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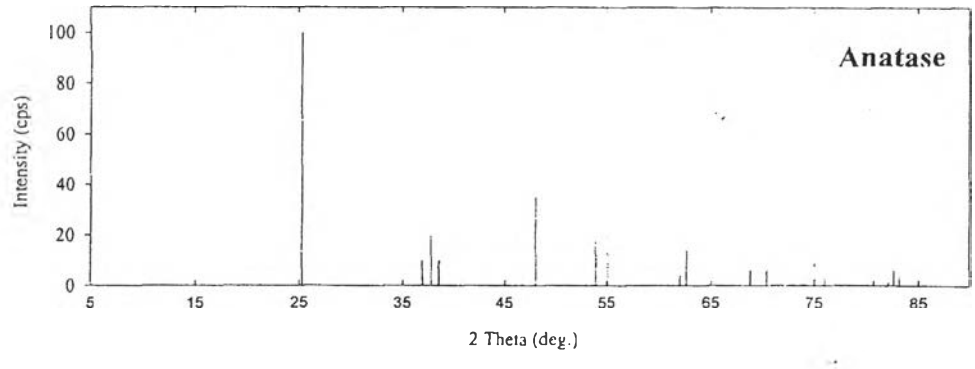
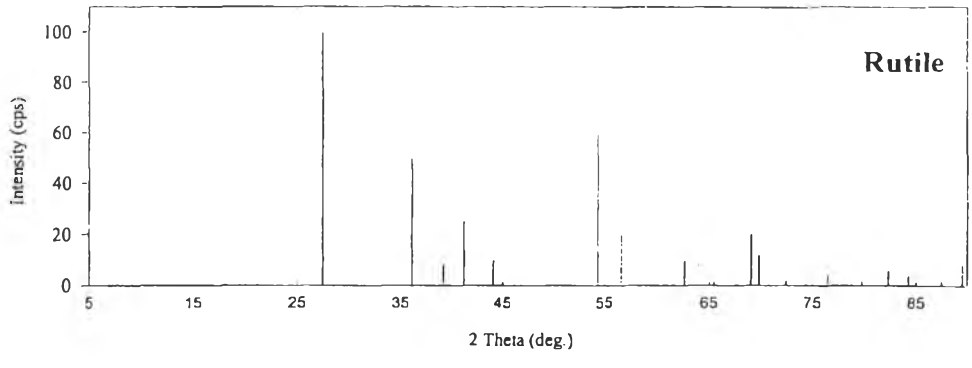
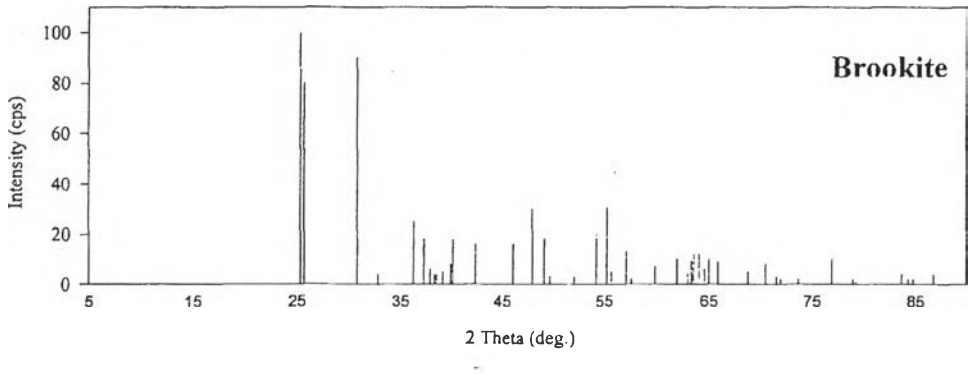
APPENDICES

Appendix A Standard TiO_2 XRD patterns, calculation of crystallite size of TiO_2 catalysts and reaction path way.

