PHOTOCATALYTIC OXIDATION OF *p*-CRESOL IN AQUEOUS TITANIUM DIOXIDE SUSPENSION

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The reaction products of the photocatalytic oxidation of *p*-cresol were characterized by high performance liquid chromatography. The influence of *p*-cresol concentration as well as the presence of dioxygen and hydrogen peroxide on the rate of photocatalytic oxidation was studied. The *p*-cresol concentration in the irradiated systems was determined by spectrophotometric method using α-nitroso-β-naphthol or by the Principal Component Regression method (in the samples with hydrogen peroxide added). The reaction pathway of the photocatalytic oxidation of *p*-cresol in TiO_2 suspension was suggested.

The photocatalytic reactions on irradiated semiconductor powders are very hopeful to remove the organic and inorganic waste materials from water[1]. Considerable interest is recently focused on the degradation of phenols and phenol derivatives by irradiation of aqueous titanium dioxide suspensions[2 - 12].

The EPR experiments confirmed that the primary process by irradiation of aqueous titanium dioxide suspensions in the presence of dioxygen is the formation of hydroxyl radicals[13]. The evolution of high concentration of hydroxyl radicals in the irradiated aqueous *p*-cresol TiO_2 suspensions in the presence of dioxygen was demonstrated[14]. Owing to its strong electrophilic character, the hydroxyl radical rapidly oxidizes a variety of organic and inorganic compounds[15].

The formation of the reactive intermediates on the irradiated titanium dioxide surface in aqueous suspension is described by the following equations[16]:

$$TiO_2 + h\nu \longrightarrow TiO_2(h^+ + e^-) \qquad (A)$$

$$O_2 + e^- \longrightarrow (O_2^{\cdot-})_s \qquad (B)$$

$$(O_2^{\cdot-})_s + H^+ \rightleftharpoons (HO_2^{\cdot})_s \qquad (C)$$

$$(HO_2^{\cdot})_s + e^- \longrightarrow (HO_2^-)_s \qquad (D)$$

$$(HO_2^-)_s + H^+ \rightleftharpoons (H_2O_2)_s \tag{E}$$

$$2\,(HO_2^\bullet)_s \longrightarrow (H_2O_2)_s + O_2 \tag{F}$$

$$(H_2O_2)_s \rightleftharpoons (H_2O_2) \tag{G}$$

$$OH^- + h^+ \longrightarrow {}^\bullet OH \tag{H}$$

$${}^\bullet OH + \text{surface/ads. compounds} \longrightarrow \text{oxidation products}, \tag{I}$$

where h^+ is a photogenerated hole, e^- is a photogenerated electron. (The surface states are labelled by the subscript s).

Kinetic studies of the photocatalytic degradation of organic compounds showed that the rate of the organic substrate removal may be expressed by means of the Langmuir–Hinshelwood kinetic model[2].

The main aim of this study is to investigate the influence of experimental conditions on *p*-cresol decomposition rate in the aqueous titanium dioxide suspensions, as well as to identify the reaction products. Based on these data the reaction mechanism might be proposed.

EXPERIMENTAL

Titanium dioxide P25 (Degussa, Germany) was used in all photocatalytic experiments. Degussa P25 titanium dioxide is predominantly anatase (80% anatase, 20% rutile), with surface area of 50 ± 5 $m^2\,g^{-1}$ and with small amounts of SiO_2 and Al_2O_3 (refs[11,13]).

The prepared aqueous dispersions of *p*-cresol and TiO_2 were stirred 20 min in ultra sound before irradiation.

The photoreactions were carried out at the temperature of 30 °C in the photochemical immersion-well (volume 120 ml) of Pyrex glass which transmits radiation over 290 nm. The aqueous suspensions were irradiated by the light of 125 W medium pressure mercury lamp (Applied Photophysics, United Kingdom) emitting light with wavelengths of 297, 303, 313, 334, 365 – 366, and 404 – 408 nm (ref.[17]). During exposure the suspensions were bubbled by carbon dioxide free air or by dinitrogen (flow rate 300 ml min^{-1}), and were stirred by magnetic stirrer. The samples removed from the reactor were immediately centrifuged 20 min at 6 400 g on the Janetzki T24 ultracentrifuge.

Carbon dioxide evolved during photocatalytic reactions was determined by means of Radelkis OK 102/1 (Hungary) conductometer as described elsewhere[18]. The pH values of centrifugates were measured on Radelkis PO 211/1 (Hungary) pH-meter, a combined glass electrode was used.

p-Cresol (Lachema, The Czech Republic) was recrystallized before use. All the chemicals used were of analytical grade purity.

