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**PHOTOCATALYTIC TREATMENT
OF C.I. REACTIVE RED 2**

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Polychromatic photo degradation of C.I. Reactive Red 2 in aqueous solutions was studied in the presence of TiO₂. The influence of several factors, such as pH value, irradiation time, amount of dye and TiO₂ was observed in the process. The dye degradation was monitored by visible absorption spectroscopy and Chemical Oxygen Demand (COD) determinations. It was found, that the mineralization of the dye strongly depends on pH value and the rate was higher at alkali conditions (pH 12 – 13). The initial quantum yields of the irradiation process were determined for the pH 12.

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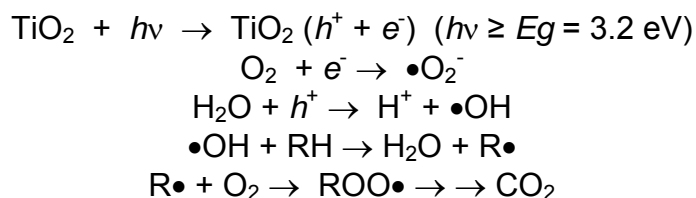
Introduction

Environmental pollution due to organic molecules creates the problem that is aggravated by the fact that biodegradation of these compounds is slow [1].

Recent developments in the domain of chemical water treatment led to an improvement in oxidative degradation procedures for organic compounds either dissolved or dispersed in an aqueous solution by photo catalytic methods. They are generally referred to as advanced oxidation processes (AOP) [2].

The AOP processes involve the oxidation of organic pollutants by the combination of ultraviolet light, oxidants (H₂O₂, O₃, etc) and/ or a catalyst (such as TiO₂) and in most cases imply the generation of hydroxyl radicals and their subsequent reactions with pollutant molecules. This will remove the organic impurities by converting them into harmless inorganic products (CO₂, H₂O, etc). It is thus a destructive purification process in contrast with adsorption processes where potentially harmful impurities are transferred from the liquid to the solid phase thereby becoming a solid waste disposal problem [3,4].

For the photo catalytic oxidation (TiO₂/UV) the semiconductor absorbs UV light and HO• radicals are generated mainly from the adsorbed H₂O and hydroxide ions. The mechanism of the TiO₂/UV degradation has been described by Bockelmann and Shugui using the band - gap model [5]. It is well established that by irradiation of an aqueous TiO₂ suspension with light energy greater than the band gap energy of the semiconductor conduction band, electrons and valence band holes are generated [6].



The ability of applying TiO₂/UV light to mineralize organic pollutants has been tested for a variety of compounds [2-4,7], including dyes [8,9].

Previously this process was applied, in the authors' research group, to azo reactive dyes, such as those derived from *meta* and *para*-aminobenzoic acid and 2-naphthol or *N,N*-dimethylaniline, and not only decolourization but also the partial degradation detected by COD decrease was measured [10].

Recently a number of research groups have dealt with the heterogenous photocatalytic decomposition of organic materials in the presence of UV or visible light with very encouraging results [11-13]. Among various semiconducting materials (oxides, sulphides, etc.) most attention has been given to TiO₂ (anatase) because of its relatively high photocatalytic activity, resistance to photo corrosion, biological immunity and low cost. On other hand, a few papers in this area determine the true quantum yield of the photo catalytic treatment [14-16] together with kinetic model of the process [17-19]. On the top of it, in the industrial applications some special optical effects (such as the dispersion of the light by particles) should be taken in the consideration [20], and, of course, the application of polychromatic irradiation [21-22].

Reactive dyes still have a medium rate of fixation in the fibres and contribute significantly to the colour in textile wastewater. One from these dyes is C.I. Reactive Red 2 used for the dyeing of cellulose fibres. The semiconductor ZnO assisted photo degradation of Reactive Red 2 was measured in aqueous solution of hydrogen peroxide [23].

The polychromatic photo catalytic degradation of the commercial dye Reactive Red 2 with TiO₂ as semiconductor has been investigated in this work and the effect of several factors such as irradiation time, pH value and concentration relations between the dye and TiO₂ are presented. Experiments were monitored by visible absorption spectroscopy and Chemical Oxygen Demand (COD) determinations. Initial quantum yields/efficiencies of the irradiation process were determined under fixed reaction conditions.

Materials and methods

Reagents

The dye C.I. Reactive Red 2 (C.I. constitution number 18200) was the commercial product of ICI corporation (United Kingdom).

Photo catalytic experiments were done with two samples of catalyst. Semiconductore TiO₂ P-25 Degussa (anatase/rutile = 3.6/1, surface area 56 m² g⁻¹) and TiO₂ Riedel de Haen (technical grade, surface area 56 m² g⁻¹). Both samples of TiO₂ have the effective diameter of particles 1206 nm, half width 676 nm, polydispersity 0.314 (measured at Department of Chemical Engineering, Faculty of Chemical Technology, University of Pardubice).

Equipment

Photochemical destruction was carried out in a commercial reactor APQ 40 (Applied Photophysics) equipped with medium - pressure Hg lamp 400 W and immersion quartz tubes (Duran) with light transparency T₁ or T₂ (Fig. 1).

