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Influence of Oxygen Pressure on the Photocatalytic Oxidation of the Azo Dye Chrome Yellow with TiO_2 As the Catalyst

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Abstract—The photocatalytic oxidation of the azo dye Chrome Yellow dissolved in water on TiO_2 at high oxygen pressures was is reported. An increase of the oxygen pressure from 0.1 to 0.7 MPa increases the rate of the reaction by a factor of 1.6.

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INTRODUCTION

The textile industry produces a considerable environmental impact mainly because of the release of large volumes of wastewater, which contains considerable amounts of organic dyes and is highly colored.

The well-known physicochemical methods for wastewater treatment in the textile industry often require the use of chemical reagents and, in some cases, high energy consumption. Therefore, photocatalytic treatment is of considerable interest because it provides an opportunity to develop energy-independent processes for the decontamination of wastewater of various compositions.

Numerous studies have been devoted to the photocatalytic oxidation of organic and inorganic compounds; the results of these studies have been reported in reviews [1–8]. For the most part, they concerned titanium dioxide photocatalysis. In particular, Zenkovets et al. [9] considered this matter, whereas Gaya and Abdullah [5] discussed fundamental problems related to progress in heterogeneous titanium dioxide photocatalysis. Mor et al. [6] published information on the highly oriented vertical nanotubes of TiO_2 and their synthesis procedures, properties, and applications in photocatalysis and solar power engineering. Konstantinou and Albanis [7] discussed the kinetics and mechanism of the photocatalytic oxidation of azo dyes in aqueous solutions with the use of TiO_2 as a catalyst.

The photocatalytic decoloration of dye solutions on TiO_2 is practically promising [10] because it provides an opportunity to perform the photocatalytic reduction of toxic transition metal salts (for example, chromium(VI)) along with dyes present in wastewater into less toxic compounds [11]. Upon the photocatalytic treatment of aqueous solutions containing azo dyes, they were completely decolorized and their toxicity decreased [12].

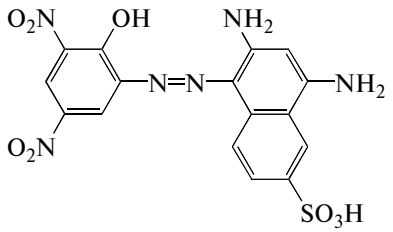
Various additives are introduced into titanium dioxide in order to increase its photocatalytic activity in the oxidation of organic compounds. In particular, Fe^{3+} and Ho^{3+} ions [13] and highly porous magnesium oxide [14] are used for this purpose. The addition of platinum nanoparticles to mesoporous titanium dioxide also increases its photocatalytic activity [15]. Nikazar et al. [16] studied the catalytic decomposition of the azo dye Disperse Yellow 23 in water. Titanium dioxide supported on clinoptilolite (Iranian natural zeolite) by solid-phase dispersion manifested itself as an active photocatalyst for this process. The maximum efficiency of photodecomposition was reached at 10 wt % TiO_2 and 90 wt % clinoptilolite concentrations in the system.

If oxygen occurs in solution in the course of a photocatalytic process, the superoxide ion is formed on the catalyst surface with the participation of oxygen. This ion can react with a dye molecule to induce its destructive oxidation.

In this work, we consider the effect of dissolved oxygen on the efficiency of a photocatalytic process occurring on titanium dioxide in the oxidation of the azo dye Chrome Yellow.

EXPERIMENTAL

The photocatalytic oxidation of the dye Chrome Yellow, whose structural formula is given below, was performed in the following manner: A dye solution with a concentration of 20 mg/l was placed in a cell, and 0.1 g of TiO_2 was added to 200 ml of the solution. Degussa P 25 titanium dioxide (Germany) as a mixture of anatase and rutile with a specific surface area of 55 m^2/g was used [5, 17]. A DRL-250 mercury lamp with a wavelength of 365 nm (OOO Svetotekhnika,



Chrome Yellow

Saransk), from which the upper luminophor layer was removed, was used as a UV-radiation source. After the irradiation of the solution for 1 h, a sample was taken and filtered, and the dye concentration was determined by spectrophotometry on a KFK-2MP photoelectric colorimeter. The analysis was performed at a wavelength of 540 nm in cells with an optical path length of 2 cm taking into account dilution and using a previously plotted calibration curve. The error in the determination of the absorbance of a solution of Chrome Yellow varied from 1 to 3%.