A.1 XRD patterns of TiO_2 reference







A.2 Calculated crystallite size

The crystallite size of TiO_2 were determined from the broadening of the anatase and rulile main peak by Debye-Scherrer equation:

$$d = \frac{k\lambda}{b\cos\theta} \qquad (3.1)$$

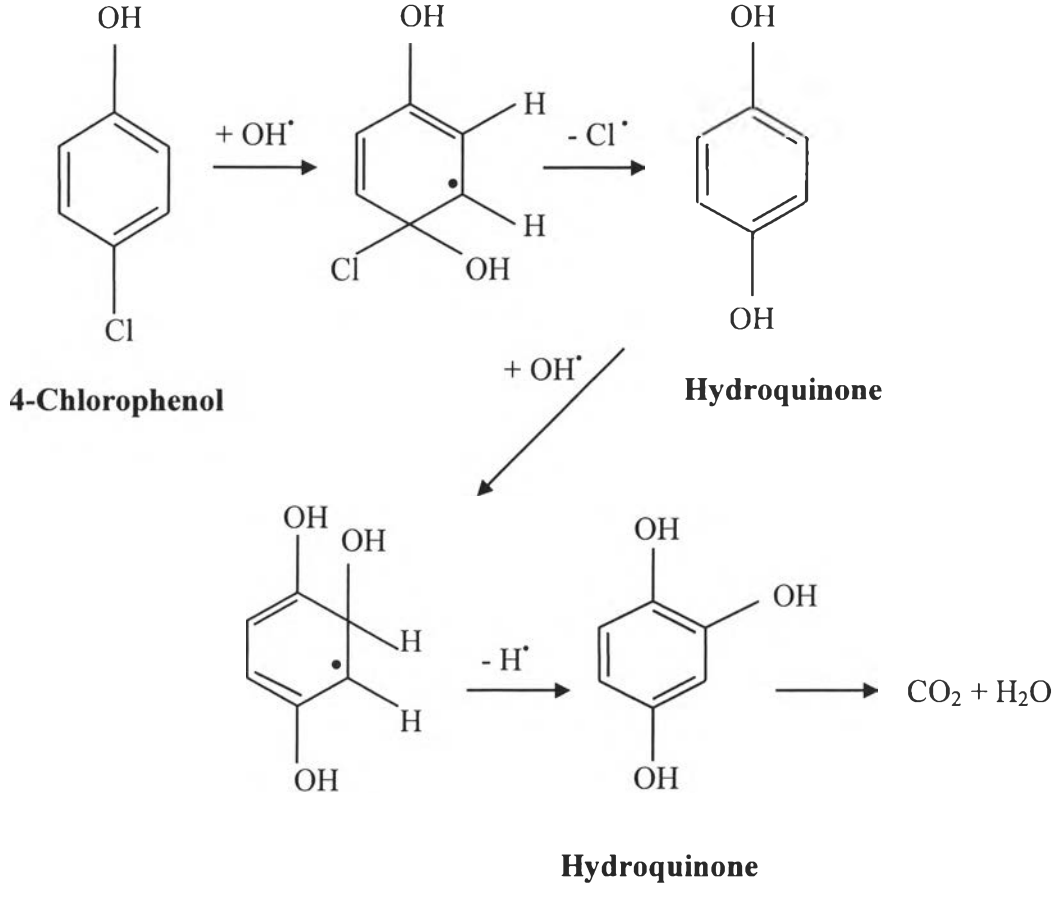
Anatase phase

Catalyst	FWHM	b	2θ(deg.)	cosθ	d (nm)
TiO_2 (Degussa P25)	0.3760	0.0066	25.26	0.9980	23.52
200 °C Calcinated TiO_2	0.3760	0.0066	25.38	0.9924	23.65
300 °C Calcinated TiO_2	0.3760	0.0066	25.28	0.9973	23.54
400 °C Calcinated TiO_2	0.3760	0.0066	25.28	0.9973	23.54
500 °C Calcinated TiO_2	0.3530	0.0062	25.28	0.9973	25.07
600 °C Calcinated TiO_2	0.3290	0.0057	25.32	0.9956	26.94
900 °C Calcinated TiO_2	-	-	-	-	-
1200 °C Calcinated TiO_2	-	-	-	-	-
0.05% Ag/TiO_2	0.3530	0.0062	25.3	0.9965	25.09
0.10% Ag/TiO_2	0.3290	0.0057	25.28	0.9973	26.90
1.00% Ag/TiO_2	0.3760	0.0066	25.36	0.9936	23.62
1.50% Ag/TiO_2	0.3530	0.0062	25.36	0.9936	25.16
0.05% Au/TiO_2	0.3530	0.0062	25.28	0.9973	25.07
0.10% Au/TiO_2	0.3530	0.0062	25.3	0.9965	25.09
1.00% Au/TiO_2	0.3760	0.0066	25.36	0.9936	23.62
1.50% Au/TiO_2	0.4000	0.0070	25.32	0.9956	22.16

