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MATHEMATICAL MODELLING OF PHOTOCATALYTIC ACTIVITY OF TIO₂ POWDERS OBTAINED BY CHEMICAL PRECIPITATION

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Abstract: The paper describes the mathematical modelling of the photocatalytic activity of TiO_2 powders obtained by chemical precipitation using titanium chloride III as precursor. The powders were characterized by X-ray diffraction and by UV-Vis spectroscopy. Using the data were modelled the structural and optical properties based on Scherrer and Tauc relations. The average of the crystallite size was calculated using Scherrer's relation. The energy band gap calculated with Tauc's relation was found to be 3.8 eV and 2.8 eV, before and after the heat treatment. The photocatalytic activity of TiO_2 has been determined by degradation of Methylene Blue in presence of TiO_2 suspension with the exposure to sunlight. Experimental data showed that the photodegradation process is described after a first order kinetic which is rationalized in terms of Langmuir-Hinshelwood model.

Key words: titanium dioxide, catalyst, Scherrer relation, Tauc low, Langmuir-Hinshelwood model.

1. INTRODUCTION

Azo dyes are organic substances, derivatives of azobenzene, resulted by diazotation of aromatic primary amines and coupling the results diazonium salts with various components. Azo dyes are used in pigmentation of textile. Wastewater from textile industry can not be treated by conventional chemical, physical and biological processes. Therefore, a series of unconventional methods were developed for treating wastewater from textile industry, based on advanced oxidation processes (AOP), process based specifically on photodegradation Photodegradation [1-3]. processes are an oxidation process which consists in mineralization of organic substances (azo dyes) following the irradiating of a semiconductor with photosensitive properties. The most investigated photocatalyst is titanium dioxide, because is non-toxic and has high chemically stability.

The photocatalytic activity of titanium dioxide by photodegradation of Methylene Blue (MB) was intensely studied [4-7]. Thus, Mathews et al [5] obtained TiO_2 films by immersing a glass substrate in a chemical bath,

using titanium butoxide as precursor. The film obtained was subjected to heat treatment at temperatures between 400 and 600 °C, and the photocatalytic activity was revealed by photodegradation of MB (100 mg/l) in a photoreactor. Irradiation was done with a UV lamp of 15 W. The author [5] observed that the film subjected to heat treatment at 600 °C has higher photocatalytic activity (efficiency of photodegradation process was 60% after 300 minutes of UV irradiation), comparative with the case of a film subjected to heat treatment at 400 °C. In the last case, the efficiency of photodegradation process was 40%. Mathews et al [5] proposed a first-order kinetic model for the degradation of Methylene Blue. With the kinetic model, author determined the efficiency of degradation and reaction constant rate, k, the value being 2.6×10^{-3} min⁻¹ for the sample photodegraded in presence of titanium dioxide film thermally treated at 600 °C [5].

Talebian et al [6] studied the photocatalytic activity of semiconductors oxides including TiO₂. The photocatalytic activity of catalysts was studied by degradation of Methylene Blue in the presence of UV radiation. The authors studied the effect of pH on the efficiency of the process and they proposed a photodegradation mechanism of reaction based on Lindemann -Hinshelwood kinetic [6].

In this paper we described the obtaining of titanium dioxide catalyst by hydrolysis of titanium chloride III and the degradation of Methylene Blue (MB) in the presence of titanium dioxide suspension under sunlight irradiation. The process of degradation (mineralization) of MB was monitored by UV-Vis spectroscopy. The kinetic model of photochemical reaction was also determined.

2. EXPERIMENTAL

2.1 The obtaining of titanium dioxide photocatalyst

Titanium dioxide with photocatalytic properties has been obtained by precipitation of titanium chloride III precursor (TiCl₃) in a solution containing ammonium hydroxide (NH₄OH), added in order to obtain an alkaline medium. The solution was prepared using 5 ml TiCl₃ 10%, containing 15% HCl (Merck) and 5 ml distilled water. The pH was adjusted to 9 with 10 ml NH₄OH (Microchim) and then 10 ml H₂O₂ 3% was added in order to achieved the rapid oxidation. Thus, a white precipitate of titanium hydroxide was obtained. The precipitate was filtered, washed vigorously with distilled water for several times and then was subjected to heat treatment at 500 °C for 1h.