The cell was depressurized before sampling; then, oxygen was pumped into the cell once again to a specified pressure and the subsequent treatment was performed (2–3 h). The suspension was intensely stirred with a magnetic stirrer in the course of photocatalysis to prevent the sedimentation of titanium dioxide. For the convenience of stirring, the cell was turned and irradiation was performed from the top (Fig. 1). Teflon vessel *6* with a volume of 200 ml served as a cell, a side of which was made of quartz glass 10 mm thick (*1*). The quartz glass was fixed with bronze rings *2* and screws *7*. The solution was poured through orifices *3*, which were than stoppered. Oxygen was pumped through valve *4*, and the pressure was measured with manometer *5*.

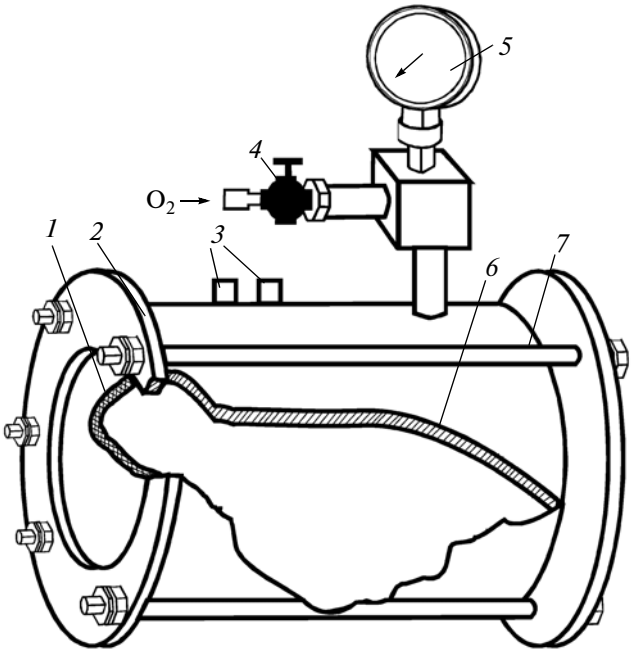


Fig. 1. Cell for the photocatalytic oxidation of dyes under oxygen pressure: (*1*) quartz window 10 mm thick, (*2*) bronze rings, (*3*) nipples for sampling and loading a suspension of titanium dioxide and a dye solution, (*4*) oxygen supply valve, (*5*) manometer, (*6*) Teflon case 20 mm thick, and (*7*) screw.

RESULTS AND DISCUSSION

The photoexcitation of a catalyst because of the formation of electrons (e^-) and holes (h^+) in the crystal lattice occurs under irradiation. They can directly interact with dye molecules or initiate the formation of highly reactive radicals, which play the main role in the photocatalytic oxidation of a dye.

Figure 2 shows the dependence of dye concentration (*C*) on irradiation time (*t*) under conditions of photocatalytic oxidation at various oxygen pressures.

Under the action of UV radiation, the solution is intensely decolorized as a result of dye molecule degradation, hypothetically, at the azo group with the formation of aromatic fragments. These fragments also undergo subsequent decomposition to form low-molecular-weight organic compounds.