Rutile phase

Catalyst	FWHM	b	2θ(deg.)	cosθ	d (nm)
TiO_2 (Degussa P25)	0.3060	0.0053	27.40	0.4234	68.12
200 °C Calcinated TiO_2	0.2820	0.0049	27.50	0.3776	82.89
300 °C Calcinated TiO_2	0.2820	0.0049	27.40	0.4234	73.92
400 °C Calcinated TiO_2	0.2820	0.0049	27.42	0.4143	75.54
500 °C Calcinated TiO_2	0.2820	0.0049	27.42	0.4143	75.54
600 °C Calcinated TiO_2	0.2590	0.0045	27.44	0.4052	84.10
900 °C Calcinated TiO_2	0.2350	0.0041	27.42	0.4143	90.65
1200 °C Calcinated TiO_2	0.2590	0.0045	27.46	0.3960	86.04
0.05% Ag/TiO_2	0.3060	0.0053	27.44	0.4052	71.18
0.10% Ag/TiO_2	0.2820	0.0049	27.44	0.4052	77.24
1.00% Ag/TiO_2	0.2820	0.0049	27.48	0.3868	80.91
1.50% Ag/TiO_2	0.2820	0.0049	27.46	0.3960	79.03
0.05% Au/TiO_2	0.2820	0.0049	27.42	0.4143	75.54
0.10% Au/TiO_2	0.3060	0.0053	27.44	0.4052	71.18
1.00% Au/TiO_2	0.2820	0.0049	27.48	0.3868	80.91
1.50% Au/TiO_2	0.2590	0.0045	27.50	0.3776	90.25

A.3 Reaction pathway for the photocatalytic degradation of 4-CP



Appendix B Experimental data from photocatalytic degradation of 4-CP in batch operation.

B.1 Photocatalytic degradation of 4-CP without TiO_2 (photolysis)

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4892	0.0000	0.0000	1.00	1.00
1	0.0109	0.1762	0.1630	0.02	0.91
2	0.0000	0.1916	0.2071	0.00	0.92
3	0.0000	0.1591	0.2094	0.00	0.91
4	0.0000	0.1313	0.1962	0.00	0.90
5	0.0000	0.1107	0.1832	0.00	0.88
6	0.0000	0.0887	0.1648	0.00	0.87

B.2 Photocatalytic degradation of 4-CP with as-received TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4857	0.0000	0.0000	1.00	1.00
1	0.0255	0.0547	0.0297	0.05	0.77
2	0.0117	0.0541	0.0497	0.02	0.61
3	0.0000	0.0295	0.0428	0.00	0.42
4	0.0000	0.0000	0.0198	0.00	0.23
5	0.0000	0.0000	0.0000	0.00	0.00
6	0.0000	0.0000	0.0000	0.00	0.00

B.3 Photocatalytic degradation of 4-CP with 200 °C calcinated TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4910	0.0000	0.0000	1.00	1.00
0.3	0.2086	0.1501	0.0248	0.42	0.85
0.7	0.0398	0.2062	0.0494	0.08	0.77
1	0.0215	0.2071	0.0620	0.04	0.73
2	0.0000	0.1481	0.0678	0.00	0.57
3	0.0000	0.0699	0.0610	0.00	0.46
4	0.0000	0.0277	0.0422	0.00	0.35
5	0.0000	0.0000	0.0210	0.00	0.24
6	0.0000	0.0000	0.0003	0.00	0.17

