Electronic Supplementary Information

Photodegradation of Imidacloprid insecticide by Ag deposited titanate nanotubes - A study of intermediates and their reaction pathways

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Scheme 1: Procedure of sample preparation for GC-MS analysis

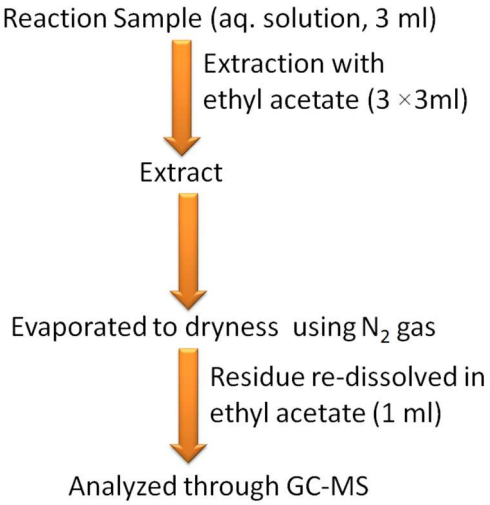


Figure S1: Kinetics for photooxidation of imidacloprid

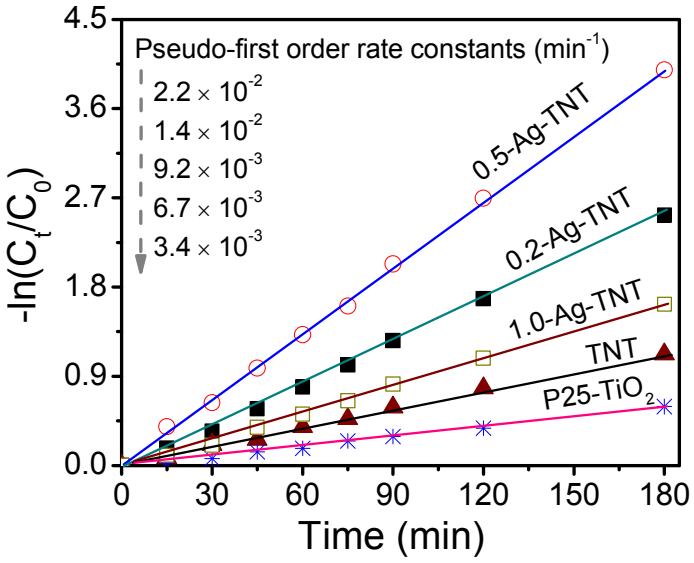


Table 1: Half-life of imidacloprid in presence of studied photocatalysts

S. No	Catalyst	Rate Constant (k, min^{-1})	Half life = 0.693/k (min)
1	P25-TiO_2	3.4×10^{-3}	204
2	TNT	6.7×10^{-3}	103
3	0.2-Ag-TNT	1.4×10^{-2}	50
4	0.5-Ag-TNT	2.2×10^{-2}	32
5	1.0-Ag-TNT	9.2×10^{-3}	75

Table 2: Calculation for mass balance of CO_2 formation by photooxidation of imidacloprid using bare titania catalysts

Initial concentration of Imidacloprid applied = 50 ppm or 0.2 mM (exact = 0.198 mM)

Amount of Imidacloprid in 5 ml = 1.0 (μmol)

Complete mineralization proceeds according as given below:

$$C_9H_{10}ClN_5O_2 + 33/2\ O_2 \longrightarrow 9CO_2 + 5NO_3^- + Cl^- + 6H^+ + 2H_2O$$

Means, 9 molecule of CO_2 produced by =1 molecules of imidacloprid

Therefore, highest amount of CO_2 could be produced = 1.0×9

= 9.0 (μ mol)