Figure 3 shows changes in the absorption spectrum of a solution of Chrome Yellow depending on photocatalytic treatment time in the presence of titanium dioxide at an oxygen pressure of 0.1 MPa. After 3 h, the dye concentration dramatically decreased and the solution was decolorized. At the same time, a new

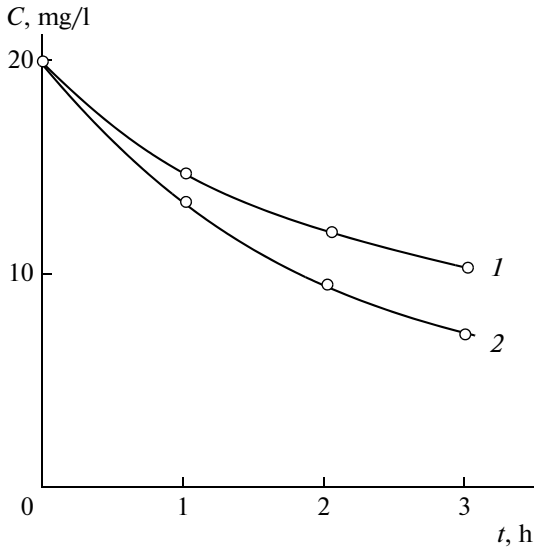


Fig. 2. Dependence of the concentration of the dye Chrome Yellow on treatment time in the course of photocatalytic oxidation at oxygen pressures of (*1*) 0.1 and (*2*) 0.7 MPa. Concentration of TiO_2, 0.5 g/l; irradiation time, 3 h.

absorption maximum appeared in the UV region of the spectrum. This absorption maximum corresponded to the destructive oxidation products of Chrome Yellow.

It is likely that the decrease in the dye concentration was more intense as the pressure of oxygen was increased to 0.7 MPa because of oxygen reduction under conditions of a photocatalytic process [8]. Moreover, the presence of oxygen dissolved under pressure facilitated the chemical oxidation of the dye. The higher the pressure of oxygen in a gas phase, the greater the concentration of oxygen in solution. An increase in the oxygen content of the solution resulted in an increase in the rate of the photocatalytic process because of the formation of active oxygen-containing species, such as $O_2^{\bullet}$, $HO_2^{\bullet}$, and $HO^{\bullet}$, which participated in the oxidation reaction, under the action of UV radiation. According to published data [8], the photocatalytic process occurred in accordance with the following reaction scheme:

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

$$h^+ + OH^- \longrightarrow {}^{\bullet}OH,$$

$$O_2 + e^- \longrightarrow O_2^{\bullet-},$$

$$CY + TiO_2(h^+) \longrightarrow \text{products}^{\bullet+} + TiO_2,$$

$$CY + O_2^{\bullet-} \longrightarrow \text{products},$$

$$CY + {}^{\bullet}OH \longrightarrow \text{products}.$$

The $O_2^{\bullet-}$ species formed in the course of the photocatalytic process facilitated the appearance of $HO_2^{\bullet}$ and $HO^{\bullet}$ radicals in the solution [18]:

$$O_2^{\bullet-} + H^+ \longrightarrow HO_2^{\bullet},$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2,$$

$$H_2O_2 + e^- \longrightarrow {}^{\bullet}OH + OH^-.$$

It is of interest to consider the effect of oxygen pressure on the kinetic parameters of the photocatalytic oxidation of Chrome Yellow. It is believed that the reaction is of first order. We plotted the dependences of $\ln \ln \frac{C}{C_0}$ (where C_0 is the initial concentration of the support) on irradiation time at various pressures of O_2. The slope of these dependences is equal to the rate constant of the reaction (Fig. 4).

The linearity of the dependence of $\ln \ln \frac{C}{C_0}$ on t demonstrates that the dye oxidation reaction is of first order. As the pressure of O_2 was increased, the initial process rate r_0 insignificantly increased; this initial rate was determined from the equation

