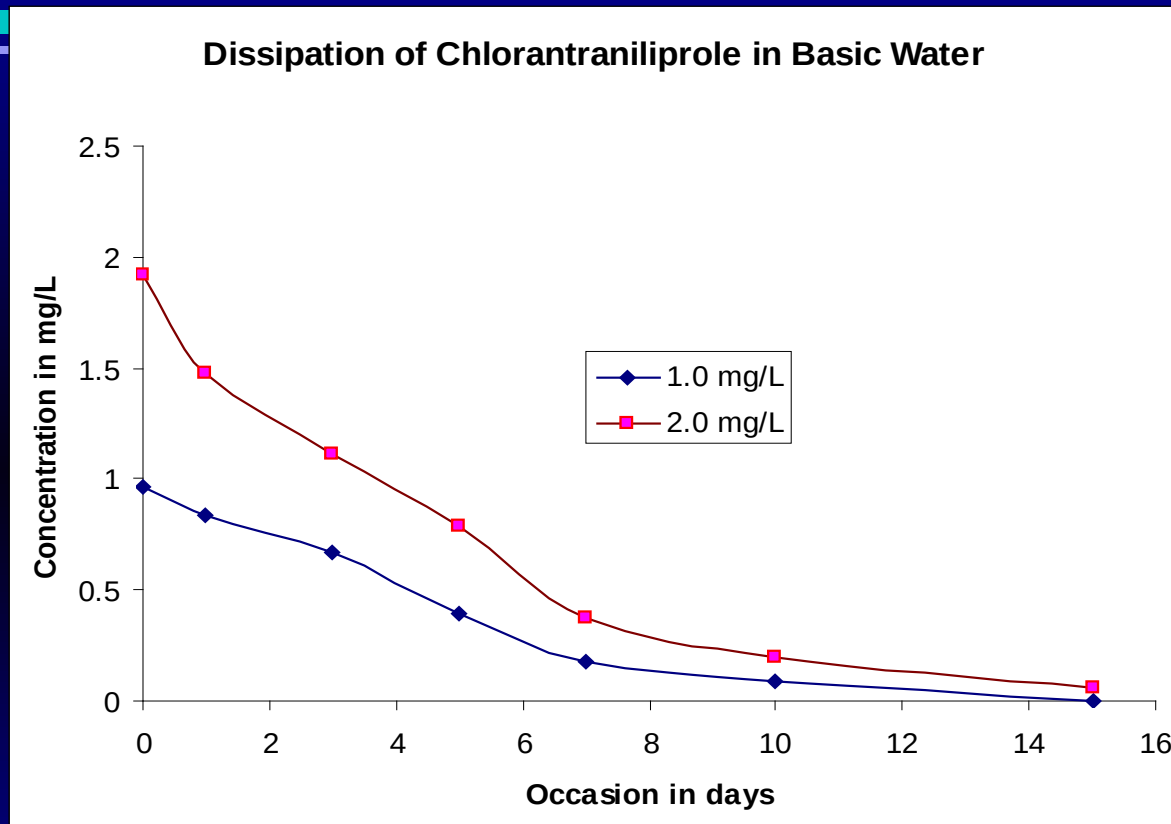
Sampling occasion (Days)	Residues (mg/L)	
	Neutral water (pH 7)	
	1.0 mg/L	2.0 mg/L
0	0.775	1.437
1	0.529	1.209
3	0.33	0.868
5	0.193	0.437
7	0.146	0.279
10	0.084	0.166
15	<LOQ	0.077
20	<LOQ	<LOQ
30	<LOQ	<LOQ
50	<LOQ	<LOQ



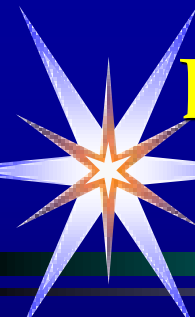
DT ₅₀ in days		DT ₉₀ in days	
1.0 mg/L	2.0 mg/L	1.0 mg/L	2.0 mg/L
4.12	4.31	13.68	14.31

DISSIPATION OF CHLORANTRANILIPROLE IN BASIC WATER WITHOUT CATALYST

Sampling occasion (Days)	Residues (mg/L)	
	Basic water (pH 9)	
	1.0 mg/L	2.0 mg/L
0	0.968	1.918
1	0.839	1.48
3	0.665	1.109
5	0.396	0.788
7	0.18	0.375
10	0.087	0.194
15	<LOQ	0.059
20	<LOQ	<LOQ
30	<LOQ	<LOQ
50	<LOQ	<LOQ

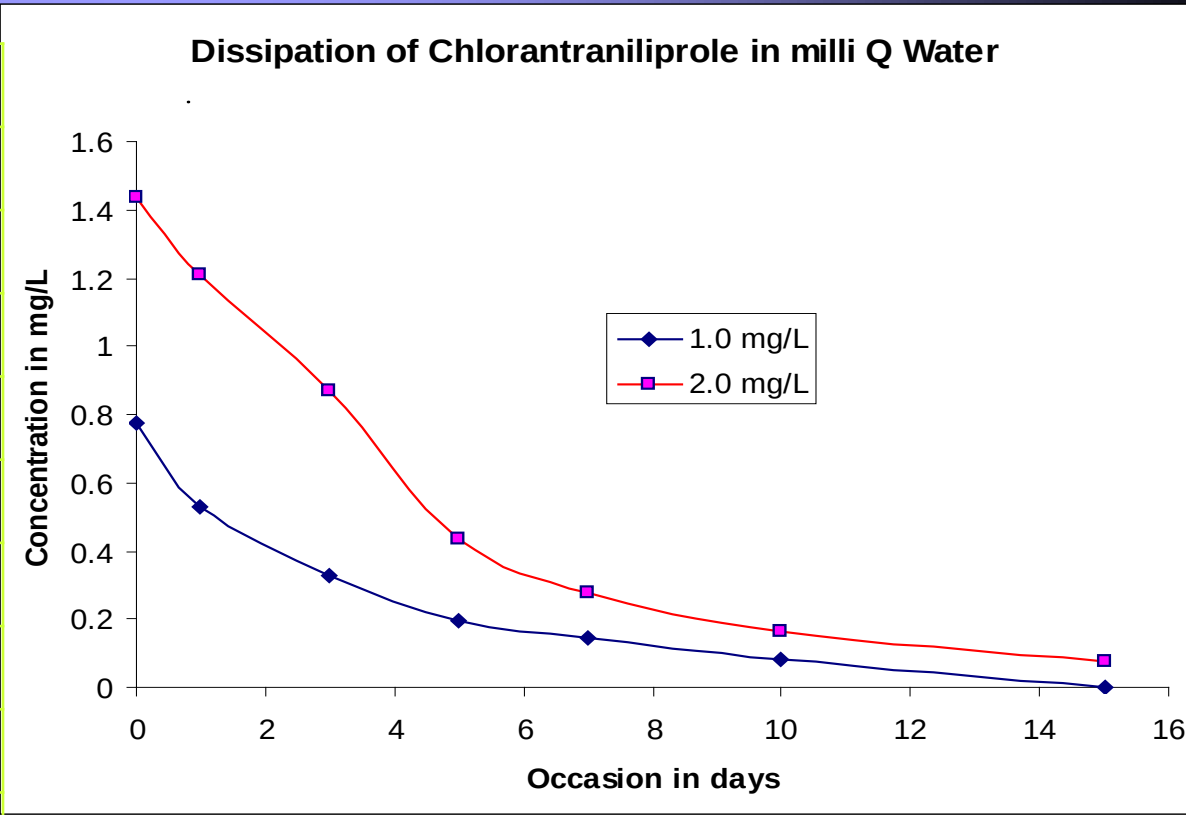


DT ₅₀ in days		DT ₉₀ in days	
1.0 mg/L	2.0 mg/L	1.0 mg/L	2.0 mg/L
4.46	4.40	14.82	14.60



