

Unusual photoreactivity of zinc oxide irradiated by concentrated sunlight

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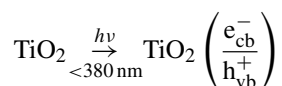
Abstract

The decrease of fluorescence emission of phenol was studied in the presence of photoactive oxides (TiO₂, ZnO and Fe₂O₃) irradiated with a sodium lamp, direct sunlight (1 sun) and concentrated sunlight (40–50 suns) in aqueous solutions. As expected photodegradation of phenol was seen to be faster for all of the oxides irradiated by concentrated sunlight. The photodegradation capacity of titanium dioxide (TiO₂) is superior to that of zinc oxide (ZnO) and ferric oxide (Fe₂O₃) under a sodium lamp and direct sunlight, but ZnO is found to be as reactive as TiO₂ under concentrated sunlight. It has been shown that ZnO is a low cost alternative solar photocatalyst to TiO₂ for degradation of organics in aqueous solutions. © 2001 Elsevier Science B.V. All rights reserved.

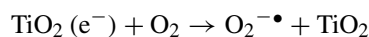
Keywords: Fluorescence emission; Titanium dioxide; Zinc oxide; Ferric oxide; Solar concentrator

1. Introduction

Catalytic transformations using photoactive oxides are of considerable interest because they can induce the indirect transformations of pollutants in water [1,2]. Among the photoactive oxides, titanium dioxide (TiO₂) is by far the most popular, which transforms organic pollutants to mineralization by an efficient electron transfer process [2,3]. Photoexcited TiO₂ exhibits strong oxidation potentials of the electron-depleted valence band on the surface of fine titanium powders.



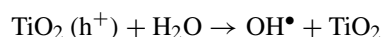
TiO₂ and platinum powders are found to be even more efficient for photocatalytic degradation of pollutants both in aqueous solution and in gas phase, due to a faster electron transfer to molecular oxygen [4,5]. Superoxide anion radicals and hydroxyl radicals, easily form in aqueous medium, accelerate the oxidation of organic pollutants, culminating in conversion to CO₂ [6,7]. However, widespread use of the expensive photoactive anatase form of TiO₂ and platinum catalyst is uneconomic for large scale water treatment operations.



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Ferric oxide (Fe₂O₃) and zinc oxide (ZnO) are known to be photoactive oxides under solar irradiation and their photodegradation mechanisms have been proven to be similar to that of TiO₂, although they exhibit less vigorous oxidation rates [8–11]. In this study we have compare the photooxidative degradation capacities of these three photoactive oxides, by monitoring the decline of fluorescence emission of phenol in water, under direct sunlight and under concentrated sunlight.

2. Experimental details

2.1. Materials

A water cooled cylindrical pyrex glass, and with a tap on the bottom was used as the photoreactor. Irradiation was accomplished using either a Philips-son-T plus-400 W sodium lamp, direct sunlight or concentrated sunlight [12] (Fig. 1). Sodium lamp irradiation was used as a simulation of solar light under laboratory conditions, because the radiation spectrum of this lamp source coincides well with the solar radiation spectrum. Concentrated sunlight experiments were performed at Fix Focus FF 3.5-HTC GmbH (Germany) instrument. Technical specifications; reflective surface area 3.68 m², usable reflector area 2.66 m² covered with a reflective aluminized polymer film, focal length 0.65 m, automatic photocell focus of sunlight on X-direction, manual focus

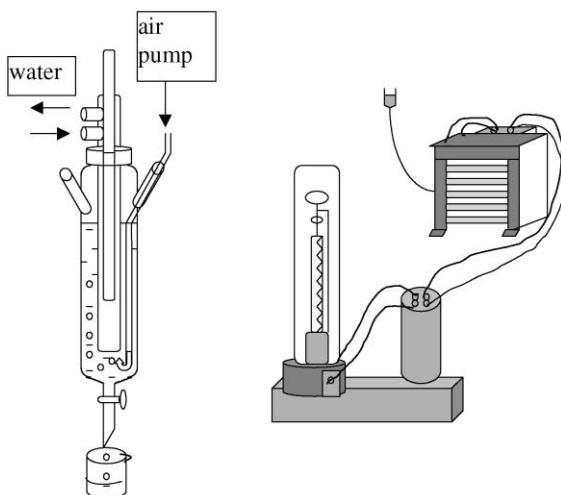


Fig. 1. Cylindrical pyrex photoreactor with inner water cooling apparatus (left), and the Philips-son-T plus-400 W sodium lamp system (right).

