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Photocatalytic degradation of Phenol Red using complexes of some transition metals and hydrogen peroxide

SAVITRI LODHA, DIPTI VAYA, RAKSHIT AMETA and PINKI B. PUNJABI*

Photochemistry and Solar Energy Laboratory, Department of Chemistry, University College of Science, M. L. Sukhadia University, Udaipur – 313002, Rajasthan, India

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Abstract: The photocatalytic degradation of Phenol Red was investigated using thiocyanate complexes of iron, copper, cobalt and hydrogen peroxide. The rate of photocatalytic degradation of the dye was followed spectrophotometrically. The effect of the variation of different parameters, such as pH, concentration of the complexes and dye, amount of H_2O_2 and light intensity on the rate of photocatalytic degradation was also studied. A tentative mechanism for the photocatalytic degradation of Phenol Red is proposed.

Keywords: photocatalytic degradation; Phenol Red; metal complexes; hydrogen peroxide.

INTRODUCTION

Water is one of the fundamental requirement of life and any undesired addition of chemical substances lead to its contamination and unfit for human use. Generally, various dyes found in industrial effluents, ultimately enter the aquatic ecosystem and can create various environmental hazards. These may have adverse, sometimes irreversible effects on animals and plants, as well. Adsorption, osmosis, flocculation and other methods have been used traditionally to remove dyes from water bodies, but all such methods suffer from various drawbacks. A group of waste treatment methods called AOPs (advanced oxidation processes), such as photo-Fenton and photocatalytic methods, are now widely used for this purpose.

The Fenton reagent is an established reagent for the degradation of dyes but main disadvantage of the reagent is that the reaction ceases after complete consumption of Fe^{2+}, whereas, in the photo-Fenton reaction, Fe^{2+} are regenerated from Fe^{3+} with the additional requirement of light. This makes the process cyclic in nature and the photochemical degradation proceeds smoothly.

Degradation of dyes employing the photo- Fenton reagent provides a newer method for the treatment of wastewater containing dye effluents. This reaction

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* Corresponding author. E-mail: pb_punjabi@yahoo.com

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involves the formation of hydroxyl and perhydroxyl radicals.[1–4]. In addition to the involvement of $^\bullet$OH, some results on the mechanism of the Fenton reaction suggests the participation of a ferryl complex.[5] Prousek *et al.*[6] reported the utilization of the Fenton reaction for the degradation of dyes present in collared waste water. Nerud *et al.*[7] investigated the decolourisation of synthetic dyes by the Fenton reagent and the Cu/pyridine/H_2O_2 system. Chen *et al.*[8] observed the electrochemical degradation of Bromopyrogallol Red in the presence of cobalt ions. Verma *et al.*[9] investigated the decolourisation of synthetic dyes using a copper complex with glucaric acid. Lunak *et al.*[10] studied the photocatalytic effects of halogen penta-amine cobalt (III) complexes and H_2O_2. The photochemistry of complexes of a number of metals, such as Cr, Fe, Co, Pt, Mo and W was studied extensively by Zhang *et al.*[11] The photocatalytic effects of Fe (III) compounds were observed to play a dominant role in the degradation of 4-chlorophenoxyacetic acid initiated by polychromatic visible radiation.[12]

In a literature survey, no attention was found to have been paid to the photocatalytic degradation of Phenol Red dye using thiocyanate complexes of iron, copper and cobalt and H_2O_2. Therefore, in the present investigation an attempt was made to carry out photochemical degradation of Phenol Red dye in a homogeneous medium using thiocyanate complexes and H_2O_2, which generates $^\bullet$OH.