DISSIPATION OF CHLORANTRANILIPROLE IN MILLI Q WATER WITHOUT CATALYST

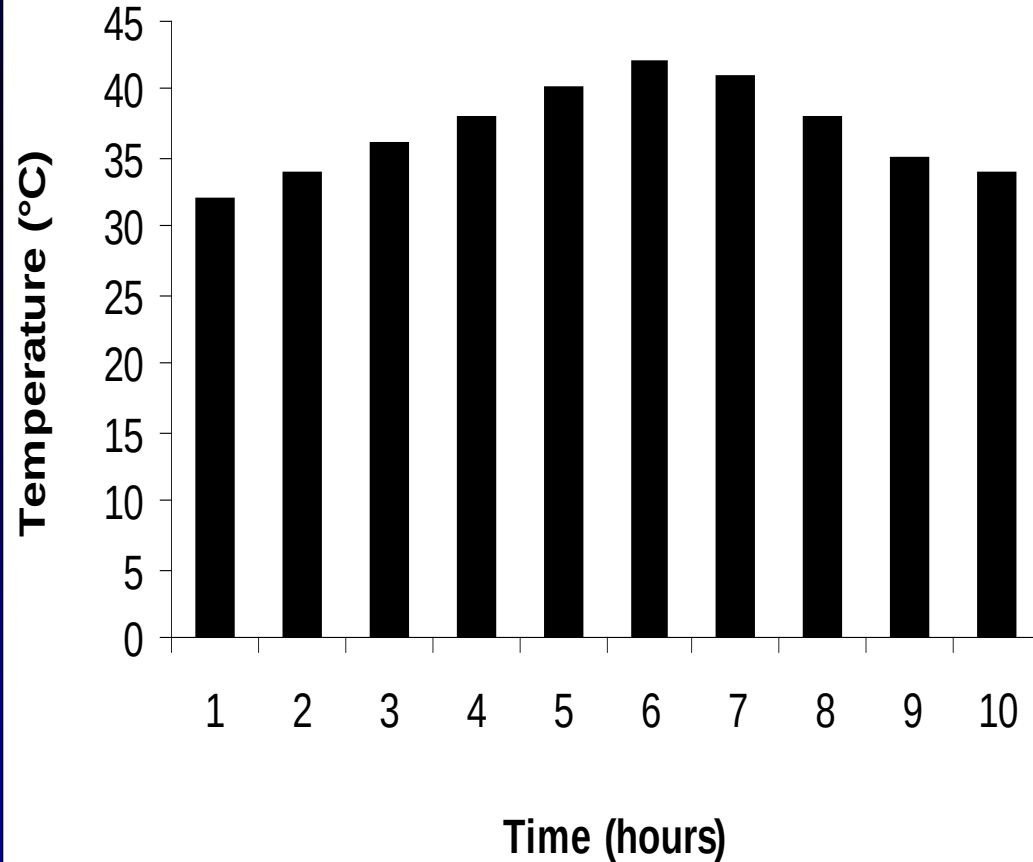
Sampling occasion (Days)	Residues (mg/L)	
	Neutral water (pH 7)	
	1.0 mg/L	2.0 mg/L
0	0.775	1.437
1	0.529	1.209
3	0.33	0.868
5	0.193	0.437
7	0.146	0.279
10	0.084	0.166
15	<LOQ	0.077
20	<LOQ	<LOQ
30	<LOQ	<LOQ
50	<LOQ	<LOQ



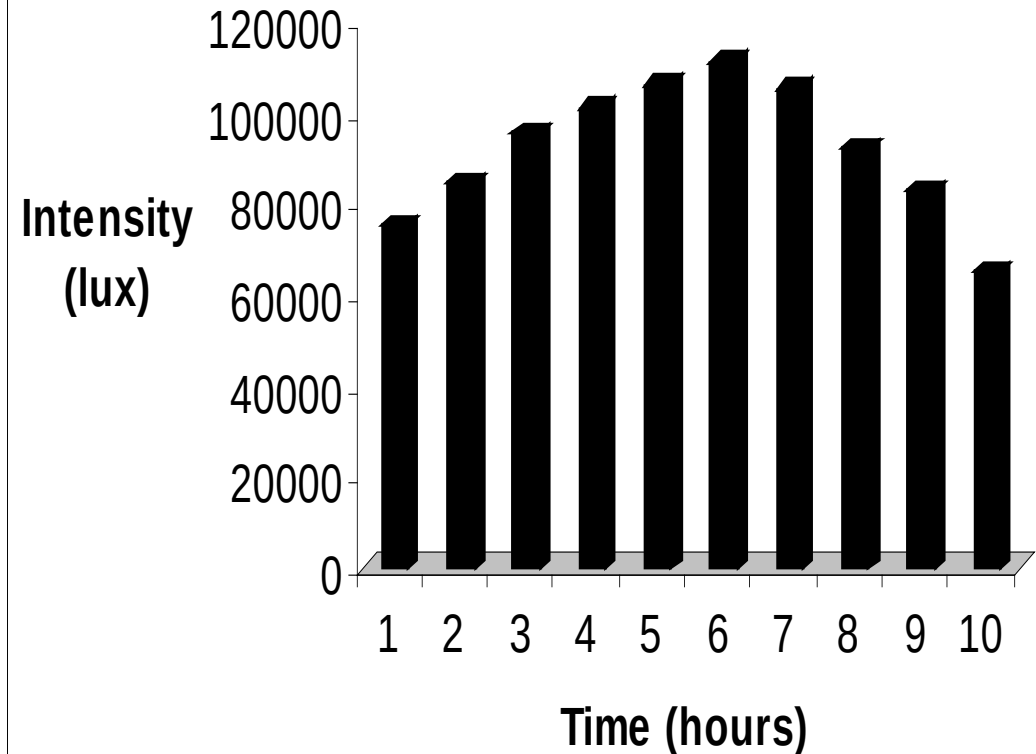
DT ₅₀ in days		DT ₉₀ in days	
1.0 mg/L	2.0 mg/L	1.0 mg/L	2.0 mg/L
2.78	2.91	9.25	9.65