2.2 Characterization of TiO₂ powder

Titanium dioxide powder was characterised by X-ray diffraction using a Shimadzu XRD-6000 diffractometer operating with CuK α radiation at angles of reflection between $10\div60^{0}$ (2 Θ). Using Scherrer's equation, the average of crystallite size has been estimated [8,9] The mass percentage of titanium dioxide sample which contained both anatase and rutile crystalline phases was also calculated [10,11].

The optical properties of TiO_2 powder were determined using a LAMBDA 35 UV-Vis spectrophotometer. Based on the graphs which showed the variation of the optical properties depending on wavelength, the energy band gap was calculated, which is the main characteristic of photocatalyst, since determines the efficiency of used radiation.

2.3 Degradation of Methylene Blue in the presence of TiO₂ photocatalyst

Photocatalytic activity of TiO₂ was studied by photodegradation of Methylene Blue dye, under sunlight irradiation. The experiment took place by exposing the samples to sunlight and for the blank experiments the samples were kept in darkness. The samples were prepared by mixing of 100 ml suspension of titanium dioxide 0.1 g/l and 100 ml containing 10.6 mg/l MB, in comparison with etalon/blank samples which contain the same concentration of MB, but without catalyst. Before the experiment, all samples were left in the dark, for 60 minutes.

For determination of the variation of Methylene Blue concentration in photodegradation process, a spectrometric quantitative method of Methylene Blue was developed. A series of MB solutions with know concentrations were prepared and a calibration curve was drawn. Calibration curve is the linear portion of the absorbance graph depending of concentration of solutions. The obtained results were presented in Figure 1.



Fig. 1. The spectrometric quantitative calibration curve of Methylene Blue

The MB concentration versus irradiation time was determined using a UV-Vis spectrometer based on the calibration curve, working at 664.2 nm because at this wavelength the MB has the maximum absorption. Based on the obtained data, the kinetic model of photodegradation process was described.

3. RESULTS AND DISCUSSION

3.1 Structural properties of TiO₂ powder

X-ray diffraction was used to determine the crystalline phases of TiO_2 obtained after heat treatment. The XRD pattern of TiO_2 sample subjected to heat treatment at 500 $^{\circ}C$ for 1 hour is presented in Figure 2. On XRD pattern was observed that the titanium dioxide sample contains both anatase (63.3%) and rutile (36.6%) crystalline phases. Table 1 showed the mass percentages of crystalline phases and the average of crystallite size calculated with Scherrer's relation [8,9]:

$$d = \frac{k \cdot \lambda}{B \cdot \cos \theta} \tag{1}$$

where: k - particle shape factor; k = 0.9; λ wavelength of CuK α radiation, λ = 1.54056 [Å]; B - the full width half maximum of the peak (FWHM); θ – Bragg's diffraction angle.



Fig. 2. XRD pattern of TiO_2 sample after heat treatment at 500 ⁰C for 1h (\bullet - anatase, \bullet - rutile)

The average of crystallites size was calculated with full width half maximum (FWHM) of the peak, using the last three maximum diffraction peaks, which correspond to (211), (200) and (111) crystallographic planes. The determinations were made at small angles 2Θ in order to reduce the errors of this calculation. The mass percentage of crystalline phases of the sample was calculated using the formulas [10,11]:

$$f_r = \frac{1.26 \cdot I_r}{I_a + 1.26 \cdot I_r} \cdot 100$$
 (2)

$$f_{a} = \left(1 + 1.26 \frac{I_{r}}{I_{a}}\right)^{-1} \cdot 100$$
 (3)

where: f_r - mass fraction of rutile [%], f_a - mass fraction of anatase [%], I_r - intensity of rutile diffraction peak on (110) crystalline plane, I_a - intensity of anatase diffraction peak on (101) crystalline plane.

 Table 1

 Average crystallite size and mass fractions of TiO₂

 powder after heat treatment

Sample	Crystalline phases	Average crystallite size [nm]	Mass fractions of crystalline phases [%]				
TiO ₂	Anatase	9*	63.3				
powder	Rutile	33**	36.68				

Note: * was calculated with (200) and (211) crystalline planes ** was calculated with (111) crystalline plane

3.2 Optical properties of TiO₂

Using a Lambda 35 UV-Vis spectrometer was determined the absorption spectra of synthesised titanium dioxide. Based on the spectra, the energy band gap of the semiconductor has been calculated. In order to be photosensitive to sunlight, the catalyst must have the values of the energy band gap between $1.4 \div 3$ eV. Energy band gap of bulk anatase TiO₂ is 3.2 eV, while the energy band gap of rutile is 3.1 eV.