EXPERIMENTAL

The photochemical degradation of Phenol Red (HIMEDIA) was studied in the presence of a transition metal complex, *i.e.*, $[Fe(SCN)]^{2+}$, $[Cu(SCN)]^+$ or $[Co(SCN)]^+$, H_2O_2 and light. A stock solution of Phenol Red (1.0×10^{-3} M) was prepared in doubly distilled water. The Complex $[Fe(SCN)]^{2+}$ was prepared by mixing $FeCl_3$ (1.0×10^{-3} M, Himedia) and KSCN (1.0×10^{-3} M, Himedia) in a 1:1 ratio. The $[Cu (SCN)]^+$ and $[Co(SCN)]^+$ complexes were prepared in a similar manner. H_2O_2 (30 %, Merck) was a commercial product and was used as received. The reaction mixture containing dye (10^{-5} M), complex (10^{-6} M) and hydrogen peroxide was exposed to light for a certain period depending on the employed complex. A 200 W tungsten lamp (Philips) was used for the irradiation. The intensity of light at various distances was measured by a "Suryamapi" (CEL Model 201). The pH of the solution was measured using a digital pH meter (Systronics Model 335). The desired pH of the solution was adjusted by the addition of previously standardised 0.050 M sulphuric acid and 1.0 M sodium hydroxide solutions. A visible spectrophotometer (Systronics Model 106) was used for measuring the absorbance of the reaction mixture at regular time intervals.

RESULTS AND DISCUSSION

A 3.0 ml aliquot was taken from the reaction mixture at regular time intervals and the absorbance measured spectrophotometrically at λ_{max} value of 430 and 560 nm for acidic and basic medium, respectively. The absorbance of the solution was found to decrease with increasing time, which indicates that the concentration of Phenol Red decreased with increasing time of exposure. A plot of 2+log A *vs.* time was linear and followed pseudo-first order kinetics. The rate constant, k, was determined using the following expression:

$$k = 2.303\times\text{slope}$$

The data for typical run are graphically presented in Fig. 1.

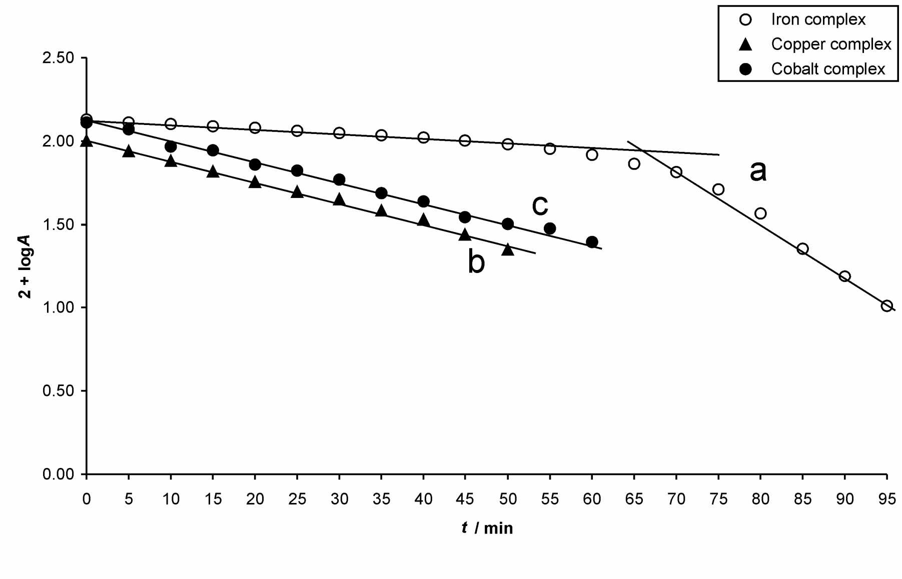

Fig. 1. 2+log *A* *vs.* time plots for different complexes; $V(H_2O_2) = 0.20$ ml; complex concentration: 1.75×10^{-5} M; dye concentration: 5.00×10^{-5} (a) and 2.50×10^{-5} M (b and c); pH: 3.0 (a), 8.0 (b) and 9.0 (c); light intensity: 60 (a), 70 (b) and 40 mW cm^{-2} (c). Rate constants, *k*: 1.53×10^{-4} and 11.05×10^{-4} (a), 5.37×10^{-4} (b) and 4.61×10^{-4} s^{-1} (c).

For iron complex/H_2O_2 system, the reaction proceeded in two phases. The first phase was an induction period,[13] in which radicals were generated, whereas the major degradation of the dye occurred in second step, as shown by the sharp decrease in the absorbance.

Effect of pH

The effect of pH on photocatalytic degradation was investigated in the pH ranges 2.0–5.0, 7.0–9.0, 7.5–10.0 for the iron, copper and cobalt complexes, respectively. The results are reported in Table I.