TEMPERATURE AND LIGHT INTENSITY DURING PHOTOCATALYTIC DEGRADATION OF RESIDUES

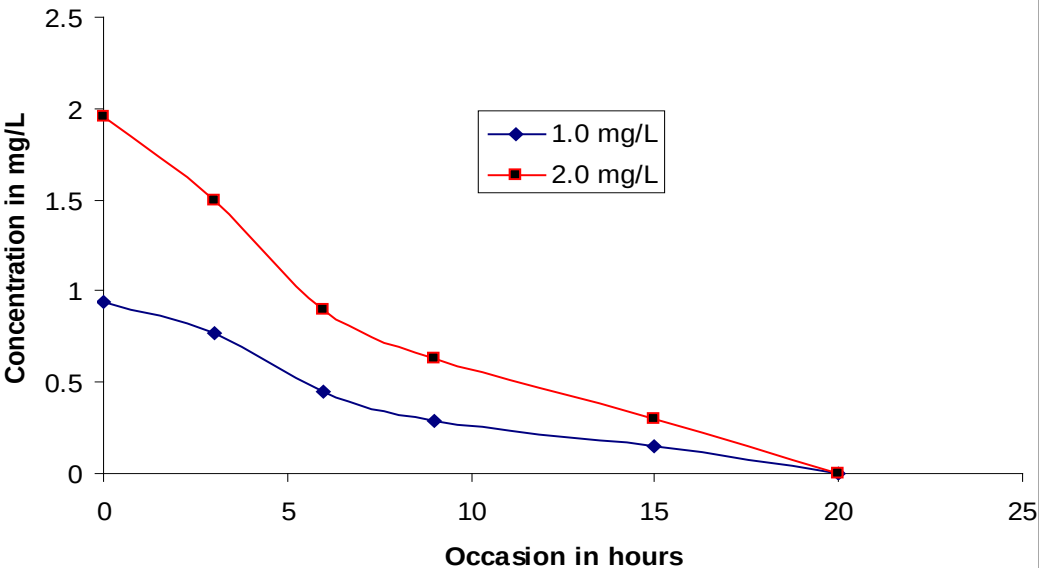
Temperature



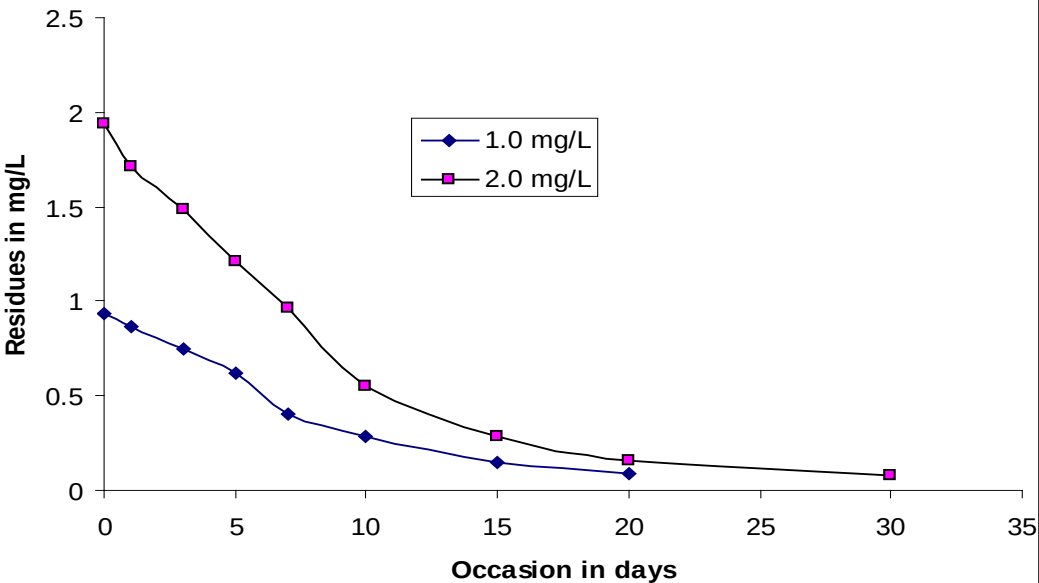
Light intensity



Photocatalytic degradation of Chlorantraniliprole in
Acidic Water with ZnO Catalyst



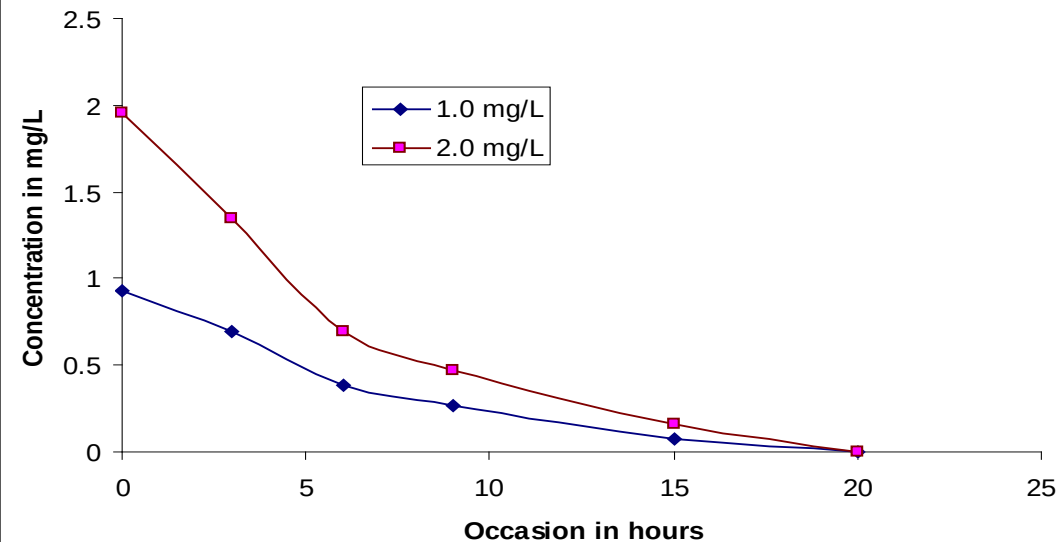
Dissipation of Chlorantraniliprole in Acidic Water without
catalyst



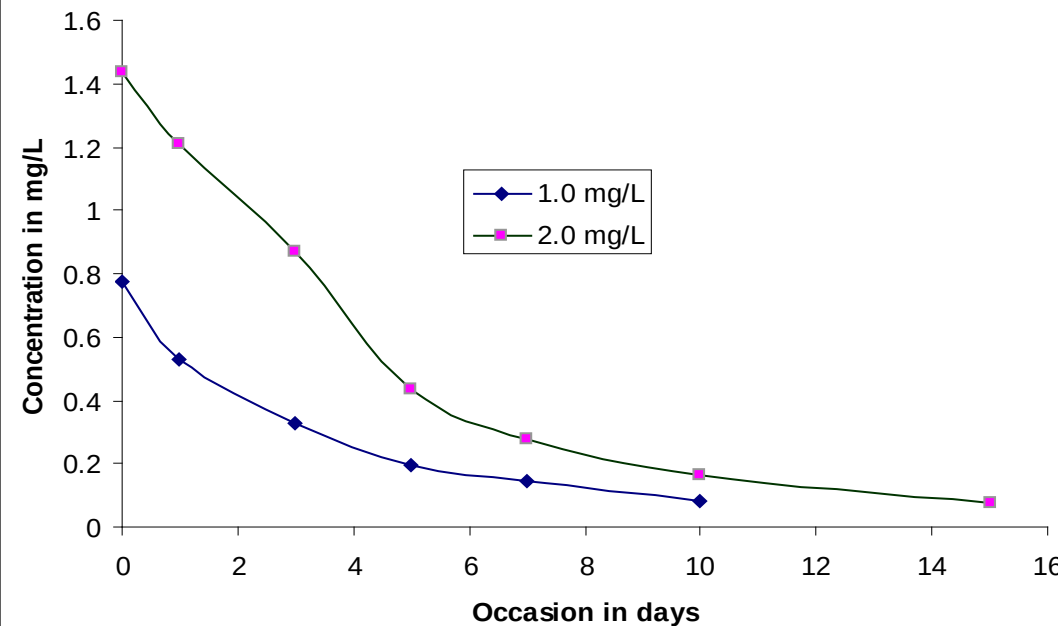
Dissipation in acidic water with ZnO catalyst

Sampling occasion (hours)	Residues (mg/L)	
	Acidic water (pH 4)	
	1.0 mg/L	2.0 mg/L
0	0.942	1.955
3	0.764	1.496
6	0.448	0.902
9	0.291	0.634
15	0.145	0.296
20	<LOQ	<LOQ

Photocatalytic degradation of Chlorantraniliprole in neutral water with ZnO Catalyst



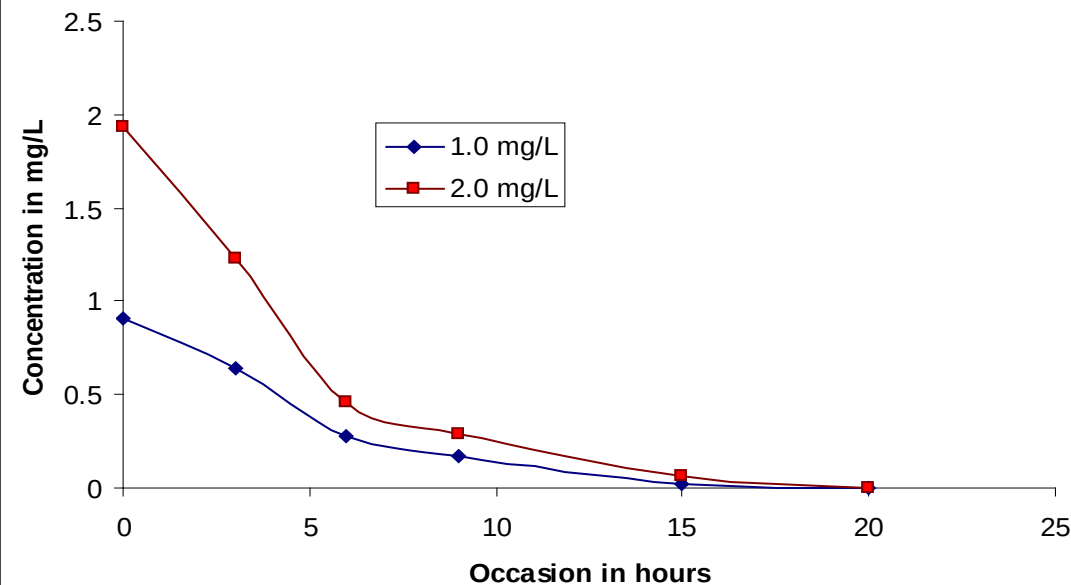
Dissipation of Chlorantraniliprole in neutral water without catalyst