All HPLC experiments were carried out using Waters HPLC modular system with Diode Array Detector (DAD) and reversed-phase column Separon SIX C-18, 15 × 0.32 cm; 5 μm (Tessek, The Czech Republic).

A mixture of 15% acetonitrile in phosphate buffer (0.01 mol dm^{-3} NaH_2PO_4 adjusted to pH 3 with H_3PO_4) was applied as a mobile phase[19]. The sample flow rate was 0.8 ml min^{-1}. The samples were injected into the loop of the injector (Rheodyne 7025) in the volume of 20 μl.

The UV-VIS spectra were measured on Philips UV-VIS spectrophotometer PU 8800 in cell path of 0.2 cm or 1 cm length.

The low concentrations of hydrogen peroxide in the irradiated suspensions were determined by spectrophotometric method of Matsubara et al.[20]. The concentrations of hydrogen peroxide added in the prepared suspensions were determined using $KMnO_4$.

The concentration of *p*-cresol in the samples were determined by improved spectrophotometric method using α-nitroso-β-naphthol[21]. Unfortunately the spectroscopic method is not suitable for the determination of *p*-cresol concentration in the aqueous systems with added hydrogen peroxide (probably due to hydrogen peroxide influence on the color formation in the reaction mixture).

The concentrations of *p*-cresol in the samples with hydrogen peroxide added were determined by the Principal Component Regression (PCR) method[22]. PCR is a multivariate calibration method utilizing a factor data compression approach.

The reliability of the PCR calibration model can be evaluated by Cross Validation method[22,23]. In this procedure the calibration is repeated NS times, each time on a subset of NS-1 standards leaving one standard out. Results of each calibration are used for "prediction" of the concentration of the leaving out standard sample. The model is characterized by the Root Mean Squared Error of Cross Validation (RMSECV)

$$\mathrm{RMSECV} = \left[\frac{1}{\mathrm{NS}} \sum_{j=1}^{\mathrm{NS}} (\hat{c}_j - c_j)^2\right]^{1/2}, \qquad (1)$$

where $\hat{c}_j$ is the predicted value and c_j is the true value of concentration of the *j*-th leaving out standard, NS is the number of the calibration standards.

Elements of the vector of standard concentrations for *p*-cresol were determined by simultaneous measurement of UV spectra and *p*-cresol concentration by HPLC in the irradiated titanium dioxide suspensions with added hydrogen peroxide.

The optimal value of a principal component space size, NF, was estimated by performing the PCR modeling for several NF values. For each NF the value of RMSECV was determined and RMSECV 0.018 for NF 4 was found to be optimal. The comparison of the predicted vs true values of concentrations for this calibration model is shown in Fig. 1.

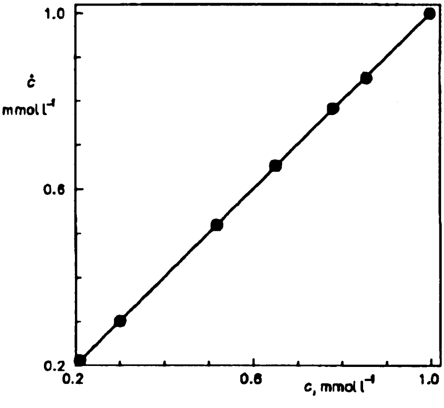


FIG. 1

Predicted concentration vs true concentration for PCR calibration model of spectrophotometric *p*-cresol determination in samples with hydrogen peroxide added

RESULTS AND DISCUSSION

Blank Experiments

The results of the blank experiments have shown that the simultaneous presence of both titanium dioxide, and light and electron acceptor (dioxygen, H_2O_2) is necessary for the effective photocatalytic removal of *p*-cresol.

High Performance Liquid Chromatography

All products of the photocatalytic degradation of *p*-cresol in irradiated TiO_2 suspensions were studied by HPLC. Reversed-phase chromatography has been recommended for the successful simultaneous separation of *p*-cresol residues and all degradation products[19]. DAD has enabled to confirm the presence of the reaction products not only comparing the retention characteristics (retention times, t_R, capacity ratios) of the degradation products and pure standards but also obtaining normalized UV spectra during the chromatographic process.