on Y-direction (Fig. 2). Aluminized PVC polymer film, with a $40 \mu\text{m}$ thick layer of alumina and 0.91 g cm^{-3} , was obtained from the POLINAS corporation in Turkey. The intensity of concentrated sunlight was determined by using Vilbert Loumart radiometers at 254 and 312 nm radiation wavelengths, and comparing the measured intensities with the intensity of direct sunlight (1 sun) using same radiometers. Irradiation intensity was found to vary between 40 and 50 suns at the focal point of the concentrator under experimental conditions. The radiation intensity striking the sample was measured before and after each experiment. In order to compare results, the irradiation intensity was kept between 40 and 50 suns by adjustments at the focal point of the solar concentrator. The intensity of the radiation emitted by the sodium lamp source was also measured by using Vilbert Loumart radiometers at 312 and 365 nm radiation wavelengths, and the measured intensities were compared to direct sunlight (1 sun) as described earlier. The effective

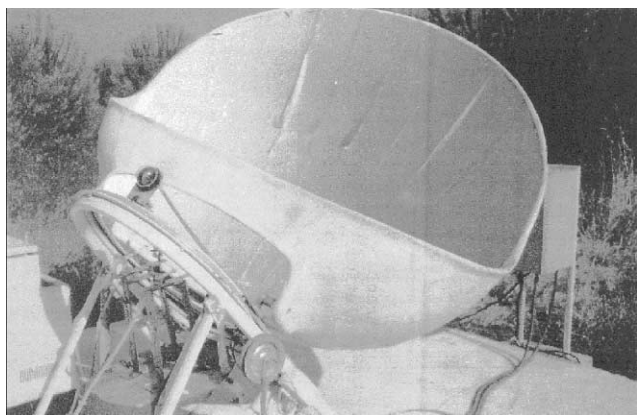


Fig. 2. Solar concentrator instrument of Fix Focus FF 3.5-HTC GmbH (Germany) at Ege University.

radiation intensity striking the cylindrical glass photoreactor was found to be about 0.2 sun at 4 cm distance between photoreactor and 400 W sodium lamp. Direct and concentrated sunlight experiments were done during the months of April–September, and between 11.00 and 15.00 h. P25 grade TiO_2 was obtained from Degussa. ZnO , 99% from Merck, Fe_2O_3 , and phenol each, 98% from Surechem were used without further purifications. Colloidal Fe_2O_3 particles were prepared by the hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99% from Merck in a water bath. The pH of the aqueous solutions were measured using a Bilmar model 101 Tacussel Electronique TS 60 N pH meters. Distilled water was used for the preparation of all solutions.

2.2. Irradiations

Aqueous solutions, 125 ml, were irradiated in the photoreactor (Fig. 1), under sodium lamp, direct sunlight and a concentrated sunlight system (Fig. 2). Phenol solutions between 10^{-4} and $2 \times 10^{-5} \text{ M}$ concentrations, were prepared fresh for every experiment, and kept in the dark until photoreacted. TiO_2 and ZnO were added such that the concentration in the resulting phenolic aqueous solutions would be 0.5 g l^{-1} . Colloidal Fe_2O_3 solutions were prepared to be 0.04 g l^{-1} . The pH of the solutions of phenol in the presence of metal oxides were found to range from 6.4 to 7.0. Aeration was accomplished by air pumping which also helped to prevent the precipitation of semiconductor metal oxides from the suspensions. The absorption and fluorescence emission spectra of phenol for all the samples were measured, before and after irradiation. A 5 ml sample was removed after irradiation periods of 5, 10, 15, 20, 25, 30, 45, 60 and 90 min for studies under sodium lamp and direct sunlight. Irradiation periods of samples were 3, 6, 9, 12 and 15 min under concentrated sunlight. Phenol solutions were irradiated with the same cylindrical glass photoreactor system in all experiments (Fig. 1). The temperature of the solutions were found to increase only about $3\text{--}4^\circ\text{C}$ under concentrated sunlight, while internal water cooling was in progress.