The photochemical degradation of Phenol Red was maximal at pH 3.0, 8.0 and 9.0, with the iron, copper and cobalt complexes, respectively. The photochemical degradation depended strongly on the pH of the reaction medium. This can be explained based on Eqs. (1) and (2), which are part of the mechanism discussed later in the text:

$$\text{Me}^{n+} + \text{H}_2\text{O}_2 \rightarrow \text{Me}^{(n+1)+} + \text{OH}^- + {}^\bullet\text{OH} \quad (1)$$

$$\text{Me}^{(n+1)+} + \text{H}_2\text{O} \xrightarrow{h\nu} \text{Me}^{n+} + {}^\bullet\text{OH} + \text{H}^+ \quad (2)$$

TABLE I. Effect of pH on the degradation rate of Phenol Red. $V(H_2O_2) = 0.20$ ml; complex concentration: 1.75×10^{-5} M; dye concentration: 5.00×10^{-5} (iron complex) and 2.50×10^{-5} M (copper and cobalt complex); light intensity: 60 (iron complex), 70 (copper complex) and 40 mW cm^{-2} (cobalt complex)

pH	k / 10^{-4} s^{-1}			
	Iron complex		Copper complex	Cobalt complex
	k_1	k_2		
2.0	0.26	0.81	–	–
2.5	0.75	2.1	–	–
3.0	1.5	11.0	–	–
3.5	0.10	0.16	–	–
4.0	0.040	0.13	–	–
4.5	0.030	0.10	–	–
5.0	0.020	0.060	–	–
7.0	–	–	2.82	–
7.5	–	–	4.80	3.65
8.0	–	–	5.37	3.94
8.5	–	–	3.96	4.27
9.0	–	–	3.66	4.61
9.5	–	–	–	3.61
10.0	–	–	–	1.97

In case of the iron complex, it was observed that rate of degradation of the dye increased on decreasing the pH from 5.0 to 3.0. This may be due to the dominance of Eq. (1) over Eq. (2), where OH^- are generated. These OH^- are removed on increasing the H^+ concentration with decreasing pH. This will facilitate *via* Eq. (1) the formation of more $^\bullet OH$, which are utilized for the oxidative degradation of Phenol Red and thiocyanate radicals. On decreasing the pH further, *i.e.*, below 3.0, the reaction rate decreased again. This may be attributed to the fact that Eq. (2) commences to dominate over Eq. (1), as $Fe(OH)_3$ is less soluble than $Fe(OH)_2$ and the generation of $^\bullet OH$ *via* Eq. (2) is retarded at pH values lower than 3.0.[14]

In cases of the copper and cobalt complexes, the reaction proceeds faster in basic media. The rate of degradation of dye increased on increasing the pH from 7.0 to 8.0 and from 7.5 to 9.0 for copper and cobalt complexes, respectively. This may be due to the dominance of Eq. (2) over Eq. (1), in which H^+ are generated. These H^+ are removed by increasing the concentration of OH^-. This will facilitate Eq. (2), forming more $^\bullet OH$, which are utilized for the oxidative degradation of Phenol Red as well as the thiocyanate radical. Above pH 8.0 and 9.0 for the copper and cobalt system, respectively, increasing the pH further resulted in a decrease in the rate of degradation, which can be attributed as the dominance of Eq. (2) over Eq. (1), in which H^+ are generated.

Effect of hydrogen peroxide

The effect of amount of H_2O_2 on the rate of photocatalytic degradation of Phenol Red was also investigated. The results are reported in Table II.

TABLE II. Effect of the concentration of H_2O_2 on the degradation rate of Phenol Red. Complex concentration: 1.75×10^{-5} M; dye concentration: 5.00×10^{-5} (iron complex) and 2.50×10^{-5} M (copper and cobalt complex); pH: 3.0 (iron complex), 8.0 (copper complex) and 9.0 (cobalt complex); light intensity: 60 (iron complex), 70 (copper complex) and 40 mW cm^{-2} (cobalt complex)