UV-visible spectra were determined on a Hitachi U-2000 UV spectrophotometer.

Effective diameter of particles was measured on ZetaPals Brookhaven Instruments Corp. equipped with a Zeta Potential Analyser.

Other instruments which were used: Hanna Instruments pH meter, Sigma 2-15/B Braun centrifuge, Hach Chemical Oxygen Demand (COD) reactor and Dr-2000 spectrophotometer and vessels with standard digestion solutions for low range (0 -150 ppm) measurements.

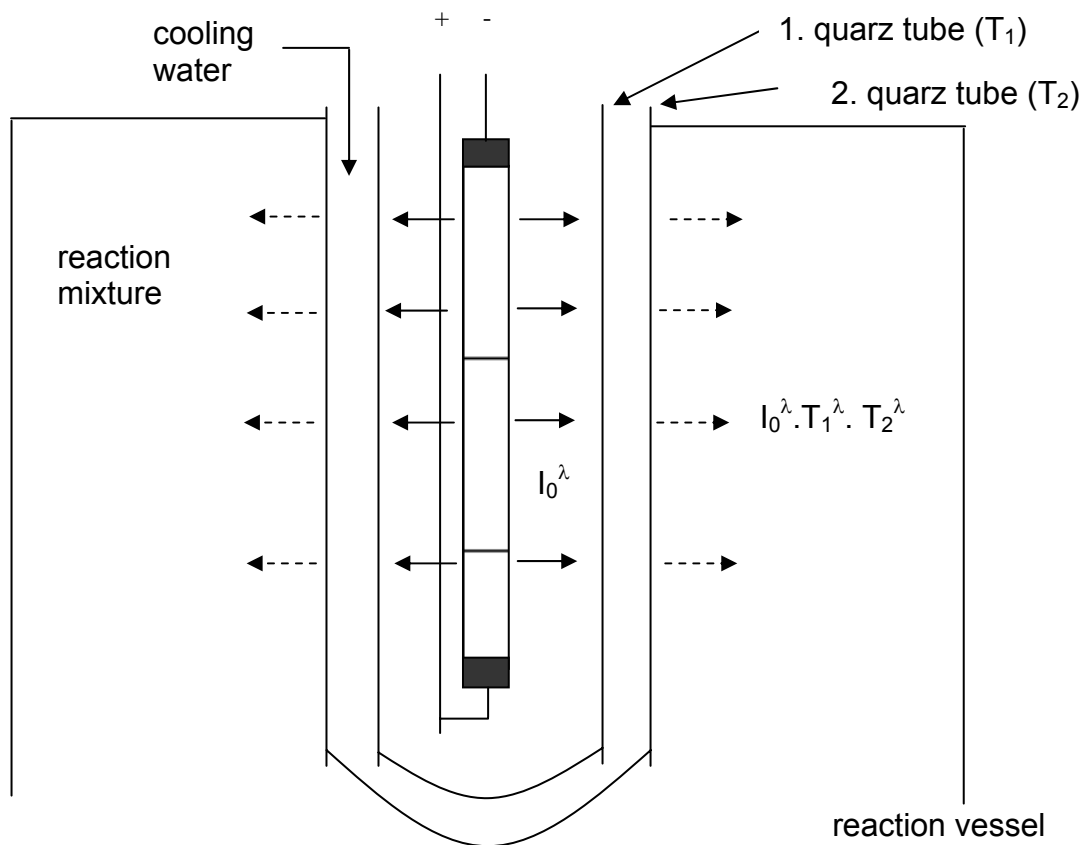


Fig. 1. Laboratory photochemical reactor APQ 40

Experimental Methods

The dye was dissolved in distilled water (1000 ml). After adjusting the pH to the desired value with 6M NaOH or 6M HCl, the absorbance was measured (A_0). The experiments were carried out at acid, neutral and basic pH values at the laboratory temperature of cooling water (20°C). TiO₂ powder was placed in the solution of the dye and the suspension was irradiated in the photochemical reactor with magnetic stirring. During the process, aliquots (2.5 ml) were taken at known intervals, the TiO₂ powder was separated by centrifugation and the absorbance (A) of the clear solution was measured.

The COD determinations were carried out with the initial solution and after various periods of irradiation. The samples were also centrifuged to remove the TiO₂. COD values were determined according to Hach procedures and obtained directly as $\text{mg dm}^{-3} \text{O}_2$.

Results and discussion

Kinetic Model of Photo Catalytic Process

The photo catalytic treatment of wastewater with a polychromatic source, where a dye is dissolved and a semiconductor is present, has very complicated mathematical description (kinetic model).

In this model we assume that:

- the dye (D) is completely dissolved in water and TiO₂ (T) is in the form of very fine dispersion;
- the irradiation is switched on after intensive stirring and after formation of adsorption equilibrium on the TiO₂ surface (Langmuir adsorption isotherm), where complex dye-TiO₂ (TD) comes into existence;
- there is no energy transport from excited dye (dissolved or adsorbed) to the semiconductor;
- the photochemical reaction does not occur if TiO₂ is not present in the batch.