$$r_0 = -\frac{dC}{dt} = k_{exp}C_0,$$

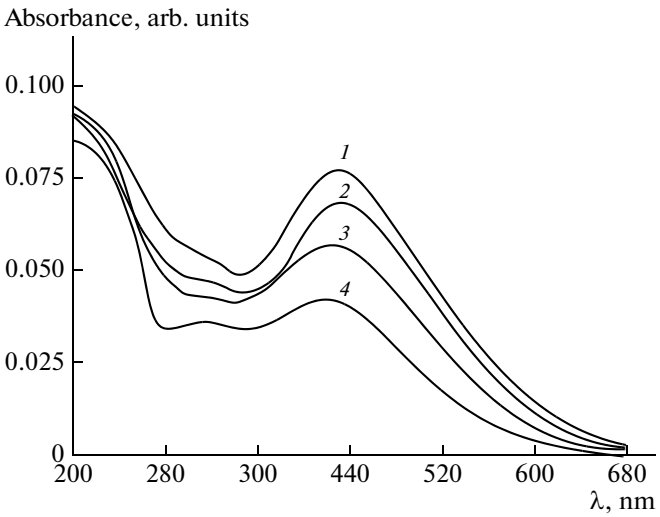


Fig. 3. Absorption spectra of a solution of Chrome Yellow measured at various photocatalytic treatment times: (*1*), 0, (*2*) 1, (*3*) 2, and (*4*) 3 h. Dye concentration, 20 mg/l; TiO_2 content, 0.5 g/l; $P_{O_2} = 0.1$ MPa.

where k_{exp} is the experimental rate constant, and C_0 is the initial concentration of the dye.

The table summarizes the rate constants of the photocatalytic oxidation of the dye Chrome Yellow at various oxygen pressures.

Figure 5 shows the dependence of the rate of oxidation on oxygen pressure. At a pressure of 0.7 MPa, the dye solution was decolorized by 50%. The dependence had an inflection point at $P_{O_2} \approx 0.5$ MPa. It was adequately approximated by the Langmuir–Hinshelwood model assuming the competitive adsorption of the dye and oxygen:

$$r_0 = k\frac{K_{CY}C_0K_{O_2}P_{O_2}}{(1 + K_{CY}C_0 + K_{O_2}P_{O_2})^2},$$

where K_{CY} is the adsorption constant of the dye Chrome Yellow on the surface of titanium dioxide; K_{O_2} is the adsorption constant of oxygen, and P_{O_2} is the pressure of oxygen.

Dependence of the rate constant of the photocatalytic oxidation of Chrome Yellow on oxygen pressure

P_{O_2}, MPa	k_{exp}, h^{-1}
0.1	0.383 ± 0.030
0.3	0.484 ± 0.028
0.5	0.530 ± 0.031
0.7	0.606 ± 0.029

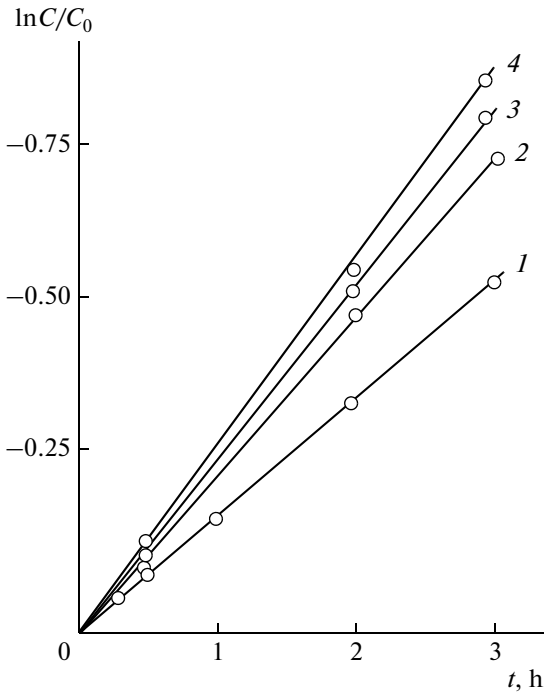


Fig. 4. Dependence of ln lnC/C_0 on the time of photocatalytic oxidation of the dye Chrome Yellow on TiO_2 under the action of UV radiation at oxygen pressures of (*1*) 0.1, (*2*) 0.2, (*3*) 0.4, and (*4*) 0.7 MPa.