2.3. Spectroscopic measurements

Prior to spectroscopic measurements, all of the aqueous solution samples were filtered with 5893 blue ribbon filter paper in order to remove suspended particles. The absorption spectra of the phenolic solutions were measured using a Jasco V-530 UV–VIS or Milton-Roy Spectronic-601 UV–VIS spectrophotometers. The fluorescence emission spectra were recorded using a PTI-QM1 fluorescence spectrophotometer. Fluorescence emission spectra were measured using an excitation wavelength of 268 nm (absorption band of phenol) and the emission band was recorded at $\lambda_{\text{max}} = 296 \text{ nm}$ in aqueous solutions. The ratio of remaining phenol concentration to the original concentration of phenol was calculated by correlating the measured area of

the fluorescence emission band in irradiated phenol/metal oxide samples to the area of fluorescence emission band of non-irradiated sample (in absence of metal oxide) at initial phenol concentration (1×10^{-4} to 2×10^{-5} M), for each experiment. The results are given in Tables 1–9.

3. Results and discussions

3.1. Irradiations under sodium lamp

Prior to irradiation the absorption and fluorescence emission spectra of the phenol in the presence of photoactive oxides were compared with the spectra of phenol in absence

Table 1

The percentage of remaining phenol concentration after irradiation with 400 W sodium lamp in 0.5 g l^{-1} TiO_2 solutions

Initial concentration of phenol (M)	Irradiation time (min)									
	0	5	10	15	20	25	30	45	60	90
2×10^{-5}	65	57	40	35	28	23	20	18	10	6
3×10^{-5}	63	60	49	42	38	34	31	28	21	13
4×10^{-5}	70	62	54	49	44	39	36	28	23	16
5×10^{-5}	74	66	58	49	42	34	31	28	24	18
6×10^{-5}	77	69	60	51	46	41	36	28	25	18
8×10^{-5}	79	77	71	65	61	57	55	48	35	30
1×10^{-4}	82	80	74	71	67	63	60	52	43	36

Table 2

The percentage of remaining phenol concentration after irradiation with 400 W sodium lamp in 0.5 g l^{-1} ZnO solutions

Initial concentration of phenol (M)	Irradiation time (min)									
	0	5	10	15	20	25	30	45	60	90
2×10^{-5}	87	60	45	37	30	27	23	21	19	16
3×10^{-5}	89	70	54	47	43	40	38	30	26	18
4×10^{-5}	89	78	70	61	53	46	40	34	29	21
5×10^{-5}	90	76	67	59	51	46	40	35	28	22
6×10^{-5}	90	84	76	63	53	47	42	37	31	25
8×10^{-5}	91	86	76	67	62	58	56	50	44	37
1×10^{-4}	91	90	85	80	75	69	65	60	54	44

Table 3

The percentage of remaining phenol concentration after irradiation with 400 W sodium lamp in 0.04 g l^{-1} Fe_2O_3 solutions

Initial concentration of phenol (M)	Irradiation time (min)									
	0	5	10	15	20	25	30	45	60	90
2×10^{-5}	87	85	82	79	76	74	72	70	67	64
3×10^{-5}	86	83	81	78	75	73	72	69	65	63
4×10^{-5}	85	82	78	75	71	70	68	67	64	62
5×10^{-5}	83	80	76	72	70	67	65	62	61	57
6×10^{-5}	78	75	70	64	58	57	54	53	51	50
8×10^{-5}	80	78	73	69	65	63	60	58	53	52
1×10^{-4}	88	85	82	78	75	72	67	63	61	59

Table 4

The percentage of remaining phenol concentration after irradiation under direct sunlight (1 sun) in 0.5 g l^{-1} TiO_2 solutions

Initial concentration of phenol (M)	Irradiation time (min)									
	0	5	10	15	20	25	30	45	60	90
2×10^{-5}	65	48	41	32	25	18	10	5	1	1
3×10^{-5}	63	55	44	39	35	30	27	23	18	09
4×10^{-5}	70	56	52	47	38	31	26	20	16	11
5×10^{-5}	74	61	53	46	41	34	28	23	17	14
6×10^{-5}	77	66	55	48	43	38	30	24	19	15
8×10^{-5}	79	70	59	53	47	43	41	32	24	19
1×10^{-4}	82	73	64	59	58	51	47	39	29	21