B.4 Photocatalytic degradation of 4-CP with 300 °C calcinated TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4692	0.0000	0.0000	1.00	1.00
0.3	0.2084	0.1221	0.0302	0.44	0.91
0.7	0.0423	0.1770	0.0646	0.09	0.85
1	0.0184	0.2017	0.0795	0.04	0.83
2	0.0000	0.1742	0.1083	0.00	0.76
3	0.0000	0.1111	0.1095	0.00	0.62
4	0.0000	0.0490	0.0865	0.00	0.50
5	0.0000	0.0000	0.0416	0.00	0.35
6	0.0000	0.0000	0.0067	0.00	0.23

B.5 Photocatalytic degradation of 4-CP with 400 °C calcinated TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4823	0.0000	0.0000	1.00	1.00
0.3	0.1889	0.1269	0.0631	0.39	0.89
0.7	0.0369	0.1816	0.0950	0.08	0.87
1	0.0162	0.2069	0.1106	0.03	0.84
2	0.0000	0.1902	0.1327	0.00	0.77
3	0.0000	0.1228	0.1251	0.00	0.69
4	0.0000	0.0655	0.1081	0.00	0.52
5	0.0000	0.0000	0.0666	0.00	0.49
6	0.0000	0.0000	0.0260	0.00	0.33

B.6 Photocatalytic degradation of 4-CP with 500 °C calcinated TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4834	0.0000	0.0000	1.00	1.00
0.3	0.1948	0.1256	0.0506	0.40	0.89
0.7	0.0395	0.1782	0.0902	0.08	0.86
1	0.0178	0.1986	0.1040	0.04	0.84
2	0.0000	0.1946	0.1250	0.00	0.76
3	0.0000	0.1331	0.1235	0.00	0.67
4	0.0000	0.0726	0.1018	0.00	0.58
5	0.0000	0.0284	0.0718	0.00	0.44
6	0.0000	0.0000	0.0386	0.00	0.33

B.7 Photocatalytic degradation of 4-CP with 600 °C calcinated TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4757	0.0000	0.0000	1.00	1.00
0.3	0.2269	0.1074	0.0728	0.48	0.89
0.7	0.0588	0.1622	0.1113	0.12	0.87
1	0.0290	0.1865	0.1259	0.06	0.86
2	0.0000	0.1938	0.1493	0.00	0.84
3	0.0000	0.1754	0.1553	0.00	0.78
4	0.0000	0.1416	0.1524	0.00	0.75
5	0.0000	0.1094	0.1445	0.00	0.71
6	0.0000	0.0751	0.1308	0.00	0.69

B.8 Photocatalytic degradation of 4-CP with 900 °C calcinated TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4786	0.0000	0.0000	1.00	1.00
0.3	0.2356	0.0804	0.0758	0.49	0.91
0.7	0.0598	0.1303	0.1208	0.12	0.88
1	0.0293	0.1566	0.1381	0.06	0.91
2	0.0000	0.1836	0.1645	0.00	0.89
3	0.0000	0.1698	0.1638	0.00	0.88
4	0.0000	0.1511	0.1620	0.00	0.82
5	0.0000	0.1296	0.1629	0.00	0.82
6	0.0000	0.1071	0.1613	0.00	0.83

B.9 Photocatalytic degradation of 4-CP with 1200 °C calcinated TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4770	0.0000	0.0000	1.00	1.00
0.3	0.2475	0.0817	0.0829	0.52	0.96
0.7	0.0616	0.1287	0.1325	0.13	0.95
1	0.0343	0.1576	0.1572	0.07	0.93
2	0.0000	0.1759	0.1718	0.00	0.90
3	0.0000	0.1689	0.1823	0.00	0.89
4	0.0000	0.1540	0.1900	0.00	0.90
5	0.0000	0.1395	0.2004	0.00	0.89
6	0.0000	0.1194	0.1925	0.00	0.86

B.10 Photocatalytic degradation of 4-CP with 0.05% Ag/TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4773	0.0000	0.0000	1.00	1.00
0.3	0.1779	0.1318	0.0658	0.37	0.89
0.7	0.0337	0.1748	0.1062	0.07	0.86
1	0.0142	0.1954	0.1335	0.03	0.86
2	0.0000	0.1658	0.1608	0.00	0.81
3	0.0000	0.1024	0.1669	0.00	0.74
4	0.0000	0.0440	0.1331	0.00	0.63
5	0.0000	0.0000	0.0804	0.00	0.50
6	0.0000	0.0000	0.0306	0.00	0.38