S. No	Catalyst	Amount of CO_2 produced (ppm) **(A)**	Amount of CO_2 produced in 5ml $\frac{A}{1000*1000*44} * 5$ (μ mol) **(B)**	Percentage of CO_2 formed $\frac{(B)}{4.5} * 100$
1	P25-TiO_2	5.8	0.66	7.3
2	TNT	12.3	1.4	15.5
3	0.2-Ag-TNT	22.4	2.5	28.3
4	0.5-Ag-TNT	29.6	3.5	37.4
5	1.0-Ag-TNT	18.2	2.0	23.0

Table 3: Rate of CO_2 formation during photooxidation of imidacloprid by studied photocatalysts

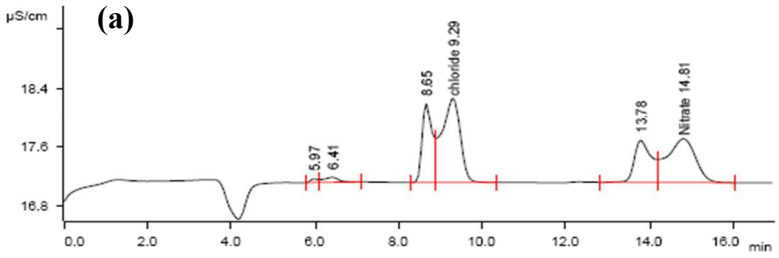
Balanced chemical equation expected after complete mineralization of imidacloprid

$$C_9H_{10}ClN_5O_2 + 33/2\ O_2 \longrightarrow 9CO_2 + 5NO_3^- + Cl^- + 6H^+ + 2H_2O$$

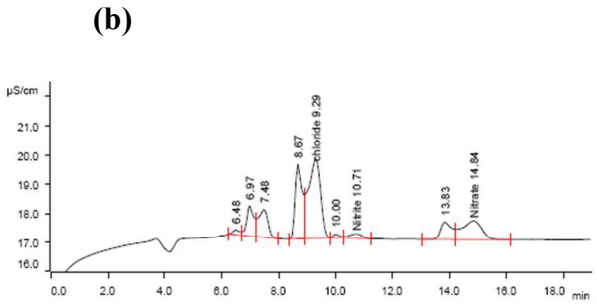
Rate of CO_2 formation **(k_1) = (1/9)** rate of degradation of imidacloprid **(k)**

S. No	Catalyst	Rate Constant (k, min^{-1})	Rate of CO_2 formation (k_1, min^{-1})
1	P25-TiO_2	3.4×10^{-3}	3.7×10^{-4}
2	TNT	6.7×10^{-3}	7.4×10^{-4}
3	0.2-Ag-TNT	1.4×10^{-2}	1.0×10^{-3}
4	0.5-Ag-TNT	2.2×10^{-2}	1.6×10^{-3}
5	1.0-Ag-TNT	9.2×10^{-3}	2.4×10^{-3}

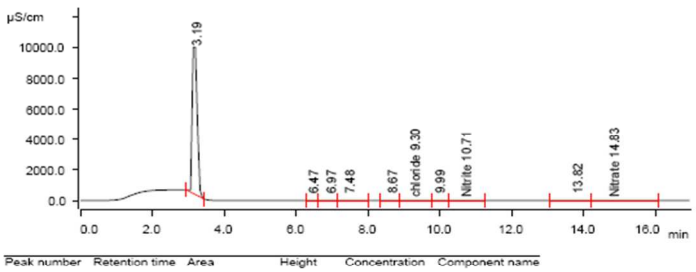
Figure S2: Ion Chromatograms for (a) Blank water, photooxidation of imidacloprid using 0.5 wt% Ag-photodeposited sodium titanate nanotubes after (b) 60 min, (c) 120 min, (d) 180 min and (e) after 180 min of photoreaction in presence of P25-TiO_2 catalyst.



