PHENOL DEGRADATION ON GLASS FIBRES WITH IMMOBILIZED TITANIUM DIOXIDE PARTICLES

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The photocatalytic mineralization of phenol in aqueous solutions under various experimental conditions was employed, to test the activity of the prepared immobilized fibreglass/TiO_2 photocatalysts. The particles of titanium dioxide P25 were coated on the surface of commercial fibreglass fabric by dipping in ethanolic TiO_2 suspensions and were fixed by firing 6 h at 500 °C.

The photocatalytic water purification on the irradiated titanium dioxide surface in the presence of oxygen is very effective process resulting in the complete mineralization of organic pollutants[1]. Recently the attention is especially focused on the degradation of phenols and phenol derivatives in TiO_2 aqueous suspensions[2–13]. The photocatalytic mineralization of organic substrates in aqueous titanium dioxide suspensions is very efficient. These systems, however, require the pretentious removing of TiO_2 particles from the solutions. Thus the technological utilization of photocatalytic processes for water purification demands the fixation or preparation of active TiO_2 surface on the suitable supporting materials[1]. The thin TiO_2 films were prepared on the glass wall of photoreactors by dipping in TiO_2 suspensions[14,15] or the particles of active TiO_2 were fixed on the sand by heating at 400 °C (ref.[16]). The immobilized TiO_2 particulate films were produced from suspensions on an optically transparent electrode[17]. The fixed titanium dioxide layers may be obtained also by the anodic oxidation[18], by the oxidation in plasma[19] or by electron-beam evaporation[20]. Sol-gel techniques were employed to coat the glass supports with colloidal solutions, subsequent firing leads to the formation of photocatalytic TiO_2 ceramic membranes[21,22]. The firing temperature dominantly determines the structure of TiO_2; the temperature below 600 °C guarantees the formation of active anatase structure[23,24].

EXPERIMENTAL

Phenol, (Reactivul, Romania) was used without further purification. All the chemicals were of analytical grade purity. The commercial fibreglass fabric V 131350/651 (Skloplast, The Slovak Republic) was applied as the supporting material for the titanium dioxide P25 particles (Degussa, Germany) immobilization. The fundamental properties of the glass fabric were: thickness, 0.4 mm; fibre diameter, 13 μm; surface weight, 350 g m^{-2}; coating material, methacryl silane.

After removal of the coating material from the technical fibreglass fabric by firing at 400 °C for 4 h, the fabric was coated by titanium dioxide particles. The glass fibres were dipped into TiO_2 suspension (TiO_2 concentration 5 g l^{-1}) in ethanol and the dried composition was calcinated 6 h at 500 °C. Non-fixed particles were removed from the surface by rewashing in water. TiO_2 particles fixation was sufficiently stable, the particles remained at the surface of the fibreglass even in a common aqueous ultrasonic bath. The concentration of supported TiO_2 was determined by measuring the turbidity (λ 530 nm) of the suspension obtained by removing the TiO_2 particles from fibreglass fabrics (2 h sonification in concentrated H_2SO_4 was the only successful method of the particles removing).

The photocatalytic activity of TiO_2 immobilized on glass fibres (area 1 dm^2) was tested in the phenol degradation reaction. The photoreactions (sample volume 130 ml) were carried out in a photochemical immersion well (Applied Photophysics, United Kingdom) using a Pyrex sleeve for cutting out the radiation below 300 nm and for inhibiting any direct photochemical transformations of phenol. A 125 W medium-pressure mercury lamp (Applied Photophysics, United Kingdom) inserted in the central part of photoreactor was employed as a radiation source. The irradiated systems were continuously saturated by dioxygen during the exposure (flow rate 200 ml min^{-1}).

The photoexperiments with the circulating phenol solutions (sample volume 300 ml) were performed in a flat photoreactor with Pyrex window (area 1 dm^2) irradiated by the external radiation source (400 W medium-pressure mercury lamp RWL, Tesla, The Czech Republic). Under these experimental conditions the prepared phenol solutions were saturated by dioxygen (flow rate 200 ml min^{-1}) in the stock vessel outside of the active irradiated zone of photoreactor.

The phenol concentration in the samples was determined by HPLC (FPLC Pharmacia, Sweden) using a Separon SIX C-18 column (Tessek, The Czech Republic) and UV detector (λ 280 nm). The mixture of methanol–water–H_3PO_4 (35 : 65 : 0.1) was applied as a mobile phase.