As P_{O_2} was increased, the amount of oxygen adsorbed on the photocatalyst surface also increased to cause an increase in the rate of reaction.

Note that the appearance of an inflection point in the dependence of the initial rate of reaction on oxygen pressure cannot be associated with the competitive adsorption of dye oxidation products. During the initial period of the process, the concentration of products was very low, and it could not have a considerable effect on the rate of reaction. This conclusion is consistent with experimental data [19].

As the pressure of O_2 was increased, the degree of solution decoloration increased with increasing the rate of reaction. This can be seen in Fig. 6, which shows the dependence of the degree of decoloration on P_{O_2} at a catalyst concentration of 0.5 g/l and a treatment time of 3 h. The degree of decoloration was determined using the equation

$$\alpha = \frac{C_0 - C_f}{C_0} \times 100,$$

where C_0 and C_f are the initial and final concentrations of the dye, respectively.

Thus, the experimental data obtained in this study indicate that active oxygen-containing species can be formed under conditions of the photocatalytic oxidation of the dye Chrome Yellow on TiO_2 in the presence of oxygen. These species participate in the degradation of dye molecules to intensify the process.

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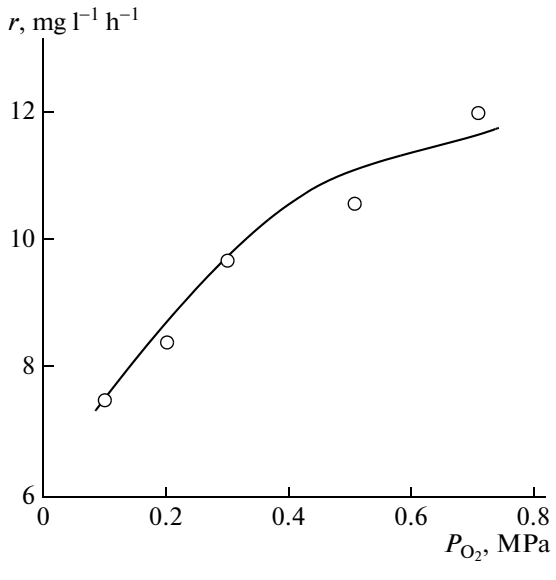

Fig. 5. Dependence of the rate of photocatalytic oxidation of Chrome Yellow on oxygen pressure under the action of UV radiation. C_0 = 20 mg/l; TiO_2 content, 0.5 g/l; and irradiation time, 3 h.

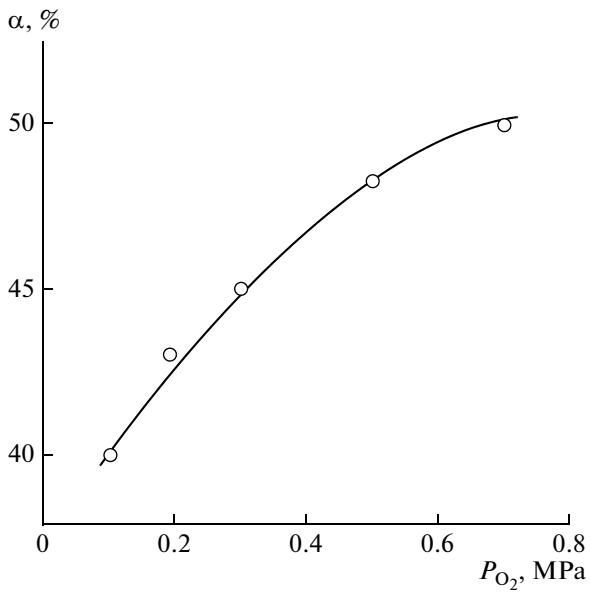

Fig. 6. Dependence of the degree of decoloration of a solution of the dye Chrome Yellow on oxygen pressure under the action of UV radiation. C_0 = 20 mg/l; TiO_2 content, 0.5 g/l; and irradiation time, 3 h.

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