Energy band gap was calculated based on absorption spectra [12], when was plotted the absorbance versus wavelength and was extrapolated the linear portion of the curve, with absorbance equal to zero. The wavelength was read from the graph and the energy band gap was calculated with Equation (4). The obtained values are presented in Table 2.

$$E_{g} = \frac{h \cdot c}{\lambda} \cong \frac{1240}{\lambda} \tag{4}$$

where: h – Planck's constant, h = $4.135 \cdot 10^{-15}$ [eV·s], c - speed of light, c = $3 \cdot 10^8$ [m/s], λ - wavelength of TiO₂ [nm].

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From Figure 3 was observed that the absorption peak of TiO_2 sample moves from 350 nm corresponding to as-prepared sample to 375 nm for the sample thermal treated.

Another method for calculation of the energy band gap was based on Tauc's law, using the absorption coefficient α [13]:

$$(\alpha h \nu)^{1/n} = A(h \nu - E_g)$$
⁽⁵⁾

where: α - the absorption coefficient, (hv) - photon energy, A – a constant which does not depend on photon energy, E_g - band gap energy [eV], n – a constant, which depends on the type of transition. For indirect allowed transition n = $\frac{1}{2}$ and for direct allowed transition n = 2.



Fig. 3. UV-Vis spectra of TiO_2 sample (BHT - before heat treatment, AHT - after heat treatment at 500 ^{0}C)

The absorption coefficient α was calculated using the Equation (6) [5]:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \tag{6}$$

where: α – absorption coefficient, d – the path length, d = 1 [cm], T – transmittance.

Appling this method, was plotted $(\alpha hv)^{1/n}$ vs. photon energy (hv) and the energy band gap was read from the graph by extrapolating of the linear portion of the curve with $\alpha = 0$. Figure 4 presents the graph for the variation of $(\alpha hv)^2$ vs. (hv) of TiO₂ samples before (BHT) and after heat treatment (AHT). The band gap values are presented in Table 2.

It was observed that the band gap energy for the sample before heat treatment was higher than those obtained after heat treatment. Energy band gap decrease from 3.3 eV (determined using Equation (4)) and 3.8 eV (determined by Tauc's low) to 2.25 eV and 2.8 eV respectively.

 Table 2

 The values of the energy band gap, Eg, determined using the absorbance and Tauc's low

using the absorbance and rade slow							
Sample	E _g determined based on absorption spectra [eV]		E_{g} determined with Tauc's low				
			[eV]				
	BHT	AHT	BHT	AHT			
TiO ₂ powder	3.3	2.25	3.8	2.8			

Note: BHT – before heat treatment; AHT – after heat treatment

Because the difference between this tow methods was quite high (0.5 eV) we will take



Fig. 4. The plots of $(\alpha h\nu)^2$ vs. $(h\nu)$ of TiO₂ sample, BHT - before heat treatment and AHT - after heat treatment

into consideration the values obtained using Tauc's law, because is a method recognized in the scientific world. For a quick estimation of the energy band gap one can apply the method based on absorption spectra.

The decrease of energy band gap following the heat treatment was attributed to the reduction of quantum size effect. In literature was reported that heat treatments lead to the increasing of crystallites size and the energy band gap of semiconductors decreased [14].

3.3 Degradation of Methylene Blue in presence of TiO₂ suspensions

The stages of photocatalytic heterogeneous processes, generally accepted [4,15,16] were exemplified using titanium dioxide as a photocatalyst:

1. Generation of electrons with different charge, under the photon radiation (hv) [4,15]:

$$2\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(e) + \text{TiO}_2(h^+)$$
(7)

2. Recombination of electron/hole pair [4]:

$$\text{TiO}_2(e) + \text{TiO}_2(h^+) \rightarrow 2\text{TiO}_2(\text{heat, light})$$
 (8)

3. Surface reactions: The holes have powerful reducing properties, and directly oxidize the compounds, or react with electron donors (Equation (9)), as - for example - water or hydroxide ions, to form hydroxyl radicals. Hydroxyl radicals can be formed on the surface of TiO₂ by the reaction of valence-band holes with water molecules or hydroxide ions adsorbed on the surface of the catalyst [16].