$V(H_2O_2)$ / ml	k / 10^{-4} s^{-1}			
	Iron complex		Copper complex	Cobalt complex
	k_1	k_2		
0.0	0.060	0.16	0.66	0.38
0.10	0.45	0.81	1.4	2.3
0.20	1.5	11.0	3.1	2.9
0.30	1.4	10.2	3.4	3.1
0.40	1.4	10.0	3.7	3.3
0.50	1.3	9.8	3.8	3.4
0.60	1.2	9.4	4.0	4.2
0.70	1.1	7.4	5.4	4.6

The rate of photochemical degradation of Phenol Red was maximal with 0.20 ml H_2O_2 for the iron complex, This may be explained because increasing the amount of H_2O_2 would result in more $^{\bullet}OH$, responsible for the oxidative degradation of Phenol Red, being formed. However, after a certain amount of H_2O_2 (0.20 ml), a further increase in the amount of H_2O_2 would produce more OH^- ions together with $^{\bullet}OH$ and, as a result, the pH of the medium would increase, resulting in a decrease in the rate of degradation.

A different kind of behaviour was observed for the copper and cobalt complex systems. In these cases, a continuous increase in the rate of degradation of Phenol Red was observed with increasing amount of H_2O_2 in the range from 0.0 to 0.70 ml. This may be attributed to the fact that Eq. (1) does not dominate over Eq. (2) in these cases and hence no decrease in the rate was observed with increasing amount of H_2O_2.

Effect of the concentration of the complexes

The effect of the concentration of the complexes on the rate of photocatalytic degradation of Phenol Red was studied by keeping all other factors identical. The results are given in Table III.

It is clear from the data that the rate of photocatalytic degradation increases with increasing concentration of the complexes. The rates were determined up to concentrations of 1.75×10^{-5}, 4.37×10^{-5}, 1.75×10^{-5} M for the iron, copper and cobalt complexes, respectively. Above these limits, the rates were extremely fast and it was not possible to study the rates satisfactorily due to experimental limitations. This increasing trend may be explained by more molecules of the complexes being available to participate in the reaction. This results in an enhanced generation of $^{\bullet}OH$ and, therefore, the rate of photocatalytic degradation of the dye increases.

TABLE III. Effect of complex concentration on the degradation rate of Phenol Red. $V(H_2O_2)$ = 0.20 ml; dye concentration: 5.00×10^{-5} (iron complex) and 2.50 ×10^{-5} M (copper and cobalt complex); pH: 3.0 (iron complex), 8.0 (copper complex) and 9.0 (cobalt complex); light intensity: 60 (iron complex), 70 (copper complex) and 40 mW cm^{-2} (cobalt complex)

Complex concentration ×10^5 M	k / 10^{-4} s^{-1}			
	Iron complex		Copper complex	Cobalt complex
	k_1	k_2		
0.0	0.22	0.25	0.83	0.85
0.25	0.38	0.80	–	2.3
0.50	0.46	0.90	–	2.9
0.62	–	–	2.9	–
0.75	0.75	3.0	–	3.4
1.0	1.1	6.0	–	4.0
1.2	1.5	7.0	3.3	4.3
1.5	1.5	9.0	–	4.4
1.8	1.5	11.0	–	4.6
1.9	–	–	4.1	–
2.5	–	–	4.3	–
3.1	–	–	4.5	–
3.8	–	–	4.7	–
4.4	–	–	5.4	–

Effect of the Phenol Red concentration

The effect of the Phenol Red concentration on the rate of photocatalytic degradation was also examined and the results are given in Table IV.

TABLE IV. Effect of the dye concentration on the degradation rate of Phenol Red. $V(H_2O_2)$ = = 0.20 ml; complex concentration: 1.75×10^{-5} M; pH: 3.0 (iron complex), 8.0 (copper complex) and 9.0 (cobalt complex); light intensity: 60 (iron complex), 70 (copper complex) and 40 mW cm^{-2} (cobalt complex)

Dye concentration ×10^5 M	k / 10^{-4} s^{-1}			
	Iron complex		Copper complex	Cobalt complex
	k_1	k_2		
1.50	–	–	4.02	1.03
2.00	1.42	7.66	4.70	3.07
2.50	–	–	5.37	4.61
3.00	1.48	9.68	5.04	4.10
3.50	–	–	4.76	3.94
4.00	1.53	10.1	4.56	3.85
4.50	–	–	4.35	3.58
5.00	1.53	11.0	4.23	3.07
6.00	1.02	10.2	–	–
7.00	0.760	10.9	–	–
8.00	0.500	10.1	–	–