Dissipation in neutral water with ZnO catalyst

Sampling occasion (hours)	Residues (mg/L)	
	Neutral water (pH 7)	
	1.0 mg/L	2.0 mg/L
0	0.931	1.951
3	0.692	1.346
6	0.383	0.692
9	0.264	0.474
15	0.071	0.158
20	<LOQ	<LOQ

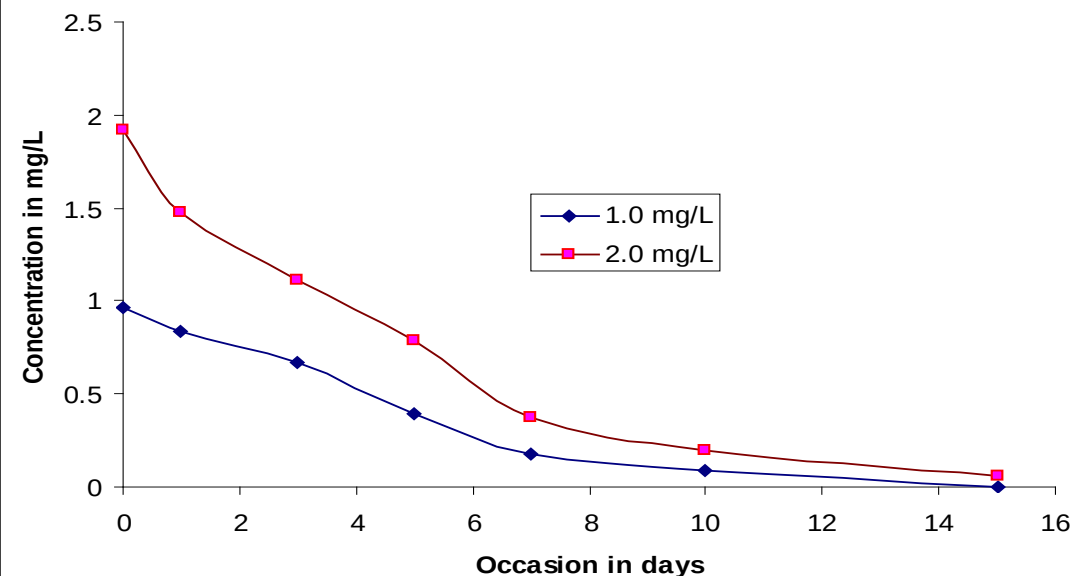
Photocatalytic degradation of Chlorantraniliprole in Basic Water with ZnO Catalyst



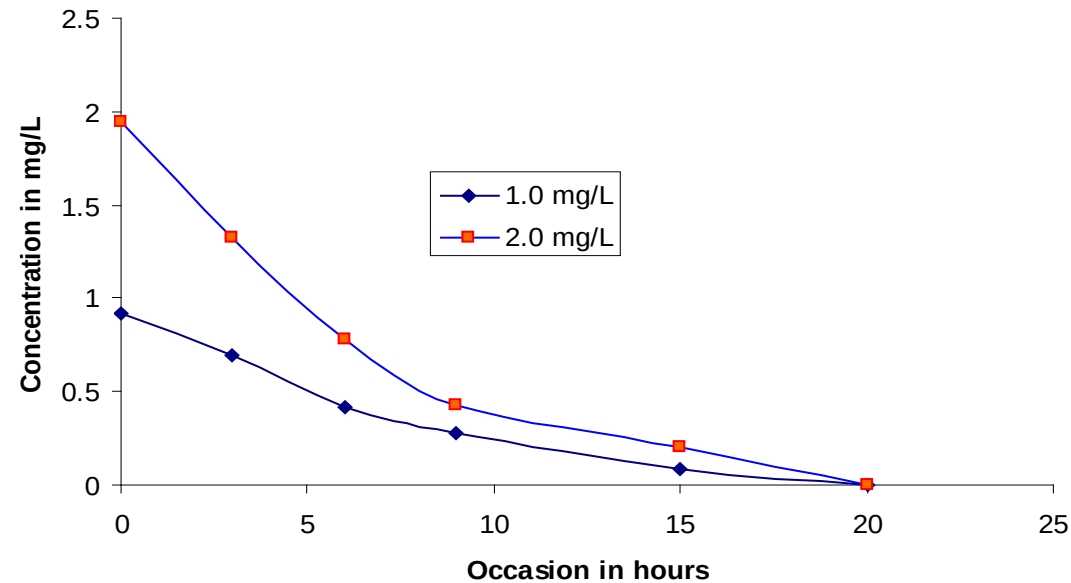
Dissipation in Basic water with ZnO catalyst

Sampling occasion (hours)	Residues (mg/L)	
	Basic water (pH 9)	
	1.0 mg/L	2.0 mg/L
0	0.909	1.937
3	0.641	1.228
6	0.274	0.461
9	0.168	0.293
15	0.026	0.065
20	<LOQ	<LOQ

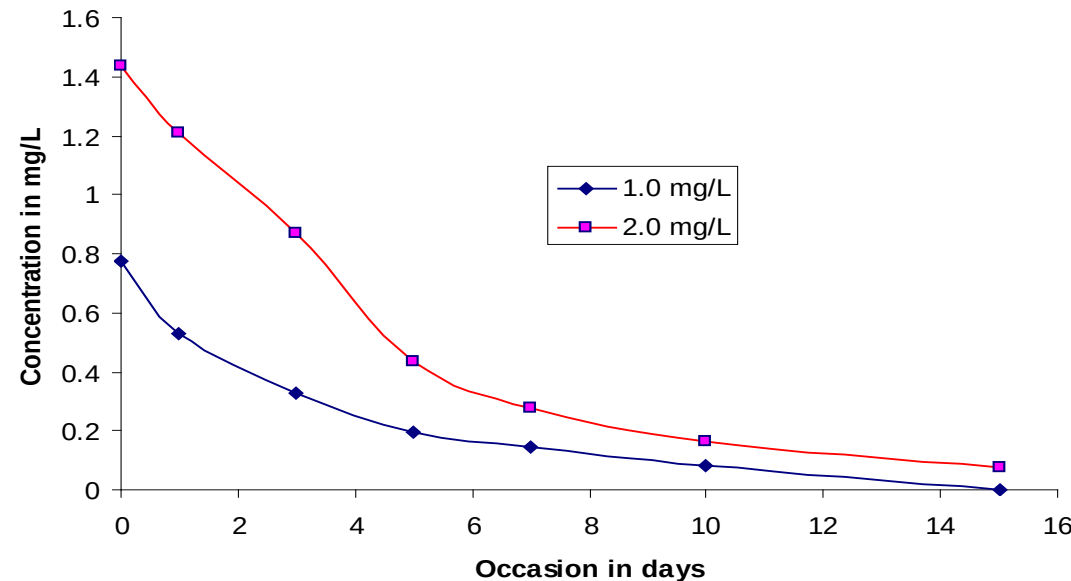
Dissipation of Chlorantraniliprole in Basic Water without Catalyst



Photocatalytic degradation of Chlorantraniliprole in Milli Q Water with ZnO catalyst



Dissipation of Chlorantraniliprole in milli Q Water without catalyst



Dissipation in Milli Q Water with ZnO catalyst

Sampling occasion (hours)	Residues (mg/L)	
	Milli Q water	
	1.0 mg/L	2.0 mg/L
0	0.924	1.943
3	0.691	1.322
6	0.414	0.781
9	0.277	0.432
15	0.088	0.207
20	<LOQ	<LOQ



RATE CONSTANT, DT50 AND DT90 VALUES FOR DISSIPATION OF CHLORANTRANILIPROLE IN WATER

Substrate	Rate constant (k) day ⁻¹		DT ₅₀ in days		DT ₉₀ in days	
	1.0 mg/L	2.0 mg/L	1.0 mg/L	2.0 mg/L	1.0 mg/L	2.0 mg/L
Acidic Water	0.12	0.11	5.68	6.04	18.87	20.08
Neutral Water	0.17	0.16	4.12	4.31	13.68	14.31
Basic Water	0.16	0.16	4.46	4.40	14.82	14.60
Milli Q Water	0.25	0.24	2.78	2.91	9.25	9.65