Table 5

The percentage of remaining phenol concentration after irradiation under direct sunlight (1 sun) in 0.5 g l^{-1} ZnO solutions

Initial concentration of phenol (M)	Irradiation time (min)									
	0	5	10	15	20	25	30	45	60	90
2×10^{-5}	87	52	44	35	29	26	22	19	17	13
3×10^{-5}	89	65	54	45	41	38	32	29	24	16
4×10^{-5}	89	69	63	58	51	44	38	33	30	20
5×10^{-5}	90	70	65	60	50	43	37	32	27	25
6×10^{-5}	90	76	69	62	52	46	40	35	30	25
8×10^{-5}	91	79	72	65	58	52	49	46	43	33
1×10^{-4}	91	84	80	77	72	66	61	57	51	43

Table 6

The percentage of remaining phenol concentration after irradiation under direct sunlight (1 sun) in 0.04 g l^{-1} Fe_2O_3 solutions

Initial concentration of phenol (M)	Irradiation time (min)									
	0	5	10	15	20	25	30	45	60	90
2×10^{-5}	87	82	77	69	64	61	58	55	52	48
3×10^{-5}	86	81	75	70	66	62	59	56	53	50
4×10^{-5}	85	80	74	70	66	61	57	53	50	47
5×10^{-5}	83	79	74	70	67	62	58	53	49	45
6×10^{-5}	78	72	68	63	59	55	51	48	44	44
8×10^{-5}	78	73	67	62	58	54	50	47	45	44
1×10^{-4}	88	83	79	72	69	64	59	55	51	47

Table 7

The percentage of remaining phenol concentration after irradiation under concentrated sunlight (40–50 suns) in 0.5 g l^{-1} TiO_2 solutions

Initial concentration of phenol (M)	Irradiation time (min)					
	0	3	6	9	12	15
2×10^{-5}	65	39	10	6	3	1
3×10^{-5}	66	28	7	4	2	1
4×10^{-5}	72	24	6	3	2	1
5×10^{-5}	75	22	4	2	1	1
6×10^{-5}	79	27	9	4	2	1
8×10^{-5}	81	32	13	7	2	1
1×10^{-4}	84	34	12	6	2	1

Table 8

The percentage of remaining phenol concentration after irradiation under concentrated sunlight (40–50 suns) in 0.5 g l^{-1} ZnO solutions

Initial concentration of phenol (M)	Irradiation time (min)					
	0	3	6	9	12	15
2×10^{-5}	87	20	10	7	3	1
3×10^{-5}	87	17	9	5	3	1
4×10^{-5}	85	16	8	2	1	1
5×10^{-5}	83	15	8	2	1	1
6×10^{-5}	78	19	8	2	2	1
8×10^{-5}	80	23	6	4	2	1
1×10^{-4}	87	23	11	6	2	1

Table 9

The percentage of remaining phenol concentration after irradiation under concentrated sunlight (40–50 suns) in 0.04 g l^{-1} Fe_2O_3 solutions

Initial concentration of phenol (M)	Irradiation time (min)					
	0	3	6	9	12	15
2×10^{-5}	86	71	40	28	17	12
3×10^{-5}	85	70	37	27	16	11
4×10^{-5}	85	59	34	26	20	14
5×10^{-5}	83	56	47	32	21	18
6×10^{-5}	77	47	36	30	24	19
8×10^{-5}	80	49	40	33	28	24
1×10^{-4}	87	63	39	33	30	27

of photoactive oxides. Fluorescence emission measurements revealed that the phenol concentration was diminished about 10–35%, (Fig. 3) before any irradiation, following the addition of the photoactive oxides, aeration and filtration in dark. Phenol/oxide samples kept in dark for longer periods