It was proved that the following degradation products have been formed,

p-hydroxybenzoic acid (t_R = 2.9 min),
p-hydroxybenzaldehyde (t_R = 3.6 min),
4-methylcatechol (t_R = 4.4 min),

and one till now unknown product (t_R = 1.9 min). The retention time of *p*-cresol was t_R = 8.9 min. The formation of *p*-hydroxybenzaldehyde has not been reported by Terzian et al.[10,11].

It is obvious that all products are successfully separated, chromatographic resolutions were in all cases sufficient for the quantitative analysis ($R_{ij} > 1.5$). The kinetic curves of *p*-cresol decomposition and products formation obtained by HPLC after irradiation of the aqueous *p*-cresol TiO_2 suspension are presented in Fig. 2.

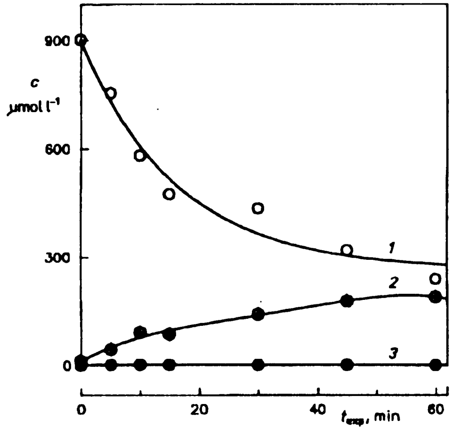
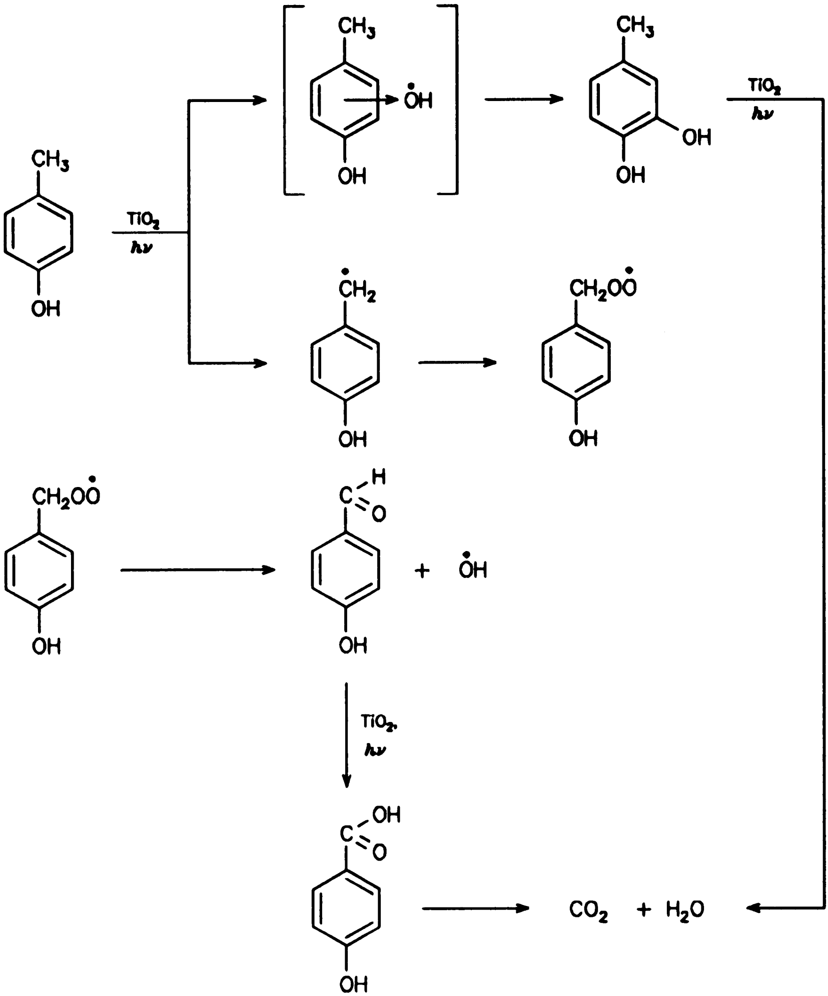


FIG. 2
The kinetic curves of *p*-cresol removal and the products formation determined by HPLC in the irradiated aqueous *p*-cresol/TiO_2 suspension bubbled with air; c(cresol) = 0.001 mol dm^{-3}, $c(TiO_2)$ = 0.8 g dm^{-3}. *1* *p*-cresol, *2* *p*-hydroxybenzaldehyde, *3* *p*-hydroxybenzoic acid

The concentration of 4-methylcatechol was negligible in the irradiated systems bubbled with air without addition of H_2O_2.