The following Eqs (1) - (9) can express the photochemical destruction of a dye on the surface of TiO₂ in the water.

Adsorption process (before irradiation)

Process	Reaction rate	Eq.
$T + D \rightarrow TD$ (resp. $D_{adsorbed}$)	$k_1[T][D]$	(1)
$TD \rightarrow T + D$	$k_{-1}[TD]$	(2)

Photochemical ineffective light absorption

$D + h\nu \rightarrow D^*$	I_{abs}^D	(3)
$D^* \rightarrow D + \Delta$	$k_D[D^*]$	(4)
TD (resp. $D_{adsorbed}$) $+ h\nu \rightarrow TD^*$	I_{abs}^{TD}	(5)
$TD^* \rightarrow TD + \Delta$	$k_{TD}[TD^*]$	(6)

Photochemical process

$T + h\nu \rightarrow T^*$	I_{abs}^T	(7)
$T^* \rightarrow T + \Delta$	$k_T[T^*]$	(8)
$T^* + D \rightarrow Prod$	$k_R[T^*][D]$	(9)

I_{abs}^X is the molar photonic flux of monochromatic light (wavelength λ) absorbed by the compound X (mole of photons.s⁻¹.dm⁻³);

[X] is the actual concentration of compound X in the reaction time t (mol.dm⁻³);

Prod is a primary product of photochemical reaction.

The reaction rate (r) of dye destruction is described by the equation (10)

$$r = -\frac{d[D]}{dt} = \frac{d[\text{Prod}]}{dt} = \frac{k_R K_1 c_0^T [D]}{k_T + k_T K_1 [D] + k_R K_1 c_0^T [D]} * I_{\text{abs}}^T \quad (10)$$

where $K_1 = k_1/k_{-1}$, $c_0^T = [T] + [TD]$, $c_0^D = [D] + [TD]$,

and

$$[TD] = \frac{K_1 c_0^T [D]}{1 + K_1 [D]}$$

The reaction rate at the beginning of irradiation ($r(0)$) is then described by Eq. (11).

$$r(0) = \frac{k_R K_1 c_0^T [D]_0}{k_T + k_T K_1 [D]_0 + k_R K_1 c_0^T [D]_0} * I_{\text{abs}}^T(0) \quad (11)$$

Complex TD (with molar absorption coefficient ε_{TD}), semiconductor TiO_2 (ε_T) and the dissolved dye D (ε_D) absorb the monochromatic light in the reaction mixture (Eq. (12)), where L is the optical length.

$$A_{\text{total}}(0) = (\varepsilon_{TD} \cdot [TD]_0 + \varepsilon_D \cdot [D]_0 + \varepsilon_T \cdot [T]_0) \cdot L \quad (12)$$

The total absorbed light is given by equation (13), where I_0 is the molar photonic flux of incident light ($\text{mole of photons} \cdot \text{s}^{-1} \cdot \text{dm}^{-2}$), S is the area of illumination (dm^2), V is the reaction volume (dm^3).

$$I_{\text{abs}}^{\text{total}}(0) = \frac{S}{V} I_0 \left(1 - 10^{-A_{\text{total}}(0)}\right) \quad (13)$$

Note: Usually we can assume, that all the light is absorbed in the reaction mixture ($A_{\text{total}}(0) > 2$) at the beginning of illumination, so that Eq. (13) can be simplified to Eq. (14). The relation (14) is frequently used for the chemical actinometry.

$$I_{\text{abs}}^{\text{total}}(0) = \frac{S}{V} I_0 \quad (14)$$

The monochromatic light absorbed by titanium dioxide is given by Eq. (15). Since this absorbed light causes the primary photo chemical reaction, the differential quantum yield (φ_0) of this photo reaction can be determined (Eq. (16)).

$$I_{\text{abs}}^{\text{T}}(0) = \frac{S}{V} I_0 \frac{\varepsilon_{\text{T}} [\text{T}]_0}{\varepsilon_{\text{D}} [\text{D}]_0 + \varepsilon_{\text{T}} [\text{T}]_0 + \varepsilon_{\text{TD}} [\text{TD}]_0} \left(1 - 10^{-A_{\text{total}}(0)}\right) \quad (15)$$

$$r(0) = \frac{k_{\text{R}} K_1 c_0^{\text{T}} [\text{D}]_0}{k_{\text{T}} + k_{\text{T}} K_1 [\text{D}]_0 + k_{\text{R}} K_1 c_0^{\text{T}} [\text{D}]_0} * \frac{\varepsilon_{\text{T}} [\text{T}]_0}{\varepsilon_{\text{D}} [\text{D}]_0 + \varepsilon_{\text{T}} [\text{T}]_0 + \varepsilon_{\text{TD}} [\text{TD}]_0} * \frac{S}{V} I_0 \left(1 - 10^{-A_{\text{total}}(0)}\right)$$

$$r(0) = \varphi_0 \frac{S}{V} I_0 \left(1 - 10^{-A_{\text{total}}(0)}\right) \quad (16)$$