$$TiO_2 (h^+) + Red_1 \rightarrow Ox_1^+ + TiO_2$$
 (9)

$$TiO_2 (h^+) + H_2O \rightarrow OH \bullet + H^+ + TiO_2 \qquad (10)$$

$$\operatorname{TiO}_{2}(h^{+}) + \operatorname{HO}^{-} \rightarrow \operatorname{OH}_{\bullet} + \operatorname{TiO}_{2}$$
 (11)

Photogenerated electrons react with the oxygen to form super-oxide radicals ($\cdot O_2$), Equation (12), fulfilling the role of oxidizing agents in the reaction with neutral molecules, radicals or ions formed on the catalyst surface.

$$TiO_2(e) + O_2 \rightarrow \bullet O_2 + TiO_2$$
(12)

$$\bullet O_2^- + H^+ \to HO_2 \bullet \tag{13}$$

$$2HO_2 \bullet \to O_2 + H_2O_2 \tag{14}$$

$$\operatorname{TiO}_2(e^{-}) + \operatorname{Ox}_2 \rightarrow \operatorname{Red}_2^{-} + \operatorname{TiO}_2$$
 (15)

Conduction-band electrons react with oxidizing species according to Equation (15).

4. Degradation [4,15,16]:

Radicals and ions, formed on the semiconductor surface, can participate in the following processes:

a. reacts with adsorbed compounds on semiconductor surface;

b. in solution can diffuse on semiconductor surface, participating in chemical reactions;

c. can suffer a recombination trough electron transfer reactions; this process is responsible for the decrease of the photodegradation process and must be limited.

The suspension containing MB and TiO_2 catalyst was exposed to solar radiation to determine the effectiveness of photocatalytic activity of the obtained titanium dioxide. The conditions of synthesis of the samples subjected to degradation process were presented in Table 3.

MB concentration was plotted versus irradiation time (Figure 5), in the presence and in absence of TiO₂ catalyst. The exposure to solar radiation was made after keeping the samples in the dark for 60 minutes. The fitting was made after a third order polynomial equation with form $f(x) = ax^3 + bx^2 + cx + d$, and the correlation coefficients R² had the values of 0.9757 (photodegradation in the presence of TiO₂) and 0.9848, respectively (photodegradation without TiO₂).

Table 3

Synthesis conditions of the samples subjected to photodegradation process

photodegradation process				
Samples	Synthesis conditions of the samples	Exposure		
A ₁	- 100 ml TiO ₂ suspension (0.01 g TiO ₂) + 100 ml MB solution (0.00106 g MB)	- solar radiation		
A ₁ '	- 100 ml TiO ₂ suspension (0.01 g) + 100 ml MB solution (0.00106 g)	- darkness		
A_2	- 100 ml distilled water + 100 ml MB solution (0.00106 g)	- solar radiation		
A ₂ '	- 100 ml distilled water + 100 ml MB solution (0.00106 g)	- darkness		

It can be observed that in the presence of TiO_2 catalyst, MB dye was photodegraded after 130 minutes, while the sample without TiO_2 catalyst, MB dye was photodegraded more slowly (approx. 500 min), occurring the photolysis process.



Fig. 5. Photodegradation of Methylene Blue (MB) in the presence of TiO_2 catalyst (\blacksquare) and in absence of TiO_2 catalyst (\blacktriangle), under the solar radiation.

In order to evaluate the photocatalytic activity of obtained TiO_2 , another sample was kept in the dark, under the same conditions as in the experiments involving the exposure to solar radiation. In Figure 6 was presented the changes of MB concentration, in the presence and absence of the catalyst, for the sample kept on the dark (Figure 7).

In Figures 6 and 7 was observed a slow decrease of MB concentration, appearing at samples kept in the dark, in the presence or in the absence of the catalyst. The decrease of MB concentration was from 0.0053 mg/ml to 0.0049 mg/ml MB for the sample with TiO₂ catalyst and from 0.0053 mg/ml to 0.005 mg/ml MB for the sample without TiO₂ catalyst. The decrease of MB concentration has been caused by the adsorption of MB on TiO₂ catalyst surface and/or on the bottle surface.