B.11 Photocatalytic degradation of 4-CP with 0.10 Ag/TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4843	0.0000	0.0000	1.00	1.00
0.3	0.1759	0.1270	0.0666	0.36	0.87
0.7	0.0327	0.1750	0.1129	0.07	0.85
1	0.0124	0.2025	0.1362	0.03	0.84
2	0.0000	0.1702	0.1653	0.00	0.77
3	0.0000	0.1042	0.1586	0.00	0.68
4	0.0000	0.0062	0.1262	0.00	0.59
5	0.0000	0.0000	0.0686	0.00	0.45
6	0.0000	0.0000	0.0240	0.00	0.26

B.12 Photocatalytic degradation of 4-CP with 1.00% Ag/TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4594	0.0000	0.0000	1.00	1.00
0.3	0.1682	0.1236	0.0488	0.37	0.86
0.7	0.0363	0.1765	0.0743	0.08	0.83
1	0.0165	0.2011	0.0900	0.04	0.82
2	0.0000	0.2175	0.0994	0.00	0.80
3	0.0000	0.1778	0.1140	0.00	0.73
4	0.0000	0.1274	0.1137	0.00	0.68
5	0.0000	0.0731	0.0944	0.00	0.58
6	0.0000	0.0243	0.0677	0.00	0.48

B.13 Photocatalytic degradation of 4-CP with 1.50% Ag/TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4684	0.0000	0.0000	1.00	1.00
0.3	0.2062	0.1186	0.0539	0.44	0.86
0.7	0.0508	0.1671	0.0859	0.11	0.83
1	0.0222	0.1970	0.0976	0.05	0.83
2	0.0000	0.1889	0.1259	0.00	0.78
3	0.0000	0.1596	0.1230	0.00	0.71
4	0.0000	0.1016	0.1164	0.00	0.65
5	0.0000	0.0469	0.0902	0.00	0.54
6	0.0000	0.0000	0.0461	0.00	0.55

B.14 Photocatalytic degradation of 4-CP with 0.05% Au/TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4715	0.0000	0.0000	1.00	1.00
0.3	0.2005	0.1072	0.0674	0.43	0.88
0.7	0.0492	0.1672	0.0859	0.10	0.86
1	0.0213	0.2184	0.1009	0.05	0.85
2	0.0000	0.2212	0.1155	0.00	0.81
3	0.0000	0.1817	0.1231	0.00	0.76
4	0.0000	0.1108	0.1113	0.00	0.70
5	0.0000	0.0686	0.0928	0.00	0.63
6	0.0000	0.0000	0.0570	0.00	0.52

B.15 Photocatalytic degradation of 4-CP with 0.10% Au/TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4498	0.0000	0.0000	1.00	1.00
0.3	0.1791	0.1107	0.0524	0.40	0.91
0.7	0.0433	0.1601	0.0821	0.10	0.83
1	0.0186	0.1809	0.0927	0.04	0.83
2	0.0000	0.1950	0.1210	0.00	0.78
3	0.0000	0.1372	0.1208	0.00	0.71
4	0.0000	0.0851	0.1029	0.00	0.62
5	0.0000	0.0346	0.0777	0.00	0.54
6	0.0000	0.0000	0.0432	0.00	0.44

B.16 Photocatalytic degradation of 4-CP with 1.00% Au/TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4834	0.0000	0.0000	1.00	1.00
0.3	0.1984	0.1186	0.0441	0.41	0.84
0.7	0.0511	0.1752	0.0656	0.11	0.82
1	0.0215	0.2029	0.0768	0.04	0.82
2	0.0000	0.2108	0.0914	0.00	0.78
3	0.0000	0.1581	0.0991	0.00	0.73
4	0.0000	0.1061	0.0939	0.00	0.67
5	0.0000	0.0648	0.0830	0.00	0.62
6	0.0000	0.0288	0.0653	0.00	0.56

B.17 Photocatalytic degradation of 4-CP with 1.50% Au/TiO_2

Time (hr)	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
0	0.4766	0.0000	0.0000	1.00	1.00
0.3	0.2161	0.1038	0.0560	0.45	0.85
0.7	0.0580	0.1615	0.0811	0.12	0.82
1	0.0261	0.1883	0.0993	0.05	0.87
2	0.0000	0.1996	0.1268	0.00	0.77
3	0.0000	0.1637	0.1212	0.00	0.73
4	0.0000	0.1106	0.0899	0.00	0.76
5	0.0000	0.0782	0.0908	0.00	0.59
6	0.0000	0.0430	0.0757	0.00	0.51

Appendix C Experimental data from photocatalytic degradation of 4-CP in continuous operation.