The reflectance spectra of titanium dioxide samples were measured using UV-VIS spectrophotometer (M40, Zeiss, Germany) equipped with a reflectance accessory with an integration sphere. The UV-VIS spectra of solutions and their turbidity were measured on Philips UV-VIS spectrophotometer PU 8800 in cell path of 0.2 and 1 cm, respectively. The scanning electron microscopy of fibreglass samples was performed by Jeol JXA-840 A analyzer.

RESULTS AND DISCUSSION

The above described procedure of TiO_2 particles deposition on glass fibres results in preparation of immobilized layers characterized by titanium dioxide concentration of 6 mg per 1 g of fibreglass. The glass fibres obtained by scanning electron microscopy before (*a*) and after (*b*) titanium dioxide deposition are depicted in Fig. 1.

The normalized reflectance spectra of TiO_2 P25 powder (80% anatase, 20% rutile)[11], glass fibres with deposited TiO_2, and rutile powder are shown in Fig. 2. The obtained reflectance spectra confirmed only negligible transformation of P25 to rutile structure by calcination (6 h at 500 °C).

Rapid decrease of phenol concentration in aqueous solutions during irradiation at various temperatures using TiO_2 immobilized on glass fibres is illustrated in Fig. 3. The dependence of phenol concentration on the irradiation time was successfully fitted (by the non-linear least squares minimization procedure) to an exponential function using program SCIENTIST (MicroMath). Formal first-order kinetics were proposed for phenol decomposition and the formal first-order rate constants were evaluated. From these the phenol half-times, $\tau_{0.5}$, in experimental systems were calculated[25]. The obtained values of phenol half-time were used for the comparison of the efficiency of the photocatalytic process under different reaction conditions.

The release of TiO_2 particles from the fibreglass support by manipulation and/or irradiation was not observed, the solutions remained transparent all the time and no turbidity was measured in UV spectra as shown in Fig. 4. Consequently the stability of the fibreglass/TiO_2 photocatalyst was sufficient, but surprisingly the phenol half-times became longer and longer during the repeated degradation experiments (16 cycles of 90 min exposure) as depicted in Fig. 5. The decrease of photodegradation activity is significant after 20 h irradiation. We were extensively looking for the reason of such activity decrease, and we found that during the exposure the TiO_2 surface is saturated by adsorbed intermediates

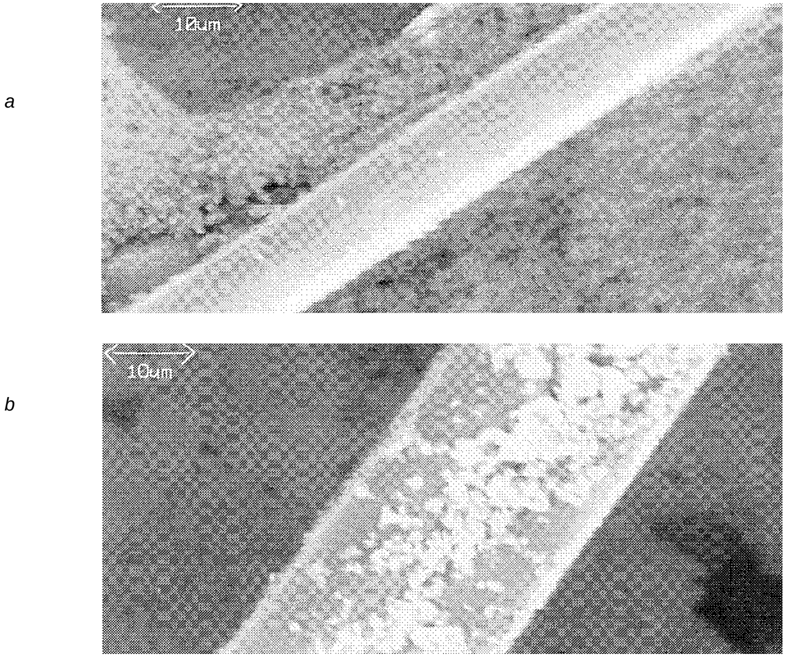

FIG. 1
Scanning electron microscopy of the glass fibres before (*a*) and after (*b*) surface deposition of TiO_2

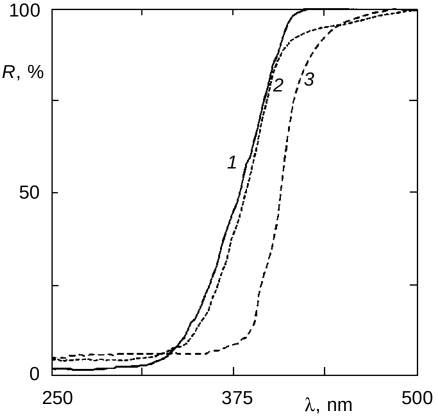

FIG. 2
The reflectance (R) spectra of TiO_2 P25 powder (*1*), glass fibres with TiO_2 deposited by calcination at 500 °C (*2*) and powder rutile (*3*)