RATE CONSTANT, DT50 AND DT90 VALUES FOR DISSIPATION OF CHLORANTRANILIPROLE IN WATER IN PRESENCE OF ZnO NANORODS

Substrate	Rate constant (k) hr ⁻¹		DT ₅₀ in hours		DT ₉₀ in hours	
	1.0 mg/L	2.0 mg/L	1.0 mg/L	2.0 mg/L	1.0 mg/L	2.0 mg/L
Acidic Water	0.13	0.13	5.33	5.39	17.69	17.90
Neutral Water	0.17	0.17	4.01	4.09	13.31	13.60
Basic Water	0.24	0.23	2.89	3.02	9.61	10.04
Milli Q Water	0.16	0.15	4.37	4.51	14.53	14.97

CONFIRMATION OF RESIDUES AND ITS BREAKDOWN PRODUCTS USING LC-ESI-MS/MS

Dry gas	: Nitrogen
Collision gas	: Helium
Nebulizer	: 40 psi
Dry gas flow	: 7 mL/min
Interface Temp	: 340°C
Scan range	: 100 to 550 m/Z



High capacity iontrap electrospray
tandem mass spectrometry



HPLC SEPARATION PARAMETERS

Instrument : Agilent 1200 series HPLC with VWD detector
Column : Xterra MS C18 (150 mm X 4.6 mm)
Mobile phase A : Acetonitrile (0.1% Formic acid)
Mobile phase B : Milli Q Water (0.1% Formic acid)
Injection volume : 50 μ L
Flow program

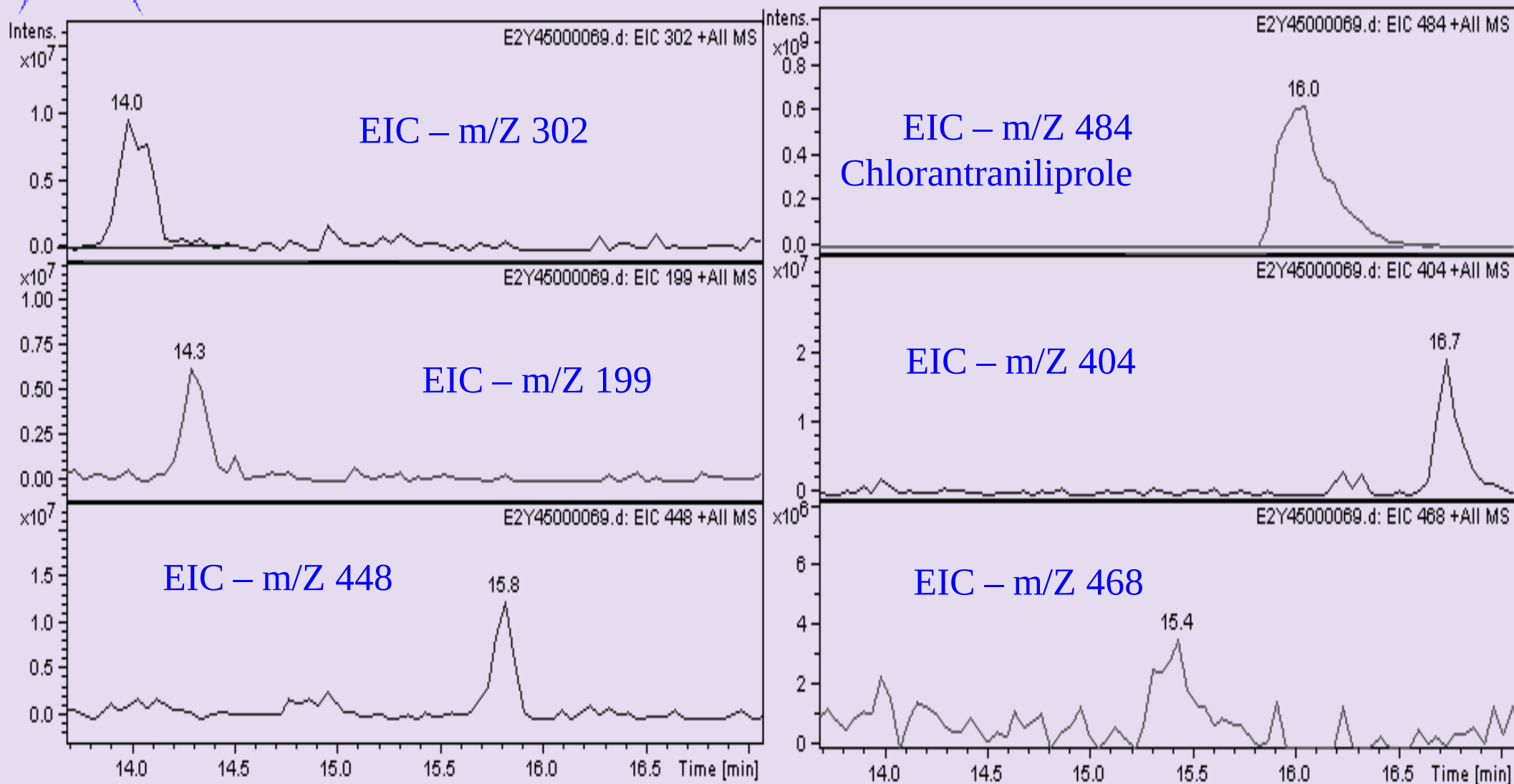
Time	%B	Flow
0	95	0.2
15	5	0.3
25	5	0.4
26	95	0.4
26.1	95	0.2

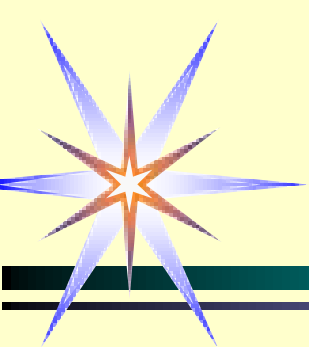


CHLORANTRANILIPROLE AND BREAKDOWN PRODUCTS IN WATER

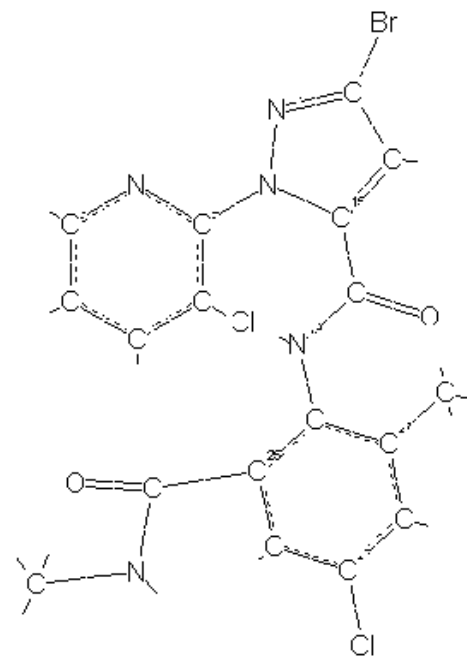
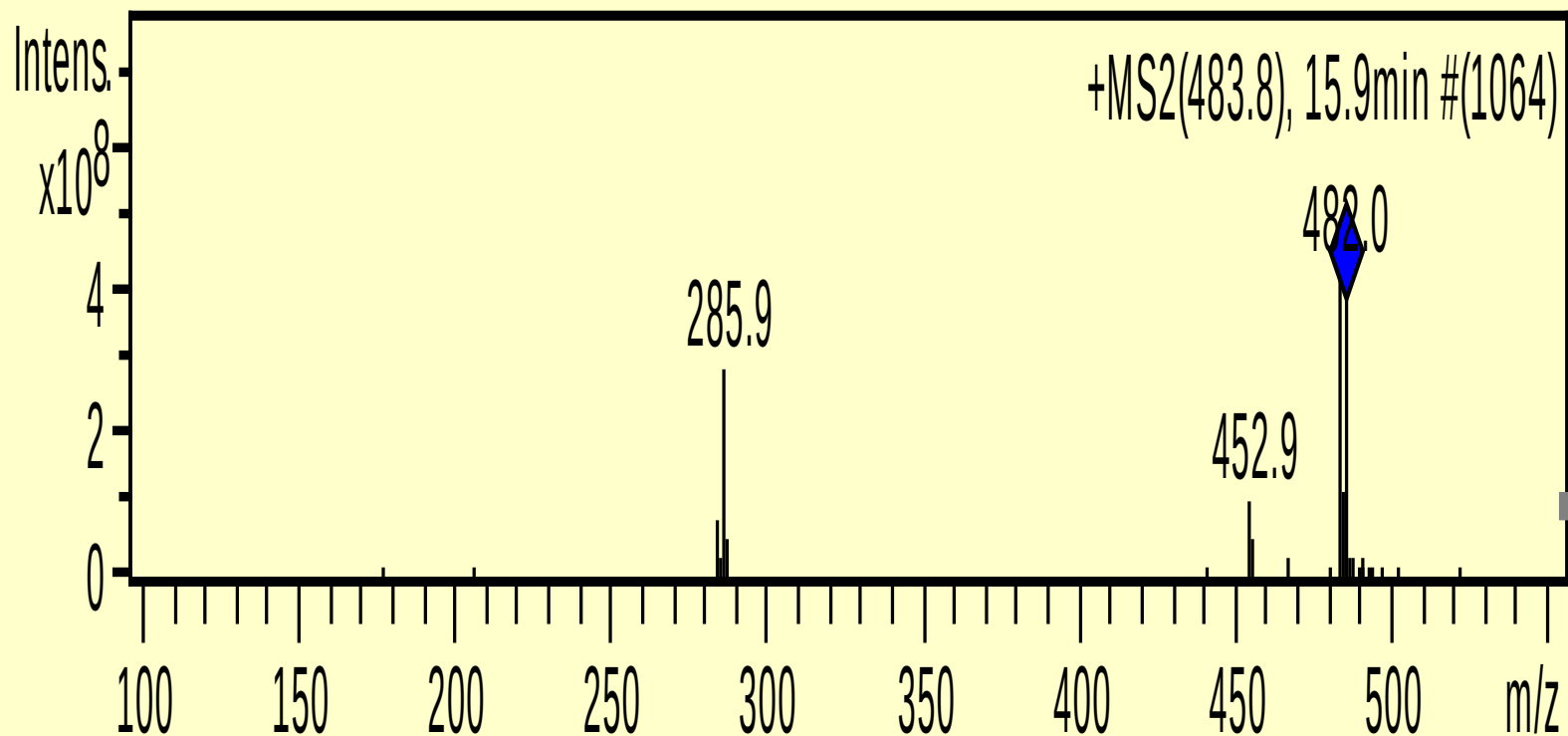
Molecular formula	Molecular weight m/Z	Retention time in min	MS2 Fragmentation ions m/Z
$C_{18}H_{14}N_5O_2Cl_2Br$	483	16.0	453 and 286
$C_9H_5N_3O_2ClBr$	302	14.0	286 and 260
$C_9H_{11}N_2OCl$	198	14.3	168
$C_{17}H_{12}N_5O_2C_{12}Br$	469	15.4	453 and 286
$C_{18}H_{15}N_5O_2ClBr$	449	15.8	419 and 250
$C_{18}H_{15}N_5O_2Cl_2$	404	16.7	372