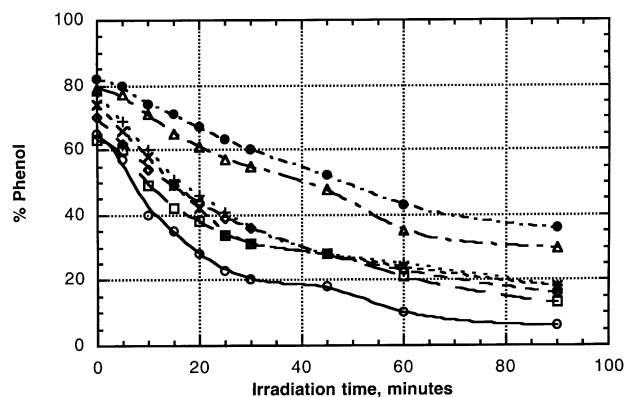


Fig. 3. The decline of phenol concentration under irradiation with 400 W sodium lamp in 0.5 g l^{-1} TiO_2 solutions, measured at 0, 5, 10, 15, 20, 25, 30, 45, 60 and 90 min, respectively from initial phenol concentrations of 1×10^{-4} M (●); 8×10^{-5} M (Δ); 6×10^{-5} M (+); 5×10^{-5} M (×); 4×10^{-5} M (◇); 3×10^{-5} M (□); 2×10^{-5} M (○) as determined by the measurement of the area of fluorescence emission band of phenol.

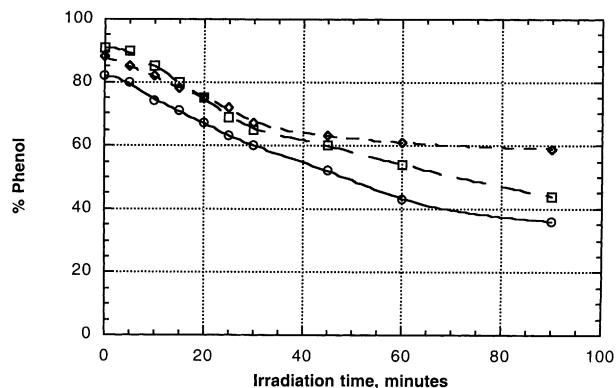


Fig. 4. Degradation of phenol at an initial concentration of 1×10^{-4} M with TiO_2 (○); ZnO (□); Fe_2O_3 (◇) by photolysis under 400 W sodium lamp.

did not exhibit any further decreases in the intensity of fluorescence emission band, unless they were exposed to light (Figs. 6 and 8). The percent ratio of final concentration of phenol in dark was taken as zero time concentration of phenol at irradiations (Tables 1–9).

The absorption and emission spectra of phenol in the presence of the three photoactive oxides, irradiated under the 400 W sodium lamp, were recorded at seven different initial phenol concentrations ranging from 1×10^{-4} to 2×10^{-5} M (Tables 1–3). The aim of the concentration variations was to observe the re-productibility of the photodegradation and to find the most effective concentration range of photodegradation. The mechanism of phenol photodegradation to mineralization was shown to follow first order kinetics by Braun and co-workers [2]. As seen in Fig. 4 and Table 1 that the phenol concentration of 10^{-4} M was shown to be the best linear degradation rate. Photodegradation capacities of all three oxides under the sodium lamp are compared at the 10^{-4} M concentration (Fig. 4). As can be seen, the order of increasing rate of phenol photodegradation follows the order: $\text{Fe}_2\text{O}_3 < \text{ZnO} < \text{TiO}_2$.

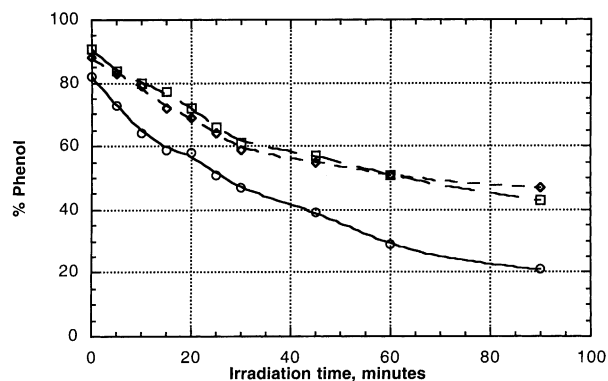


Fig. 5. Degradation of phenol at an initial concentration of 1×10^{-4} M with TiO_2 (○); ZnO (□); Fe_2O_3 (◇) by photolysis under direct sunlight (1 sun).