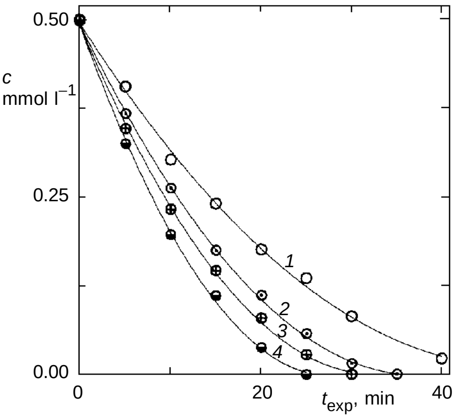

FIG. 3
The dependence of phenol concentration (c) on the irradiation time (t_{ext}) at various temperatures using TiO_2 supported on glass fibres; c_0 0.5 mmol l^{-1}. Temperature (°C): *1* 30, *2* 40, *3* 50, *4* 60

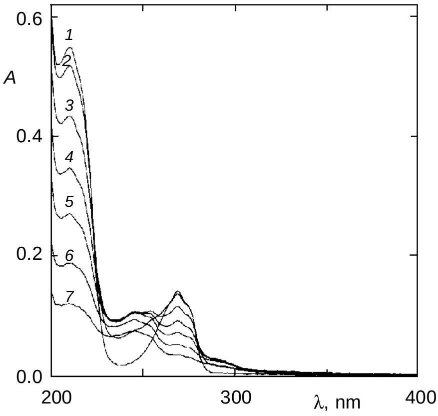

FIG. 4
Changes of absorption (A) in UV spectra in dependence on the time of irradiation in the phenol aqueous system using TiO_2 supported on glass fibres; c_0 0.5 mmol l^{-1}, cell 0.2 cm. Exposure (min): *1* 0, *2* 5, *3* 10, *4* 15, *5* 20, *6* 25, *7* 30

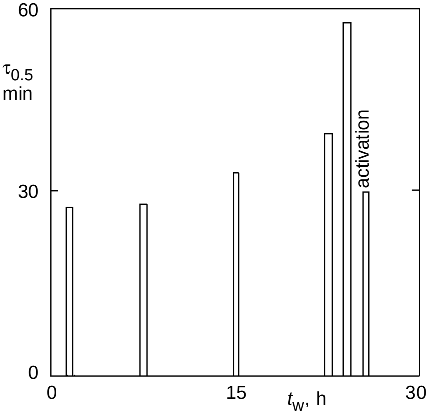

FIG. 5
The dependence of phenol half-time ($\tau_{0.5}$) on the working time (τ_w) of fibreglass/TiO_2 photocatalyst (c_0 1 mmol l^{-1}, temperature 25 °C)

of phenol degradation, e.g. hydroquinone and catechol[7]. (The formation of these intermediates was monitored in our experiments by HPLC). After removing the adsorbates from the TiO_2 surface by heating (2 h at 200 °C) or by irradiation in the acidic aqueous solution (c_{HCl} 1 mmol l^{-1}), the fibreglass/TiO_2 photocatalyst recover again the primary activity (Fig. 5). If the total working time of fibreglass/TiO_2 photocatalysts, t_w, remains below 15 h, its reactivating is not necessary.

The linear dependence of phenol half-times on the initial concentration of phenol, c_0, is illustrated in Fig. 6. Such kinetic behaviour is characteristic for Langmuir–Hinshelwood description of the surface photocatalytic reactions in systems with constant dioxygen concentration as described in the equation[22]

$$\tau_{0.5} = \frac{\ln 2}{k_1} + \frac{K_{ph}}{2k_1k_2}\,c_0 \ , \qquad (1)$$

where K_{ph} is the adsorption constant of phenol, k_1 and k_2 are formal experimental constants including the influence of experimental arrangement and the dioxygen concentration[22].

From the least-squares analysis of the data shown in Fig. 6 (intercept 4.0 min, slope 25.7 min l $mmol^{-1}$, R squared 0.98) we evaluated the phenol adsorption constant K_{ph} = 8.9 l $mmol^{-1}$. This value may be compared with adsorption constant K_{ph} = 4.07 l $mmol^{-1}$ reported for phenol decomposition in aqueous titanium dioxide suspension[2].