Theoretical relation between $r(0)$ and $[\text{D}]_0$ can be predicted, where $r(0) = 0$ if $[\text{D}]_0 = 0$ and $r(0) = 0$ if $[\text{D}]_0 \rightarrow \infty$. The function (16) has maximum ($r_{\text{max}} = [\text{D}]_0^{\text{opt}}$), which can be computed from Eq. (17)

$$\frac{dr(0)}{d[\text{D}]_0} = 0 \Rightarrow [\text{D}]_0^{\text{opt}} = \sqrt{\frac{k_{\text{T}} d}{b c}} \quad (17)$$

where $b = k_{\text{T}} K_1 + k_{\text{R}} K_1 c_0^{\text{T}}$, $c = \varepsilon_{\text{D}} - \varepsilon_{\text{TD}}$, $d = \varepsilon_{\text{T}} [\text{T}]_0 + \varepsilon_{\text{TD}} c_0^{\text{D}}$.

Equation (16) is valid for every monochromatic light λ and for the polychromatic light can be integrated (Eq. (18)), where we define the initial integral yield (Φ_0) and also the total initial reaction rate of dye destruction (R_0). The source of light we suppose to be a medium-pressure mercury lamp with "line" emission spectrum.

$$\sum_{\lambda} r_0^{\lambda} = R_0 = \sum_{\lambda} \varphi_0^{\lambda} I_0^{\lambda} = \Phi_0 \sum_{\lambda} I_0^{\lambda} = \text{constant} \quad (18)$$

The function (11) (r_0) and the maximum location (r_0^{max} , $[\text{D}]_0^{\text{opt}}$) depend upon the wavelength and the intensity of monochromatic light. The integral reaction rate for the polychromatic source R_0 is the summation of r_0^{λ} ($R_0 = \sum r_0^{\lambda}$). The functional maximum (R_0^{max}) for some concentration of dissolved dye $[\text{D}]_0^{\text{opt}}$ can

be predicted, if we know all experimental (s, V, I_0^λ), physical ($\epsilon_{D,T,TD}$) and chemical constants ($K_1, k_{d,r}$).

From the kinetic model we can see, that predicted velocity of a dye oxidation strongly depends on the affinity of the dye to the semiconductor surface.

Secondly, the concentration proportion between the dye and the semiconductor should be carefully adjusted to obtain the maximum velocity of the photo destruction.

These conclusions are generally valid for photochemical systems of this type.

Determination of Molar Photonic Flux of Incident Light

Polychromatic source for the presented photochemical study was medium - pressure mercury lamp TQ 150 (Hanau, BRD), where the producer declares radiation fluxes (mole of photons per hour) of emission lines I_0^λ (Table I). Since two quartz tubes (transparency T_1^λ, T_2^λ) were placed between lamp and reaction solution and the used lamp was not new (from the stand point of the processing age), the incident radiation flux was determined by potassium ferrioxalate actinometry (Eq. (19), Tables I and II) [24-26]

$$\left(\frac{\Delta c}{\Delta t}\right)_{total} = K \sum_{\lambda} I_0^\lambda T_1^\lambda T_2^\lambda \phi^\lambda \quad (19)$$

$\Delta c = c(\text{Fe}^{2+}) - c_0(\text{Fe}^{2+})$, where $c(\text{Fe}^{2+})$ is concentration of Fe^{2+} in the irradiated solution in the time t , $c_0(\text{Fe}^{2+})$ is the initial concentration of Fe^{2+} before the irradiation;

ϕ^λ is quantum yield of Fe^{2+} at 22°C;

K is experimental constant (dm^{-3}) and its value depends on the service age of the lamp and on the geometrical relations in photoreactor.

The reactor was filled with the solution of potassium ferrioxalate and solution was irradiated, during the processing the samples were taken and concentrations of Fe^{2+} were determined (Fig. 2).

The value of $(\Delta c/\Delta t)_{total}$ in our reactor was found to be 1.4224×10^{-5} mole. $\text{dm}^{-3} \cdot \text{s}^{-1}$ (linear regression from seven experiments with correlation coefficient $r=0.994$), thus experimental constant $K = 0.62046 \text{ dm}^{-3}$ was obtained and experimental line radiations were calculated (Table II).

Irradiation time (s)	Concentration of Fe ²⁺ (mol.dm ⁻³)
60	2.20E-04
120	7.65E-04
180	1.55E-03
240	2.69E-03
360	4.24E-03
420	4.65E-03
480	6.20E-03