Peak number	Retention time	Area	Height	Concentration	Component name
	min	(µS/cm) x min	µS/cm	ppm	
1	5.968	0.0103	0.050	invalid	
2	6.408	0.0281	0.068	invalid	
3	8.652	0.3028	1.075	invalid	
4	9.292	0.5715	1.150	2.567	chloride
5	13.782	0.2643	0.565	invalid	
6	14.807	0.4622	0.588	10.256	Nitrate

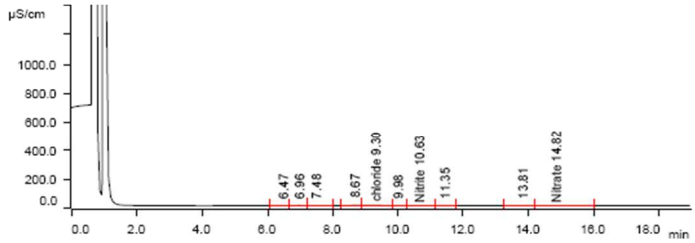


Peak number	Retention time	Area	Height	Concentration	Component name
	min	(µS/cm) x min	µS/cm	ppm	
1	6.477	0.0466	0.170	invalid	
2	6.970	0.3046	1.047	invalid	
3	7.478	0.3800	0.972	invalid	
4	8.667	0.7103	2.578	invalid	
5	9.293	1.3801	2.748	5.615	chloride
6	9.998	0.0390	0.135	invalid	
7	10.710	0.0900	0.168	1.256	Nitrite
8	13.825	0.2858	0.615	invalid	
9	14.835	0.5321	0.660	11.732	Nitrate



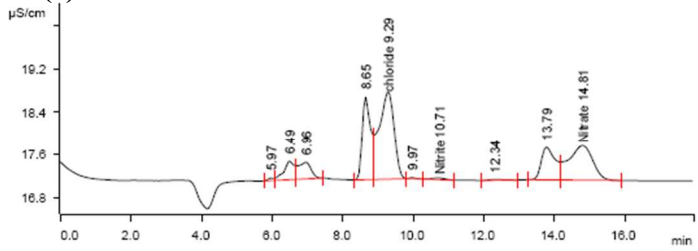
Peak number	Retention time	Area	Height	Concentration	Component name
	min	(µS/cm) x min	µS/cm	ppm	
1	3.185	1500.4794	9567.812	invalid	
2	6.465	0.0136	0.067	invalid	
3	6.965	0.2751	1.072	invalid	
4	7.480	0.4404	1.094	invalid	
5	8.665	0.7739	2.848	invalid	
6	9.297	1.4944	3.017	6.046	chloride
7	9.990	0.0557	0.199	invalid	
8	10.710	0.1294	0.243	1.516	Nitrite
9	13.815	0.3106	0.684	invalid	
10	14.830	0.5880	0.733	12.911	Nitrate

(d)



Peak number	Retention time	Area	Height	Concentration	Component name
	min	(µS/cm) x min	µS/cm	ppm	
1	6.467	0.1616	0.671	invalid	
2	6.963	0.6256	1.987	invalid	
3	7.482	0.5121	1.385	invalid	
4	8.668	0.8845	3.213	invalid	
5	9.300	1.6779	3.413	6.737	chloride
6	9.977	0.0134	0.067	invalid	
7	10.627	0.0489	0.112	0.985	Nitrite
8	11.345	0.0103	0.028	invalid	
9	13.807	0.4339	0.963	invalid	
10	14.822	0.8277	1.041	17.972	Nitrate

(e)



Peak number	Retention time	Area	Height	Concentration	Component name
	min	(µS/cm) x min	µS/cm	ppm	
1	5.972	0.0083	0.047	invalid	
2	6.492	0.1185	0.344	invalid	
3	6.960	0.1290	0.308	invalid	
4	8.652	0.4322	1.549	invalid	
5	9.292	0.8041	1.641	3.444	chloride
6	9.968	0.0045	0.022	invalid	
7	10.705	0.0132	0.031	0.749	Nitrite
8	12.343	0.0072	0.014	invalid	
9	13.785	0.2798	0.609	invalid	
10	14.808	0.5030	0.643	11.116	Nitrate