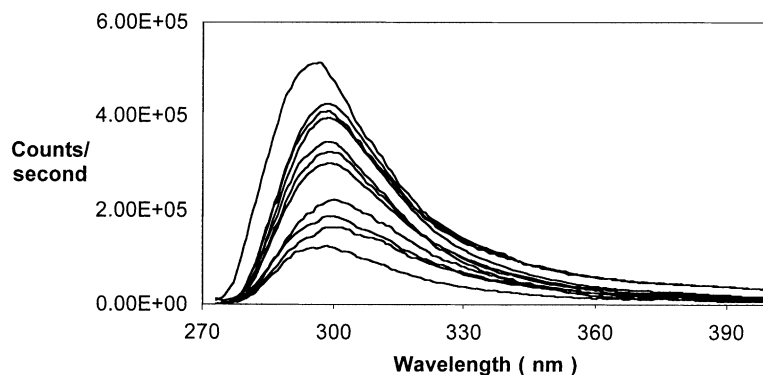


Fig. 6. Decline of fluorescence emission of a 5×10^{-5} M phenol, $\lambda_{\text{exc}} = 268$ nm, $\lambda_f = 296$ nm, in the presence of 0.5 g l^{-1} ZnO photolyzed under direct sunlight (1 sun). The traces depict phenol luminescence beginning from fluorescence in absence of ZnO in the dark and at photolysis periods of 0, 5, 10, 15, 20, 25, 30, 45, 60 and 90 min, from top to bottom, respectively.

3.2. Irradiations under direct sunlight

Experiments under direct sunlight (1 sun) with TiO_2 , ZnO and Fe_2O_3 have yielded higher ratios of phenol degradation, with respect to sodium lamp irradiations. This was observed by monitoring a decline in the intensity of the fluorescence emission band of phenol (Tables 4–6 and Figs. 5 and 6). These results further show that the 400 W sodium lamp radiation intensity is lower than direct sunlight, which was estimated to be 0.2 sun by our measurements with radiometers at 312 and 365 nm radiation wavelengths. A comparison of the photodegradation capacities of the three oxides under direct sunlight (1 sun) at 10^{-4} M phenol concentrations shows that TiO_2 is by far the most effective with respect to ZnO and Fe_2O_3 $\text{TiO}_2 > \text{ZnO} > \text{Fe}_2\text{O}_3$ (Fig. 5).

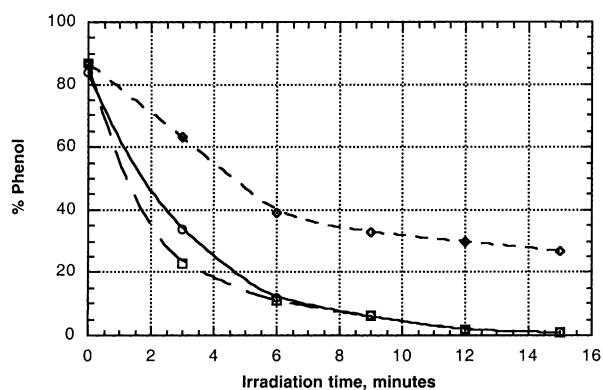


Fig. 7. Degradation of phenol at an initial concentration of 1×10^{-4} M with TiO_2 (○); ZnO (□); Fe_2O_3 (◇) under concentrated sunlight (40–50 suns).