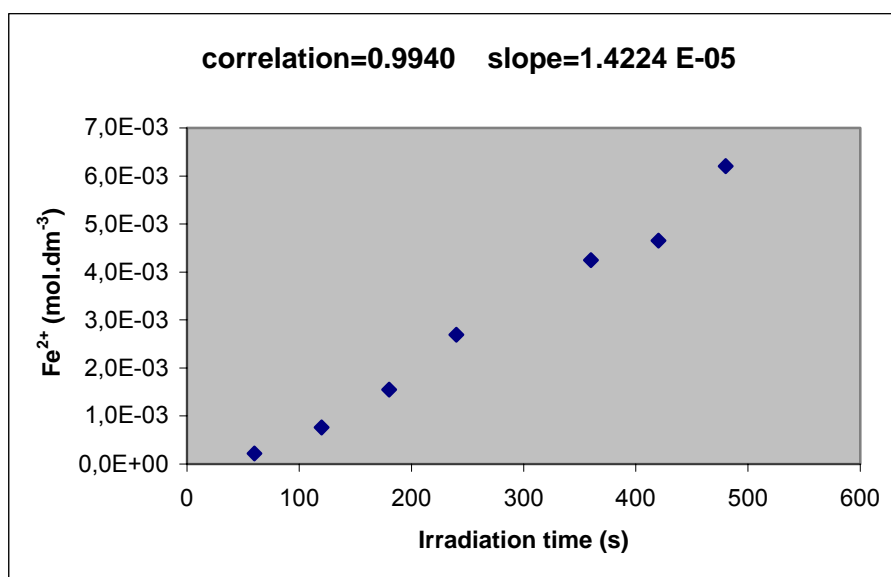


Fig. 2. Ferrioxalate actinometry (mercury lamp TQ 150)

Table I. Input data for the calculation of radiation fluxes

Emission line λ (nm)	Declared radiation flux of lamp TQ 150 I_0^λ (mole of photons.hr ⁻¹)	Tube transparency T_1^λ	Tube transparency T_2^λ	Quantum yields of Fe ²⁺ ϕ^λ	mole.hr ⁻¹ $I_0^\lambda \cdot T_1^\lambda \cdot T_2^\lambda \cdot \phi^\lambda$
238/240	8.00E-03	2.56E-01	3.30E-01	1.25E+00	8.43E-04
248	5.00E-03	2.82E-02	3.21E-02	1.25E+00	5.67E-04
254	3.00E-02	3.30E-02	3.30E-02	1.25E+00	4.08E-03
265	1.10E-02	3.93E-02	3.39E-02	1.24E+00	1.82E-03
270	5.00E-03	4.07E-02	3.37E-02	1.24E+00	8.50E-04
275	2.00E-03	4.17E-02	3.38E-02	1.24E+00	3.50E-04
280	6.00E-03	4.24E-02	3.42E-02	1.24E+00	1.08E-03
289	4.00E-03	4.32E-02	3.60E-02	1.24E+00	7.71E-04
297	9.00E-03	4.35E-02	3.84E-02	1.24E+00	1.86E-03
302	1.70E-02	4.43E-02	4.10E-02	1.24E+00	3.83E-03
313	4.10E-02	4.50E-02	4.46E-02	1.24E+00	1.02E-02
334	5.00E-03	4.86E-02	5.04E-02	1.23E+00	1.51E-03
366	7.10E-02	5.13E-02	5.17E-02	1.15E+00	2.17E-02
390	1.00E-03	5.16E-02	5.25E-02	1.10E+00	2.98E-04
405/408	3.90E-02	5.25E-02	5.30E-02	1.14E+00	1.24E-02
436	5.50E-02	5.34E-02	5.36E-02	1.01E+00	1.59E-02
480/492	1.00E-03	5.50E-02	5.45E-02	9.40E-01	2.82E-04

546	8.40E-02	5.61E-02	5.55E-02	1.50E-01	3.92E-03
577/579	8.20E-02	5.70E-02	5.55E-02	1.30E-02	3.37E-04
Total					8.253E-2 mole.hr⁻¹ 2.2925E-5 mole.s⁻¹

Table II. Experimental line radiation fluxes at the surface of reaction mixture

Emission line (nm)	Incident radiation flux (mole of photons.hr⁻¹)
238/240	4.1853E-04
248	2.8122E-04
254	2.0270E-03
265	9.0928E-04
270	4.2551E-04
275	1.7490E-04
280	5.3983E-04
289	3.8598E-04
297	9.3277E-04
302	1.9158E-03
313	5.1056E-03
334	7.5989E-04
366	1.1684E-02
390	1.6808E-04
405/408	6.7331E-03
436	9.7675E-03
480/492	1.8598E-04
546	1.6227E-02
577/579	1.6095E-02
Total	7.4737E-02 mol.hr⁻¹ 2.0760 E-05 mol.s⁻¹

The described calibration procedure neglects the changes between proportions of line radiations during the procession of the lamp, thus can be used only for approximate determination of quantum yields of photochemical reactions, or otherwise a new lamp has to be used.

Photo Destruction of Reactive Red 2 –Quantum Yields

Reactive Red 2 is a mono azo dye with absorption maximum $\lambda_{\max} = 510$ nm, $\epsilon_{\max} = 6703 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in aqueous solution (Fig.3).