The rate of degradation was found to increase with increasing concentration of Phenol Red up to 5.00×10^{-5}, 2.50×10^{-5} and 2.50×10^{-5} M for the $[Fe(SCN)]^{2+}$, $[Cu(SCN)]^{+}$, $[Co(SCN)]^{+}$ complexes, respectively. Further increasing of the concentration beyond these limits decreases the rate of degradation. This may be explained on the basis that, on increasing the concentration of Phenol Red, the reaction rate increases as more molecules of the dye were available for degradation. Further increase in the concentration causes a retardation of the reaction because at higher concentrations, the dye molecules themselves act as a filter for the incident light, thus the full intensity of the light was not employed in the photodegradation, which resulted in a decrease in the rate of degradation. Moreover, at the higher concentration, the number of collisions between dye molecules increases whereas the number of collisions between dye molecules and $^{\bullet}OH$ decreases. Consequently, the rate of the reaction is retarded. An unsuitable steric orientation is also another factor for a decrease in the rate of reaction.[15,16]

Effect of light intensity

The effect of the light intensity on the photocatalytic degradation of Phenol Red was also investigated and the results are reported in Table V.

TABLE VI. Effect of the light intensity on the degradation rate of Phenol Red. $V(H_2O_2)$ = = 0.20 ml; dye concentration: 5.00×10^{-5} (iron complex) and 2.50 ×10^{-5} M (copper and cobalt complex); complex concentration: 1.75×10^{-5} M; pH: 3.0 (iron complex), 8.0 (copper complex) and 9.0 (cobalt complex)

Light intensity mW cm^{-2}	k / 10^{-4} s^{-1}			
	Iron complex		Copper complex	Cobalt complex
	k_1	k_2		
10.0	0.43	0.57	3.87	3.86
20.0	0.65	8.1	4.19	4.04
30.0	0.87	8.2	4.48	4.32
40.0	1.1	8.4	4.65	4.61
50.0	1.3	9.6	4.78	4.43
60.0	1.5	11.0	5.07	4.32
70.0	1.3	10.9	5.37	4.20
80.0	1.3	8.8	4.78	4.04

The data indicate that an increase in the light intensity increases the rate of reaction and maxima were found at 60, 70 and 40 mW cm^{-2} for the iron, copper and cobalt complexes, respectively. This may be explained by an increase in the number of photons striking per unit area as the light intensity was increased. A further increase in the intensity beyond the maximum limits resulted in a decreease in the rate of reaction, which may be due to thermal side reactions.

MECHANISM

Based on the experimental observations and corroborating existing literature, a tentative mechanism is proposed for the degradation of Phenol Red in presence of iron and copper complexes, H_2O_2 and light:[17]

$$[\mathrm{Me(SCN)}]^{n+} \xrightarrow{h\nu} \mathrm{Me}^{n+} + {}^{\bullet}\mathrm{SCN} \qquad (3)$$

$$\mathrm{Me}^{n+} + \mathrm{H_2O_2} \rightarrow \mathrm{Me}^{(n+1)+} + \mathrm{OH}^- + {}^{\bullet}\mathrm{OH} \qquad (1)$$

$$\mathrm{Me}^{(n+1)+} + \mathrm{H_2O} \xrightarrow{h\nu} \mathrm{Me}^{n+} + {}^{\bullet}\mathrm{OH} + \mathrm{H}^+ \qquad (2)$$

$${}^{\bullet}\mathrm{SCN} + 8{}^{\bullet}\mathrm{OH} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{NH_4^+} + \mathrm{CO_2} + 2\mathrm{H_2O} \qquad (4)$$

$$\mathrm{Dye} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{Products} \qquad (5)$$

$${}^{\bullet}\mathrm{OH} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{H_2O_2} \qquad (6)$$

$$2\mathrm{H_2O_2} \rightarrow 2\mathrm{H_2O} + \mathrm{O_2} \qquad (7)$$

where Me denotes iron or copper.