EXTRACTED ION CHROMATOGRAM OF CHLORANTRANILIPROLE AND ITS BREAKDOWN PRODUCTS IN WATER



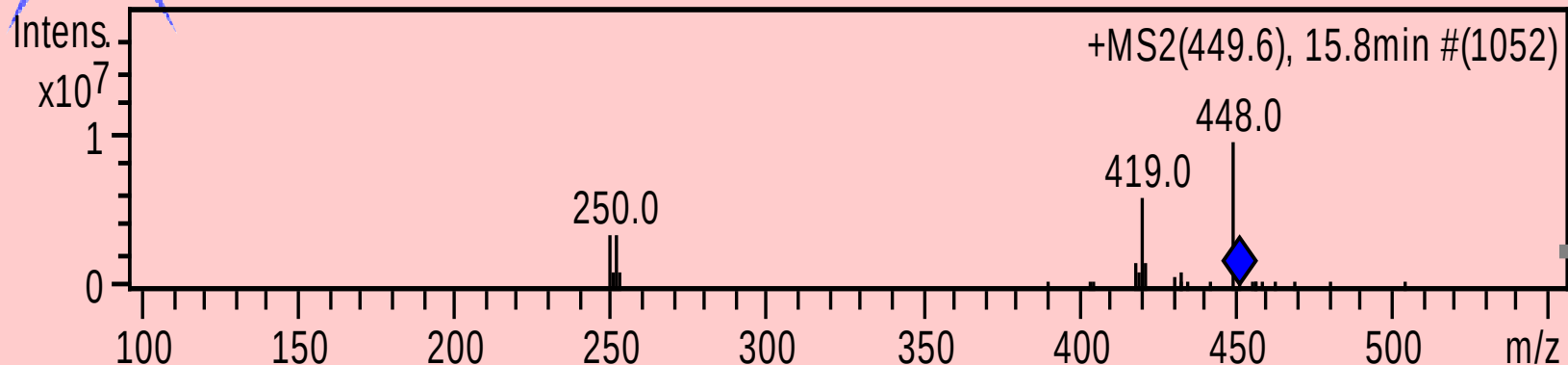


ESI-MS/MS SPECTRA OF CHLORANTRANILIPROLE

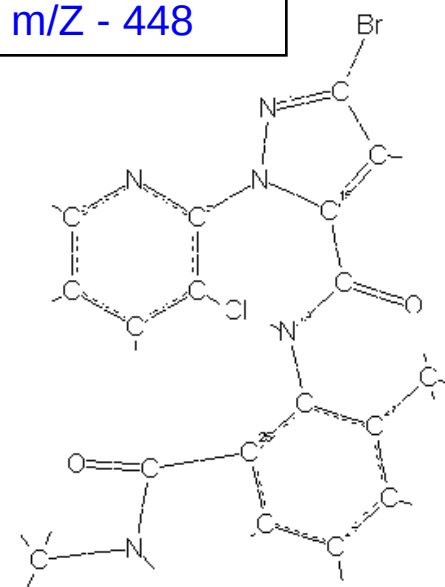


Chlorantraniliprole –
m/z – 483

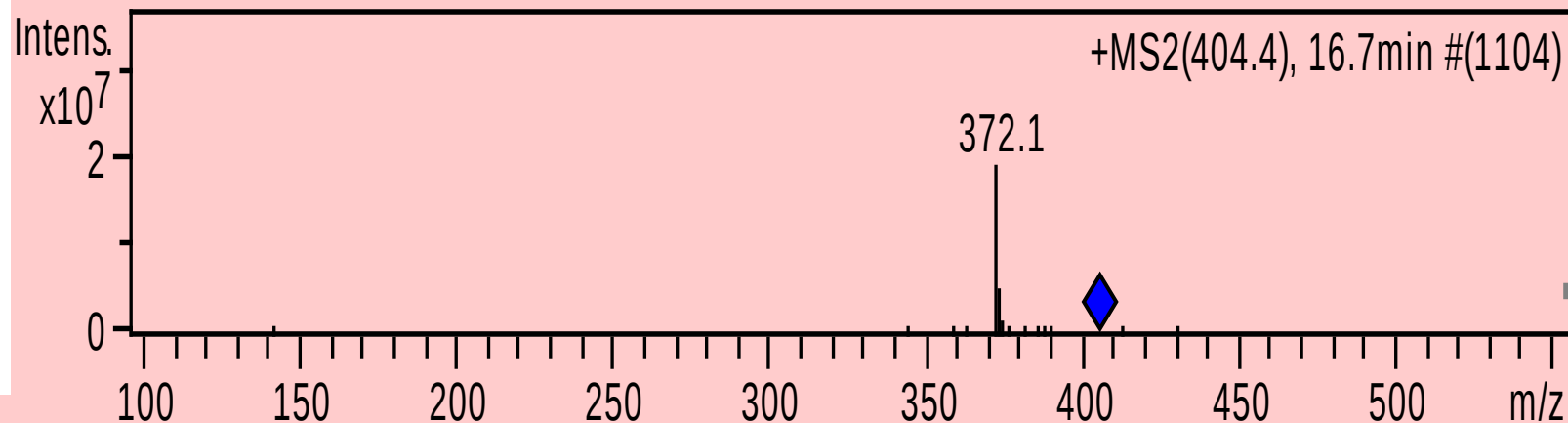
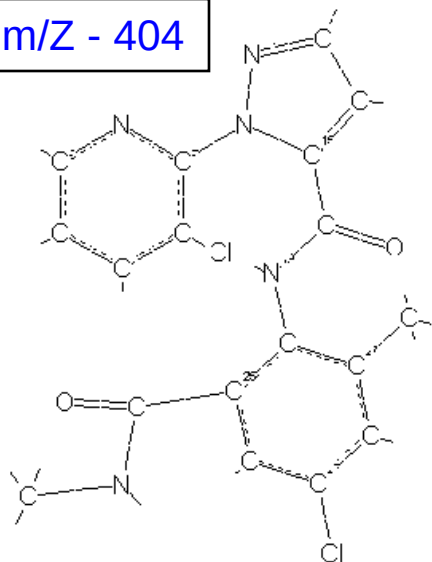
ESI-MS/MS SPECTRA OF BREAKDOWN PRODUCTS