The dispersion of semiconductor TiO_2 has the absorption in the ultraviolet and visible area of spectra (Fig. 4), where the mass (resp. molar) absorption coefficients strongly depend on the size of the particles (Degussa, Riedel de Haen, both with absorption maximum 325 nm, $\epsilon_{\max} = 2513 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

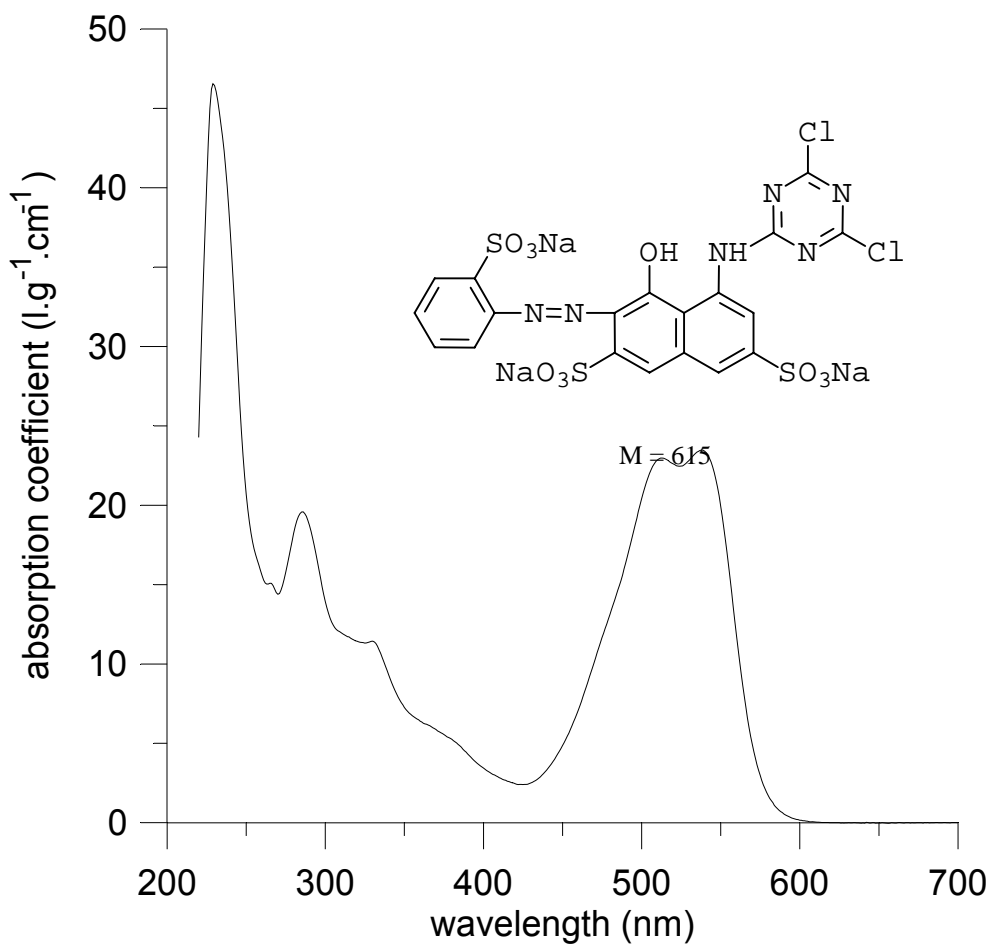


Fig. 3. Absorption spectrum of Reactive Red 2

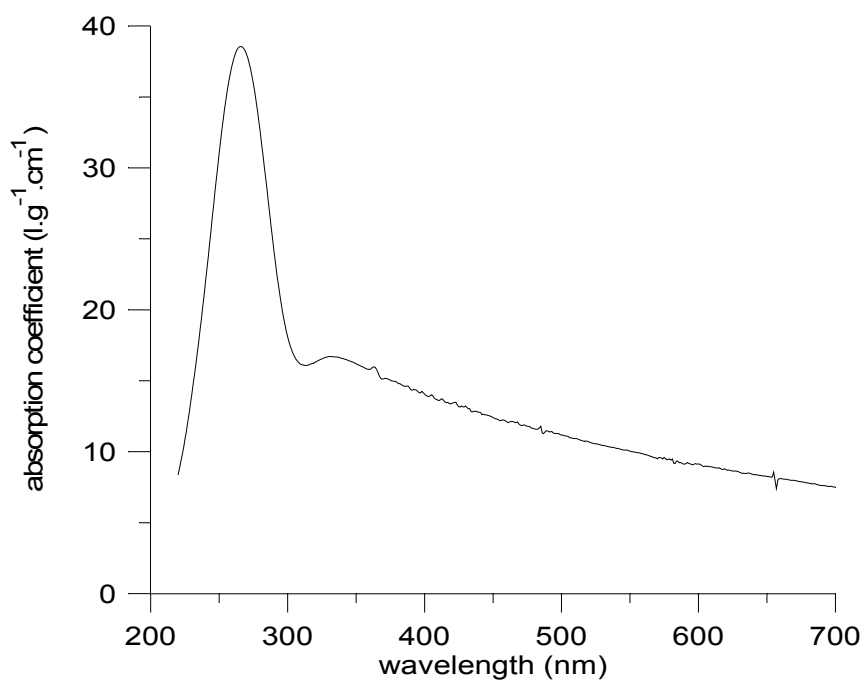


Fig 4. Absorption spectrum of TiO_2 (Degussa P25, $M = 79.88 \text{ g.mol}^{-1}$)

Firstly, photoreactions were carried out under fixed reaction conditions to confirm the suggested kinetic model and to determine the efficiency of photochemical process. The photochemical oxidation was performed in water containing various quantities of dispersed TiO_2 and dissolved Reactive Red 2. The pH 12 was adjusted by addition of alkali in all the experiments.