The temperature dependence of phenol decomposition rate was investigated in the range 25 – 60 °C. This dependence can be formally described using Arrhenius equation[15,26]

$$\tau_{0.5} = A \exp\left(-\frac{E_a}{\boldsymbol{R}T}\right) \ , \qquad (2)$$

where A is a constant, and E_a is the apparent activation energy of the photocatalytic process.

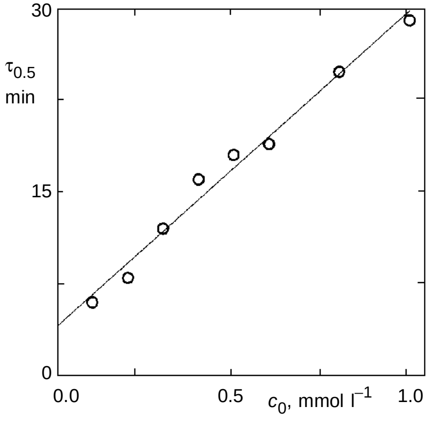

FIG. 6
The dependence of phenol half-time ($\tau_{0.5}$) on the initial phenol concentration (c_0) (dioxygen saturated systems, temperature 25 °C)

The apparent activation energy of the phenol decomposition can be calculated from the slope of the linearized Eq. (*2*) after least-squares analysis. Figure 7 illustrates such Arrhenius plot for the temperature dependence of phenol half-times (slope 1 765 K, R squared 0.96). The calculated value of the apparent activation energy of phenol degradation on irradiated fibreglass/TiO_2 is of 14.7 kJ mol^{-1} and is in a good agreement with activation energies obtained for phenol removal on immobilized TiO_2 layer by Matthews[15] and Okamoto[26].

The positive effect of higher temperature on the phenol degradation rate can be explained under assumption that the increase in temperature improve the photoreaction to compete with electron-hole recombination process[27]. The rate of formation electron-hole pairs depends also upon the temperature of semiconductor controlling its Fermi band position[28]. The increase in temperature may also increase the desorption of physisorbed species from the irradiated surface[29].

The study of the fibreglass/TiO_2 immobilized systems with circulated pollutant solution is necessary for the applications of photocatalytic processes of water purification in the future. The dependence of the phenol half-times on the flow rate of solution, *q*, through the active zone of photoreactor with external dioxygen saturation and irradiation source, is depicted in Fig. 8. The results showed the significant decrease in the phenol degradation half-time with increasing flow rate, confirming mass transfer limitations in accordance with other studies with immobilized TiO_2 photocatalysts[16,30].

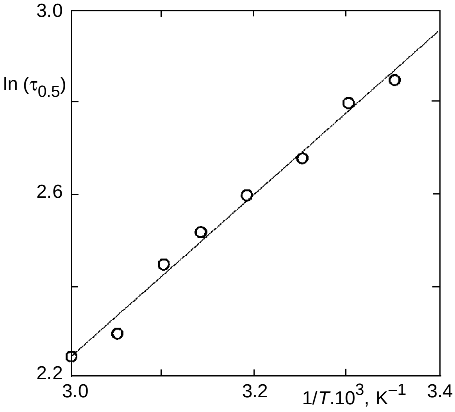

FIG. 7
The Arrhenius analysis of the dependence of phenol half-time on temperature (dioxygen saturated systems, c_0 0.5 mmol l^{-1})

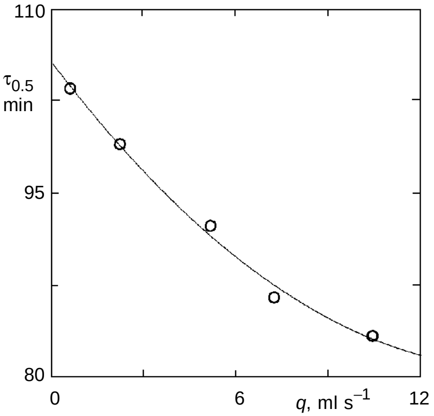

FIG. 8
The dependence of phenol half-times ($\tau_{0.5}$) on the flow rate (*q*) of solution through the active zone of flat photochemical reactor (c_0 1 mmol l^{-1}, temperature 25 °C)

The active titanium dioxide particles were fixed on the commercial glass fibres by very simple procedure. The removing of TiO_2 from the prepared fibreglass/TiO_2 photocatalyst during irradiation in aqueous solutions was fully inhibited. The immobilized photocatalysts were tested in reaction of phenol decomposition in aqueous solutions under various experimental conditions.

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