Based on the results obtained, the reaction mechanism of *p*-cresol oxidation in the titanium dioxide aqueous suspensions may be suggested (Scheme 1).



SCHEME 1

Photocatalytic Decomposition of p-Cresol in the Aqueous TiO_2 Suspension

Figure 3 shows the changes in UV spectra after various periods of the suspension irradiation in the presence of air.

During 60 min of irradiation of the 120 ml *p*-cresol TiO_2 suspension (0.0001 mol dm^{-3} of *p*-cresol, 0.8 g dm^{-3} of TiO_2) 80 μmol of carbon dioxide was evolved.

Assuming total mineralization of *p*-cresol in the system according to the following equation

$$CH_3\text{-}C_6H_4\text{-}OH \xrightarrow[TiO_2,\ O_2,\ H_2O]{h\nu} 7\,CO_2 + 4\,H_2O \qquad (J)$$

the measured amount of CO_2 corresponds to 95% mineralization of the organic substrate.

The pH values noticeably decreased during irradiation in all photocatalytic systems with various concentrations of *p*-cresol and TiO_2 (Fig. 4). The decrease in pH values can be explained by acidic products formation in the irradiated system (*p*-hydroxybenzoic acid), and by hydroxyl anions consumption according to Eq. (*H*).

The dependencies of the *p*-cresol concentration, *c*(cresol), on the irradiation time, t_{exp}, are measured in systems with various initial *p*-cresol concentration, c^0_{cresol}. The kinetic curves, $c(\text{cresol}) = f(t_{\text{exp}})$, were successfully fitted by Fletcher–Powell minimization procedure of least-squares method to exponential function (Fig. 5), i.e. formal first-order kinetics were proposed for *p*-cresol removal,

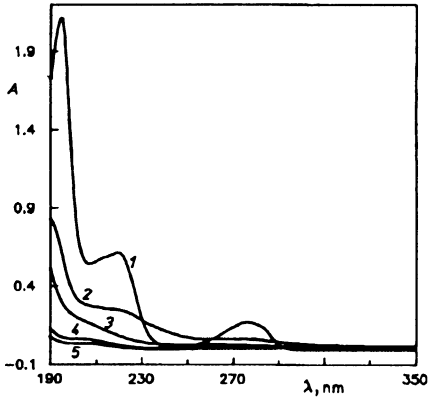


FIG. 3

Changes in UV spectra in dependence on the time of irradiation in the *p*-cresol aqueous TiO_2 suspension in the presence of air; *c*(cresol) = 0.0001 mol dm^{-3}, $c(TiO_2)$ = 0.8 g dm^{-3}, cell 1 cm. Exposure (min): *1* 0, *2* 10, *3* 30, *4* 40, *5* 60

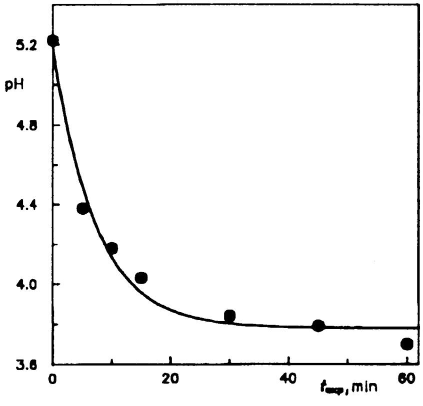


FIG. 4

Decrease of pH values in dependence on the time of irradiation in the aqueous *p*-cresol suspension; *c*(cresol) = 0.001 mol dm^{-3}, $c(TiO_2)$ = 0.8 g dm^{-3}

$$c(\text{cresol}) = A \exp(-k_f t_{exp}) + B \qquad (2)$$

and the formal first-order rate constant, k_f, was evaluated. Figure 6 shows the dependence of reciprocal values of the formal first-order rate constant on the *p*-cresol initial concentrations. The observed linear dependence confirmed the proposed Langmuir–Hinshelwood kinetic model for the photocatalytic reaction of *p*-cresol on the TiO_2 surface. The similar results were obtained for systems with various concentrations of titanium dioxide.

The influence of hydrogen peroxide addition on the *p*-cresol decomposition was also tested. Various volumes of H_2O_2 were added into the system after sonification of prepared suspensions of *p*-cresol and TiO_2 immediately before the irradiation. The measured kinetic curves for *p*-cresol removal were also fitted to exponential function and the formal first-order rate constants were calculated (Eq. (*2*)). The value of the formal first-order rate constant increases significantly with the initial concentration of hydrogen peroxide in the photocatalytic system (Fig. 7).