The following Figs 5 and 6 summarise the experimental results obtained.

Initial concentration of dye (mol.dm^{-3})	R_0 ($\text{mol.s}^{-1}.\text{dm}^{-3}$)	Origin of TiO_2 (78 mg.dm^{-3})
6.22E-05	2.4865E-08	Degussa
6.22E-05	2.2378E-08	Riedel
1.26E-04	3.4189E-08	Degussa
2.69E-04	2.3596E-08	Degussa
1.58E-04	2.5262E-08	Degussa

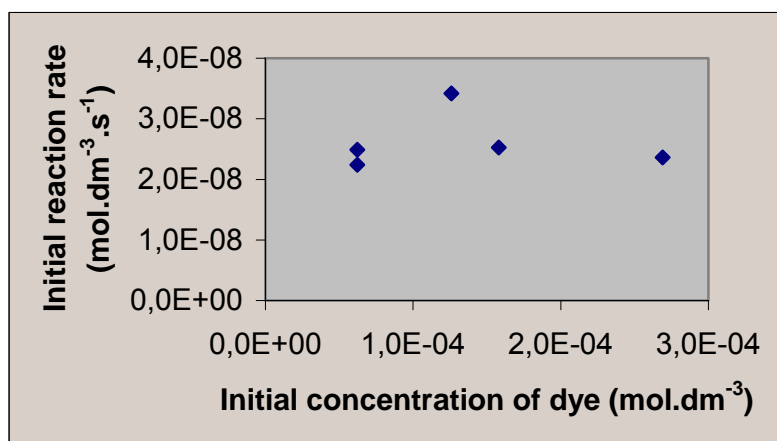


Fig. 5. Relation between initial reaction rate (R_0) and initial concentration of Reactive Red 2 (concentration of $\text{TiO}_2 = 78 \text{ mg.dm}^{-3}$, $9.76 \times 10^{-4} \text{ mol.dm}^{-3}$)

From these results we can see, firstly, that there is no difference between the individual samples of TiO_2 . Secondly, the relation between initial concentration of dye and initial reaction rate of photo destruction has a maximum (60 mg of dye / 78 mg of TiO_2 per litre).

When the concentration of TiO_2 is higher (396 mg per litre) in the reaction mixture, the concentration of the dye can be also higher (Fig. 6).

Initial concentration of dye (mol.dm ⁻³)	R ₀ (mol.s ⁻¹ .dm ⁻³)	Origin of TiO ₂ (396 mg.dm ⁻³)
4.8784E-05	3.3816E-08	Degussa
2.4959E-04	4.9505E-08	Degussa
2.6063E-04	5.0400E-08	Riedel
6.0120E-04	1.3782E-07	Degussa
1.1960E-03	1.1691E-07	Degussa

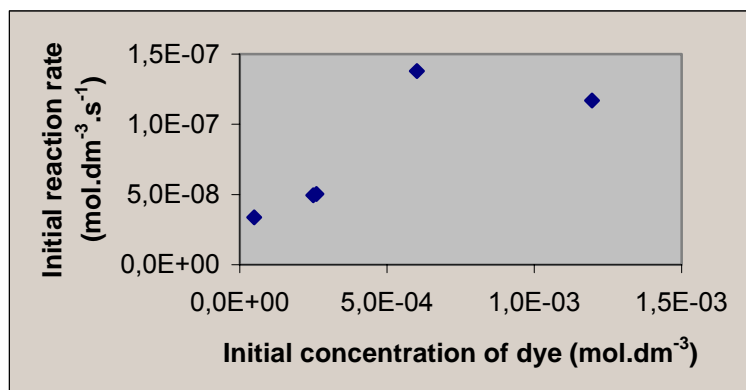


Fig. 6. Relation between initial reaction rate (R₀) and initial concentration of Reactive Red 2 (concentration of TiO₂ = 396 mg.dm⁻³, 4.96x10⁻³ mol.dm⁻³)

Since the total radiation flux of TQ150 (with quartz tubes) in UV and VIS area was 2.076x10⁻⁵ mole photons.s⁻¹ (Table II), the rough estimation of initial quantum yields (Φ₀) (Tables III and IV) was calculated.

Table III. Relation between initial concentration of dissolved dye and initial quantum yield (concentration of TiO₂ = 78 mg.dm⁻³, 9.76x10⁻⁴ mol.dm⁻³)

Initial concentration of dye (mol.dm ⁻³)	Φ ₀ (%)
6.22E-05	1.20E-01
1.26E-04	1.6469E-01
6.22E-05	1.0779E-01
2.69E-04	1.1366E-01
1.58E-04	1.2169E-01

Table IV. Relation between initial concentration of dissolved dye and initial quantum yield
(concentration of $\text{TiO}_2 = 396 \text{ mg.dm}^{-3}$, $4.96 \times 10^{-3} \text{ mol.dm}^{-3}$)

Initial concentration of dye (mol.dm^{-3})	Φ_0 (%)
4.8784E-05	1.6289E-01
2.4959E-04	2.3846E-01
2.6063E-04	2.4278E-01
6.0120E-04	6.6388E-01
1.1960E-03	5.6316E-01

From the experimental results we can see that the efficiency of photochemical destruction is very low on the surface of TiO_2 (total integral quantum yield was less than 1%). The reason for this low quantum yield is in a very low affinity of the dye to the semiconductor surface. We tried to determine the K value by classical UV/VIS spectroscopy in this work, but we were unsuccessful if K was less than 0.01. Thus, for the industrial purposes it is necessary to develop a semiconductor with a higher affinity to the water-soluble dye, which will be the first aim of our next research.