In case of cobalt complex, the following mechanism is proposed:

$$[\mathrm{Me(SCN)}]^{n+} \xrightarrow{h\nu} \mathrm{Me}^{(n+1)+} + \mathrm{SCN}^- \qquad (8)$$

$$\mathrm{Me}^{(n+1)+} + \mathrm{H_2O} \xrightarrow{h\nu} \mathrm{Me}^{n+} + {}^{\bullet}\mathrm{OH} + \mathrm{H}^+ \qquad (2)$$

$$\mathrm{Me}^{n+} + \mathrm{H_2O_2} \rightarrow \mathrm{Me}^{(n+1)+} + \mathrm{OH}^- + {}^{\bullet}\mathrm{OH} \qquad (1)$$

$${}^{\bullet}\mathrm{SCN} + 8{}^{\bullet}\mathrm{OH} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{NH_4^+} + \mathrm{CO_2} + 2\mathrm{H_2O} \qquad (4)$$

$$\mathrm{Dye} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{Products} \qquad (5)$$

$${}^{\bullet}\mathrm{OH} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{H_2O_2} \qquad (6)$$

$$2\mathrm{H_2O_2} \rightarrow 2\mathrm{H_2O} + \mathrm{O_2} \qquad (7)$$

The photo-Fenton reaction is one of the examples of classical photocatalytic process in homogeneous system that involves H_2O_2, iron(III) and visible radiation. The thiocyanate complex of Fe^{3+} gives Fe^{2+} and the thiocyanate radical on exposure to light. The Fe^{2+} decomposes hydrogen peroxide into ${}^{\bullet}OH$, OH^- and Fe^{3+}. The Fe^{3+} decomposes water photochemically to give ${}^{\bullet}OH$ and Fe^{2+}. The thiocyanate radical and the dye are decomposed by hydroxyl radicals to simpler ions/molecules, such as sulphates and ammonium ion, carbon dioxide, water, *etc.*

The above-proposed mechanism for the iron complex is also applicable for the copper complex.

The mechanism for the cobalt complex differs from that for the iron and copper complexes in that the iron and copper complexes involve thiocyanate radicals, whereas in the case of the cobalt complex, thiocyanate ions are involved. The release of thiocyanate ion from its cobalt complex was ascertained by its spot test,[18] however, the negative spot test for thiocyanate ions in the case of the iron and copper complexes indicates that ${}^{\bullet}SCN$ was involved in this reaction and not SCN^-.

CONCLUSIONS

The rate of photocatalytic degradation of Phenol Red was enhanced by metal complexes. The following order of the degradation rate with different metal complexes was found:

$$[\mathrm{Fe(SCN)}]^{2+} > [\mathrm{Cu(SCN)}]^{+} > [\mathrm{Co(SCN)}]^{+}$$

Hydroxyl radicals photocatalytically degrade Phenol Red. The participation of $^{\bullet}$OH as active oxidising species was confirmed by using hydroxyl radical scavengers, where the rate of photodegradation was drastically reduced.

Further, this method is more advantageous over other methods, since it does not add further to pollution. The active oxidising species, the hydroxyl radicals, dimerise to give hydrogen peroxide, which degrades ultimately to water and oxygen.

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ИЗВОД

ФОТОКАТАЛИТИЧКА РАЗГРАДЊА ФЕНОЛ-ЦРВЕНОГ КОМПЛЕКСИМА НЕКИХ ПРЕЛАЗНИХ МЕТАЛА И ВОДОНИК-ПЕРОКСИДОМ

SAVITRI LODHA, DIPTI VAYA, RAKSHIT AMETA и PINKI B. PUNJABI

Photochemistry and Solar Energy Laboratory, Department of Chemistry, University College of Science, M. L. Sukhadia University, Udaipur – 313002, Rajasthan, India

Фотокаталитичка разградња фенол-црвеног испитивана је помоћу тиоцијанатних комплекса гвожђа, бакра и кобалта и водоник-пероксида. Брзина фотокаталитичке разградње обојеног једињења праћена је спектрофотометријски. Такође је испитивана и утицај разних параметара на брзину фотокаталитичке разградње, као што су pH, концентрација комплекса и обојеног једињења, количина H_2O_2 и интензитет светлости. Предложен је механизам реакције фотокаталитичке разградње фенол-црвеног.

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