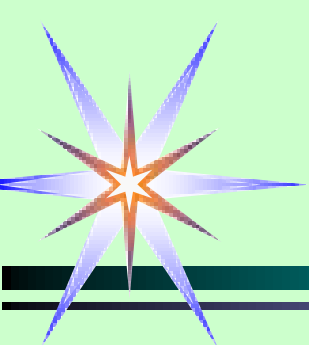


m/Z - 448

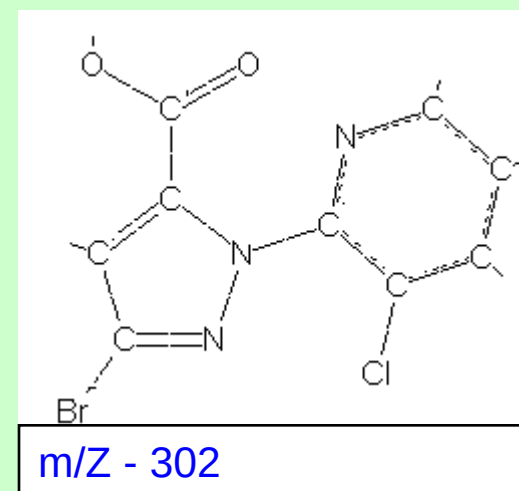
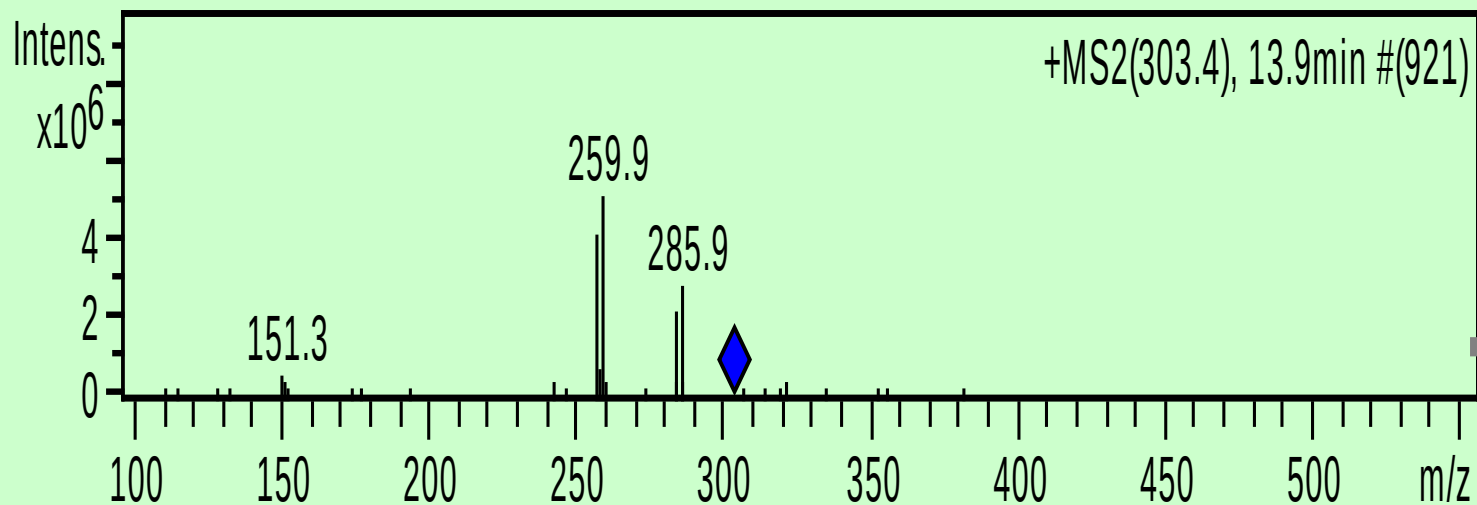
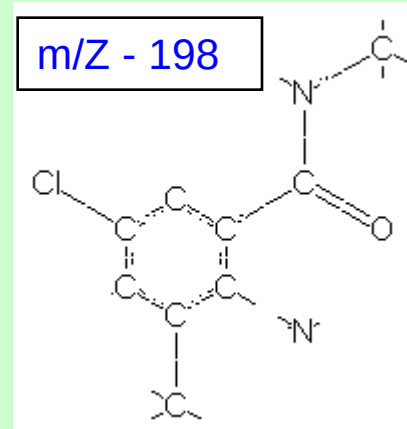
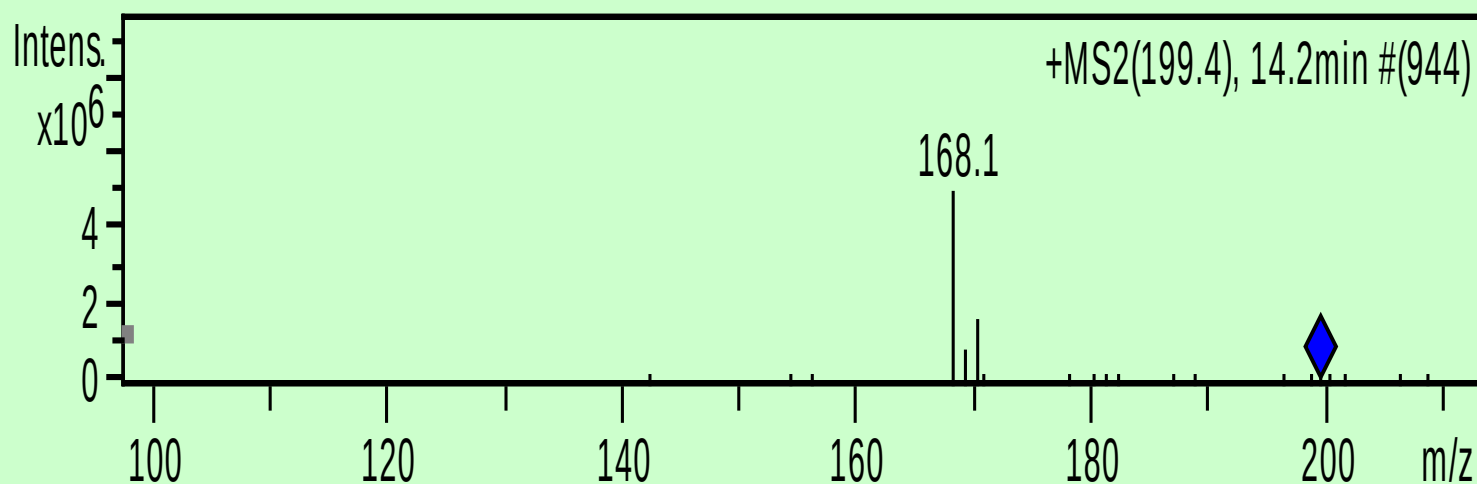