Effect of pH Value on the Photo Catalytic Treatment

The photo catalytic reaction induced by suspended semiconductor powders in aqueous solutions showed a remarkable pH dependence of the reaction rate. at various pH conditions. For practical purposes, we show the result of photo destruction of dye as decolouration ratio.

Table V. Relationship between decolouration ratio DR and pH value at room temperature
(30 mg of dye; 180 mg of TiO_2 ; irradiation time – 2 hours)
 $DR = 100 \cdot (A_0 - A) / A_0$

pH	1.4	3	5.6	10	11	12	13
DR (%)	49 *	90	84	72	93	95	99

* The dye was not completely dissolved in the batch

The results showed that the colour of Reactive Red 2 disappeared completely on the irradiation. For example, at pH 12, which is very close to the pH of dye house wastewater for Reactive Red 2, more than 80 % decolouration was observed after 30 minutes. At pH 3 irradiation for 110 minutes was needed to obtain a similar result (Fig. 7).

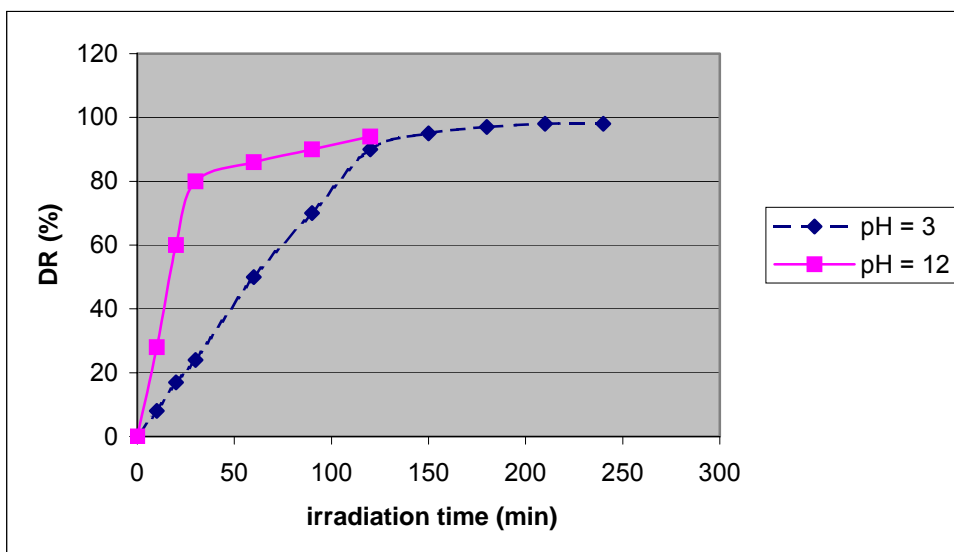


Figure 7. Effect of pH at photo destruction of dye (concentration of dye 30 mg.dm^{-3} , concentration of TiO_2 180 mg.dm^{-3})

From the time dependence (Fig. 6) we can see, that the reaction rate of photochemical reaction is constant for conversions of dye between 0 – 80%. This result is in the accordance with Eqs (14) and (16).

COD Analysis

Since the decolouration of dye solution was only the first step of mineralization, some irradiated samples were tested for COD in this work. The results of COD analysis in five experiments are shown in Table VI.

Table VI. COD results in various experiments

Dye (mg.dm^{-3})	TiO_2 (mg.dm^{-3})	pH	Irradiation time (h)	Reduction of colour (%)	COD decrease (%)
30	180	3	3.5	99	58
30	180	13	2	99	64
50	210	*	2.5	81	35
50	210	*	5	100	51
50	450	*	2.5	78	52

* distilled water pH ≈ 7

From the analysis we can see, firstly, that the decolouration (conversion of dye) corresponds to COD values. Secondly, the intermediates obtained by

photo catalytic degradation need more time to be transformed to further degradation products until complete mineralization is achieved.

Although the loss of colour for acid (pH 3) and basic (pH 13) solutions is equivalent, a higher COD decrease is observed at pH 13.

Conclusion

The efficiency of photo catalytic treatment on the surface of TiO₂ is very low in terms of quantum yields of the process. Nevertheless, the optimum treatment conditions for Reactive Red 2 using polychromatic light (Hg lamp TQ150) were: strong alkali conditions (pH ≥ 12), molar concentration ratio dye/TiO₂ in the interval from 1/7 to 1/8.

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