The hydrogen peroxide added to or produced in the photocatalytic systems acts as the electron acceptor and the hole acceptor, respectively. In the photocatalytic systems bubbled with dinitrogen, the molecular oxygen (electron acceptor) was replaced by the hydrogen peroxide. It was found that the photocatalytic removal of the *p*-cresol in these systems was stopped. The time period of the effective *p*-cresol decomposition was dependent on the initial H_2O_2 concentration. The stopping of the degradation reaction was

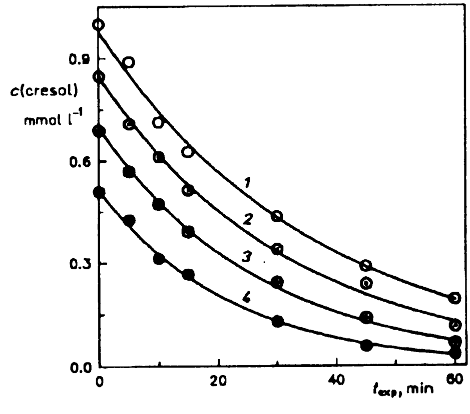


FIG. 5

The dependence of *p*-cresol concentration on the irradiation time in systems with various initial concentration of *p*-cresol; $c(TiO_2)$ = 1.7 g dm^{-3}, c^0_{cresol} (mmol dm^{-3}): *1* 1.0, *2* 0.85, *3* 0.75, *4* 0.5

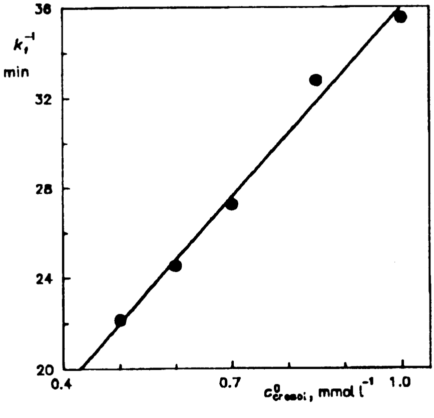


FIG. 6

The dependence of the reciprocal values of the formal first-order rate constant on the *p*-cresol initial concentrations in suspensions with $c(TiO_2)$ = 0.8 g dm^{-3}

tightly connected with the fast decrease of hydrogen peroxide concentration in the system (Fig. 8).

Finally may be concluded that the mineralization of *p*-cresol in the irradiated titanium dioxide aqueous suspensions is effective and photocatalysis may be a hopeful way of waste water purification. Further study in this field oriented in the preparation of immobilized TiO_2 photocatalyst may bring fruitful results.

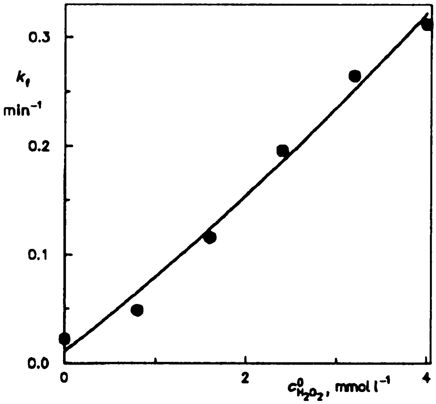


FIG. 7

The dependence of the formal first-order rate constant on the initial concentration of hydrogen peroxide in the photocatalytic systems bubbled with air; c(cresol) = 0.001 mol dm^{-3}, $c(TiO_2)$ = 0.8 g dm^{-3}

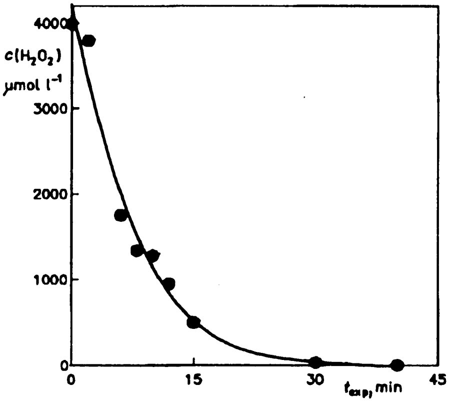


FIG. 8

Decrease of the hydrogen peroxide concentration in dependence on the time of irradiation in the photocatalytic systems bubbled with dinitrogen with added hydrogen peroxide; c(cresol) = 0.001 mol dm^{-3}, $c(TiO_2)$ = 0.8 g dm^{-3}

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