m/Z - 404



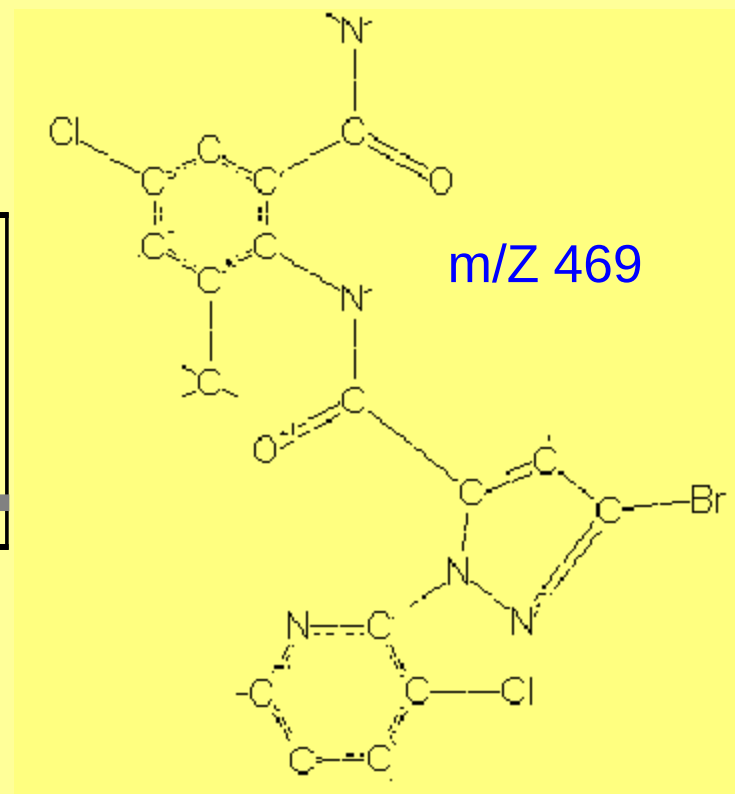
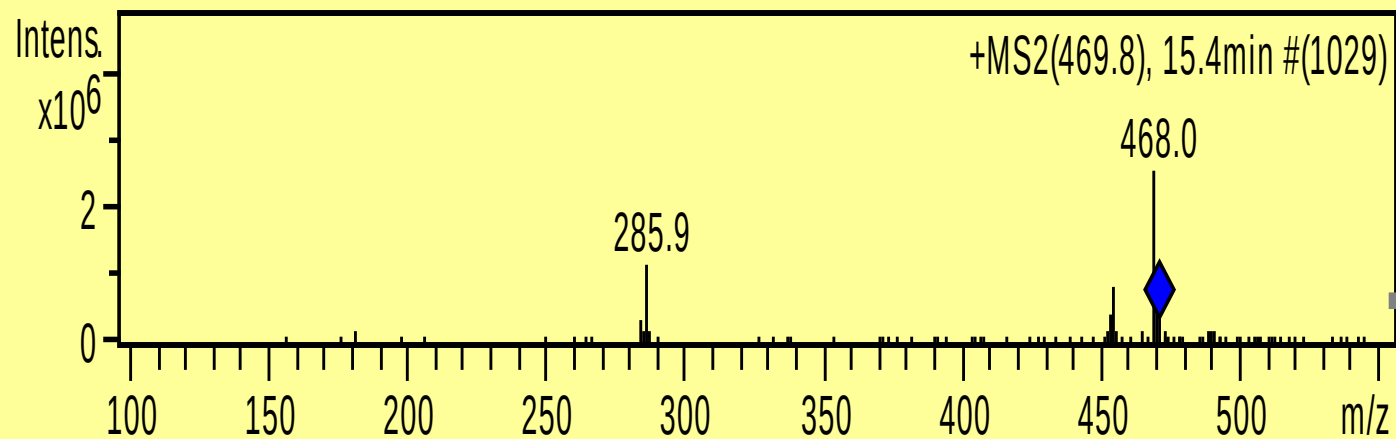


ESI-MS/MS SPECTRA OF BREAKDOWN PRODUCTS



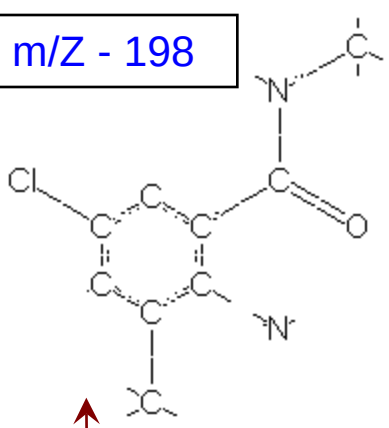


ESI-MS/MS SPECTRA OF BREAKDOWN PRODUCTS



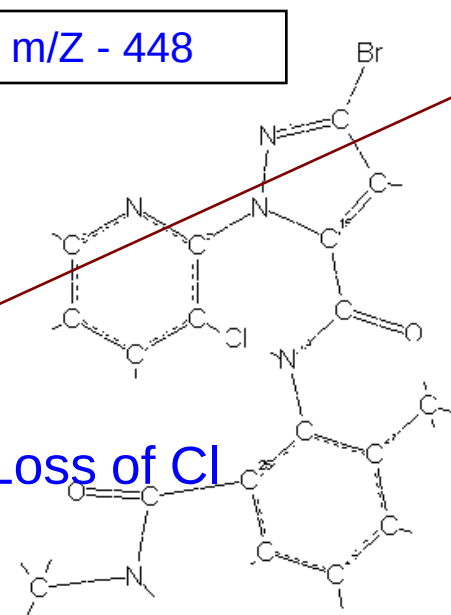
DEGRADATION PATTERN OF CHLORANTRANILIPROLE IN WATER

m/Z - 198



C-N Cleavage

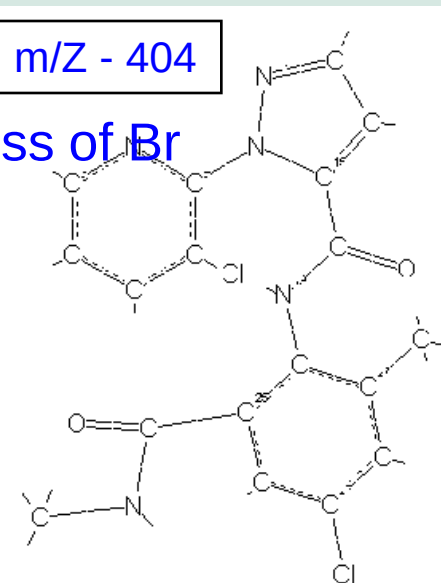
m/Z - 448



Loss of Cl

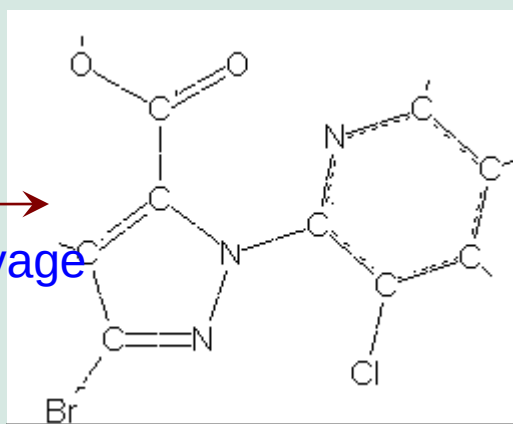
m/Z - 404

Loss of Br



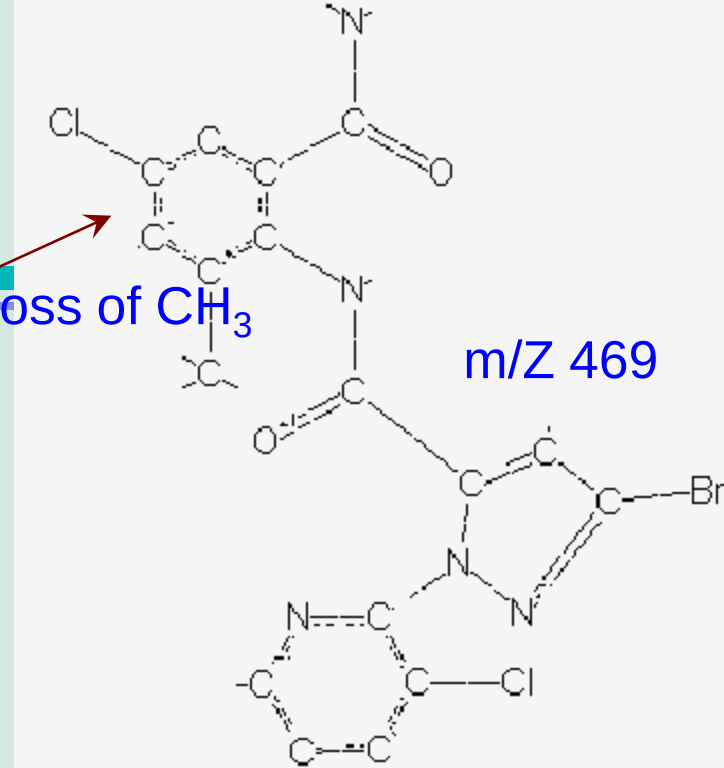
C-N Cleavage

m/Z - 302



Loss of CH₃

m/Z 469



Chlorantraniliprole
– m/Z – 483

Thank you