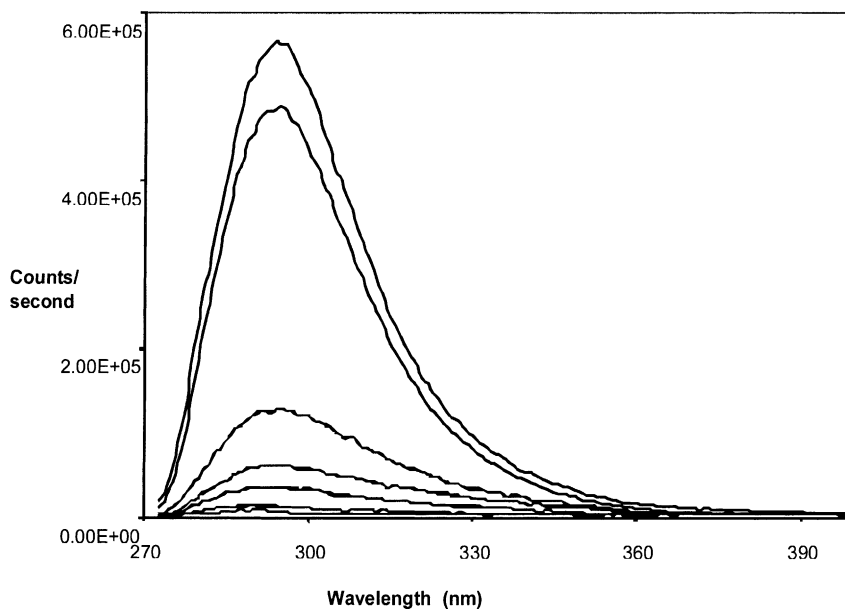


Fig. 8. Decline of fluorescence emission of 5×10^{-5} M phenol, $\lambda_{\text{exc}} = 268$ nm, $\lambda_f = 296$ nm, in the presence of 0.5 g l^{-1} ZnO photolyzed under concentrated sunlight (40–50 suns). The traces depict phenol luminescence beginning from fluorescence in the absence of ZnO in the dark and at photolysis periods 0, 3, 6, 9, 12 and 15 min, from top to bottom, respectively.

3.3. Irradiations under concentrated sunlight

Irradiations under concentrated sunlight (40–50 suns) have shown a vigorous photodegradation of phenol for all of the concentrations between 1×10^{-4} and 2×10^{-5} M (Tables 7–9). Phenol was completely degraded in less than 10 min with TiO₂ and ZnO, and only 12–27% phenol was left after 15 min of irradiation in presence of Fe₂O₃. A striking observation that can be seen in Fig. 7, the photoreactivity of ZnO is higher than Fe₂O₃, and as reactive as TiO₂ under concentrated sunlight of 40–50 suns. A complete loss of the phenol fluorescence emission band is seen in Fig. 8 upon irradiation with concentrated sunlight in presence of the ZnO photocatalyst.

4. Conclusion

It is apparent from these results that photodegradations are favored under concentrated sunlight. A most unexpected, and economically promising result is that the photoreactivity of ZnO is as high as TiO₂ under concentrated sunlight. The enhanced photocatalytic activity of ZnO under these conditions may be related to absorption characteristics of ZnO in the 300–400 nm region. Concentrated sunlight system used in these experiments has an aluminum reflector, which reflects the solar irradiation below 400 nm. Thus, ZnO is capable of being “activated” by the concentrated sunlight much more efficiently than either TiO₂ and Fe₂O₃. The air saturated aqueous ZnO suspension is reported to promote electrons effectively from the valence band to the conduction band, with the formation of free electrons and positive holes in the photoconductor upon 350 nm irradiation [10,11]. The intensity of the radiation below 400 nm under direct sunlight is low, only few percent of the total intensity of the solar radiation spectrum. As a result ZnO absorbs less under direct sunlight and under 400 W sodium lamp, and as a result, is less reactive with respect to TiO₂.

Weller and Hoyer have studied the redox potentials of ZnO colloids, and reported 29.3 Å diameter size affords the maximum redox potential [13]. Our studies have proven that the photoreactivity is sufficient under concentrated sunlight, irrespective of particle size, which is a large advantage for the practical application of this ZnO system in large scale decontamination of polluted waters. In a recent

study, Schubnell et al. studied the ZnO fluorescence emission at 370 nm ($\lambda_{\text{exc}} = 355$ nm) at elevated temperatures (310–630 K), and provided evidence for the potential photocatalytic capacity of ZnO even at very high temperature [14]. Combining these facts, one may announce that low cost, polydisperse ZnO can replace TiO₂ as the main photoactive metal oxide used for solar purification of contaminated waters under concentrated sunlight. The employment of simple parabolic mirror to concentrate direct sunlight, will prove to be an efficient and economical method for the removal of organic pollutants with aqueous ZnO suspensions.

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