C.1 Photocatalytic Degradation of 4-CP without TiO_2 and 200 ml/min solution flow rate

Reactor number	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
Feed solution	0.4758	0.0000	0.0000	1.00	1.00
1	0.4023	0.0361	0.0347	0.85	0.99
2	0.3187	0.0650	0.0806	0.67	0.97
3	0.2543	0.0832	0.0999	0.53	0.98
4	0.1898	0.0964	0.1219	0.40	0.95

C.2 Photocatalytic Degradation of 4-CP without TiO_2 and 50.00 ml/min solution flow rate

Reactor number	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
Feed solution	0.5102	0.0000	0.0000	1.00	1.00
1	0.2809	0.0890	0.0881	0.55	0.97
2	0.1544	0.1344	0.1467	0.30	0.94
3	0.0453	0.1486	0.1691	0.09	0.92
4	0.0107	0.1477	0.1894	0.02	0.91

C.3 Photocatalytic Degradation of 4-CP without TiO_2 and 25.00 ml/min solution flow rate

Reactor number	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
Feed solution	0.5110	0.0000	0.0000	1.00	1.00
1	0.2125	0.1175	0.1364	0.42	0.91
2	0.0649	0.1628	0.1915	0.13	0.87
3	0.0106	0.1720	0.2090	0.02	0.88
4	0.0000	0.1580	0.2107	0.00	0.86

C.4 Photocatalytic Degradation of 4-CP without TiO_2 and 12.50 ml/min solution flow rate

Reactor number	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
Feed solution	0.5057	0.0000	0.0000	1.00	1.00
1	0.1243	0.1424	0.1681	0.25	0.89
2	0.0094	0.1591	0.1974	0.02	0.88
3	0.0000	0.1168	0.1893	0.00	0.82
4	0.0000	0.0675	0.1561	0.00	0.78

C.5 Photocatalytic Degradation of 4-CP with TiO_2 and 25.00 ml/min solution flow rate

Reactor number	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
Feed solution	0.5045	0.0000	0.0000	1.00	1.00
1	0.1725	0.1368	0.0754	0.34	0.89
2	0.0180	0.1492	0.1023	0.04	0.86
3	0.0000	0.1473	0.1028	0.00	0.81
4	0.0000	0.1254	0.0941	0.00	0.75

C.6 Photocatalytic Degradation of 4-CP with TiO_2 and 12.50 ml/min solution flow rate

Reactor number	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
Feed solution	0.4854	0.0000	0.0000	1.00	1.00
1	0.0377	0.1313	0.1172	0.08	0.84
2	0.0000	0.0996	0.1188	0.00	0.73
3	0.0000	0.0362	0.0751	0.00	0.59
4	0.0000	0.0000	0.0089	0.00	0.28

C.7 Photocatalytic Degradation of 4-CP with TiO_2 and 12.50 ml/min solution flow rate (Repeat Experiment)

Reactor number	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
Feed solution	-	-	-	-	1.00
1	-	-	-	-	0.82
2	-	-	-	-	0.73
3	-	-	-	-	0.59
4	-	-	-	-	0.34

C.8 Photocatalytic Degradation of 4-CP with TiO_2 and 6.25 ml/min solution flow rate

Reactor number	Concentration (mM)			Remaining fraction	
	4-CP	HQ	HHQ	4-CP	TOC
Feed solution	0.504	0.000	0.000	1.00	1.00
1	0.012	0.095	0.105	0.02	0.67
2	0.000	0.000	0.013	0.00	0.22
3	0.000	0.000	0.000	0.00	0.01
4	0.000	0.000	0.000	0.00	0.00

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