

Photodegradation of Halogen Derivatives of Phenol in Aqueous Photocatalytic Suspension-Solution

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The rates of photodegradation, reactivities, and mechanisms of photooxidation for the aqueous TiO₂ -solution containing with halogen derivatives of phenol have been discussed by TOC and GCMS.

Aqueous slurries(1.5L) of TiO₂(0.5g/L), and 2-chlorophenol(93~113ppm-TOC), 2-bromophenol(98~109 ppm-TOC), 3 - bromophenol(98~104 ppm-TOC), 4-bromophenol(100~103 ppm-TOC), 2,4-dibromophenol(68~75 ppm-TOC) or 2,6-dibromophenol (40~48 ppm-TOC) were prepared, respectively. The stirred aqueous slurries were bubbled with humid O₂ (10mL min⁻¹) for 240min. prior to and during the irradiation to maintain oxygenated condutions. These aqueous slurry solutions were illuminated with wavelength of 184nm, of 253.7nm controlled by 450W Hg-low lamp, and \geq 320 nm, controlled by 450W- Xe arc. lamp at 25°C, respectively.

At periodic time intervals, aliquots(100 μ L) of the slurry were extracted through 0.45 μ m syringe filters. nylon filters (Nalgene) were used for organic analysis.

Separation and quantification of organic intermediated was accomplished by GCMS and TOC meter(SHIMADZU).

These aqueous saturated solutions suspended with 0.5 g L⁻¹-TiO₂ powder have been photodecomposed in the range of 74.60 and 34.96 % when it is illuminated by the wavelength of 253.7 nm, for 4 hours.

The rates of photodegradation were increased in the order of 2-chlorophenol > 3-bromophenol \geq 2-bromophenol > 4-bromophenol > 2,4-dibromophenol > 2,6-dibromophenol. at 253.7 nm. and the rates of photodegradation were increased in the following order of illuminating

wavelength, 253.7nm > 184nm.

Particularly, all of pollutants were not nearly photodecomposed at the wavelength above 320 nm (Table 1).

For the photolysis of chloro- or bromophenols, the decrease of this substrate did not match the CO₂ production during the first 240min. of irradiation. the difference between this decrease and increase of stoichiometric amounts of CO₂ gives evidence for the formation of intermediates which are generated from the beginning, reach a maximum concentration after 10 minutes, undergo themselves a photooxidation and are completely photooxidized at the end (240min.). it is quite understandable that larger molecules such as halogen phenols are not photooxidized in one step. Ten intermediates are detected by GCMS under the indicated. By far, the two main ones are chlorohydroquinon (CQQ), or bromohydroquinon (BQQ) and hydroxyhydroquinon (HQQ), dihydroxybenzene, trihydroxybenzene, or benzoquinone.

Table 1. Photodegradation for halogen-derivatives of phenol in aqueous solution under the various experimental conditions.

Pollutants	Time of illumination	184 nm				253.7 nm				450W (≥320nm)			
		None TiO ₂		TiO ₂ 0.5g/L		None TiO ₂		TiO ₂ 0.5g/L		None TiO ₂		TiO ₂ 0.5g/L	
		Conc. (ppm)	Rem. (%)	Conc. (ppm)	Rem. (%)	Conc. (ppm)	Rem. (%)	Conc. (ppm)	Rem. (%)	Conc. (ppm)	Rem. (%)	Conc. (ppm)	Rem. (%)
2-chloro-phenol	0	93.17	0	93.44	0	104.9	0	104.4	0	112.9	0	99.18	0
	120	77.28	17.06	68.29	26.92	88.10	16.01	66.44	36.36	110.1	2.480	93.80	5.425
	180	70.02	24.85	55.99	40.08	79.54	24.18	45.78	56.15	107.7	4.606	90.81	8.439
	240	63.32	32.04	42.13	54.91	71.09	32.23	26.52	74.60	107.0	5.226	88.08	11.19
2-bromo-phenol	0	98.59	0	98.32	0	109.7	0	99.45	0	106.5	0	102.3	0
	120	83.41	15.40	73.32	25.43	102.2	6.837	76.54	23.04	104.6	1.784	96.32	5.846
	180	79.01	19.86	60.24	38.73	99.56	9.243	60.71	38.95	102.5	3.756	94.65	7.478
	240	75.32	23.60	48.26	50.92	97.46	11.16	49.55	50.18	101.0	5.164	90.46	11.58
3-bromo-phenol	0	98.41	0	93.93	0	101.2	0	100.7	0			104.6	0
	120	96.07	2.378	83.32	11.30	98.04	3.123	75.47	25.06	☆	☆	103.3	1.243
	180	93.01	5.487	76.79	18.24	94.46	6.660	60.56	39.86			100.4	4.015
	240	90.82	7.713	67.60	28.03	91.62	9.466	46.51	53.81			99.09	5.268
4-bromo-phenol	0	100.1	0	101.9	0	102.2	0	103.0	0				
	120	95.62	4.476	83.92	17.65	97.86	4.247	88.89	13.70	☆	☆	☆	☆
	180	93.51	6.583	74.90	26.50	95.27	6.791	78.67	23.62				
	240	93.64	6.454	67.79	33.47	93.45	8.562	66.99	34.96				
2,4-dibromophenol	0	74.91	0	75.16	0	68.68	0	72.92	0				
	120	68.03	9.184	60.03	20.13	65.73	4.295	51.66	29.16	☆	☆	☆	☆
	180	66.79	10.84	52.38	30.31	61.58	10.34	46.05	36.85				
	240	65.12	13.07	43.97	41.50	60.02	12.61	36.90	49.40				
2,6-dibromophenol	0	43.74	0	45.46	0	41.53	0	36.99	0	48.77	0	46.30	0
	120	40.16	8.185	32.49	28.53	38.00	8.500	20.61	44.28	47.51	2.5843	45.54	1.641
	180	36.48	16.60	25.63	43.62	35.42	14.71	14.76	60.01	47.21	.199	45.09	2.614
	240	32.81	24.99	22.88	49.67	34.54	16.83	11.436	69.07	47.55	2.502	43.02	7.084