At high concentrations of dye, reagent molecules adsorbed on catalyst surfaces can occupy all the active positions on the surface, leading to a zero-order kinetic model. At high concentrations of dye, the catalyst has no longer the ability to form the free radicals needed for photodegradation process, because all active centres were covered with dye. At low concentrations of dye, the rate of degradation is proportional to the amount of active centres on the surface of catalyst, so that the kinetics of Langmuir - Hinshelwood is reduced to a pseudo first-order kinetic model.





Fig. 6. Variation of MB concentration in the presence of TiO₂ catalyst for the solution kept on the dark



Fig. 7. Variation of MB concentration in the absence of TiO_2 catalyst, for the solution kept on the dark

act consists in the transformation of one molecule of MB into reaction products [17-20].

$$MB \xrightarrow{k} Reaction products$$
(16)

First order reactions are those reactions whose rate is proportional to the concentration of reagent at the first power [17-20].

$$\mathbf{v} = \mathbf{k}\mathbf{c}_{\mathrm{MB}} \tag{17}$$

By integration of Equation (17) as a function of time was obtained the concentration of reagent [17-20]

$$v = -kc_{MB}^{0} \left(1 - e^{-kt} \right)$$
 (18)

where: c_{MB}^{0} is MB concentration at initial time, $c_{MB} = c_{MB}^{0}(1-e^{-kt})$. MB concentration at a specific time t decreases over time, after equation (18).

The linear form of the Equation (19) was obtained from the logarithm of Equation (18) [17-20].

$$-\ln (c_{\rm MB}/c_{\rm MB}^{0}) = kt$$
 (19)

From obtained slope of plotting semilogarithmic $-\ln(c_{MB}/c_{MB}^{0})$ versus time was determined the value of the rate constant k. Rate constant does not depend on concentration.

The half time was obtained from Equation (20) assuming that $x = c_{MB}^{0}/2$ [17-20].

$$t^{1/2} = 1 - e^{-k \cdot t}, e^{-k \cdot t} = t^{1/2}, t^{1/2} = 0.693/k$$
 (20)

In order to determine the rate constant, k and half time $t^{1/2}$, $-\ln(c/c_0)$ was plotted versus irradiation time for the samples of MB in the presence and in the absence of TiO₂ catalyst, exposed to solar radiation (Figure 8) and for the samples of MB kept in the dark in the presence and absence of TiO₂ catalyst (Figure 9). The obtained values for the rate constant k and for the half time t $\frac{1}{2}$ were listed in Table 4.

In Figure 8 was observed that the fitting was done by a linear function on the form f(x) = ax + b and the correlation coefficient for the sample with TiO₂ catalyst with exposure on solar radiation was 0.9999.

From kinetic model results that for sample with TiO_2 catalyst exposed to solar radiation, the reaction rate constant k and half time t $\frac{1}{2}$ was five times higher than for the sample without TiO_2 catalyst exposed also to solar radiation.

Table 4 The values of the rate constant, k, and half time, t¹/₂, for all samples subjected to photodegradation process

Sample	$TiO_2 + MB$ (hv)	MB (hv)	TiO ₂ + MB (darkness)	MB (darkness)
k [min ⁻¹]	0.0338	0.0068	0.001	0.0004
t½ [min]	20.5	102	693	1732

The results of this experiment clearly show the photocatalytic activity of obtained TiO_2 by hydrolysis of titanium chloride III. The obtained titanium dioxide was photosensitive at solar radiation. It was assumed that the photocatalytic activity of titanium dioxide in the visible range was caused by nitrogen, from NH₃ used in preparing the photocatalyst. This theory will be discussed in our next paper.

4. CONCLUSION

dioxide powder Titanium with photocatalytic properties was obtained by precipitation of titanium chloride III in alkaline medium. The sample was treated at 500 °C for 1h. X-ray diffraction showed that after heat treatment was obtained anatase (63.3%) and rutile (36.6%) crystalline phases. Based on Scherrer's relation and Tauc's low were determined the average of crystallite size and the energy band gap respectively. The energy band gap decrease from 3.8 eV to 2.8 eV, after heat treatment, value which corresponds to solar radiation. Because the energy band gap of titanium dioxide after heat treatment was 2.8 eV, the catalyst was photosensitive at solar radiation, so the Methylene Blue dye was photodegraded by exposing to sunlight. The photodegradation efficiency was 96.9% for the sample containing TiO₂ catalyst exposed at solar radiation, after 3h 30min of irradiating time.



Fig. 8. Variation of - $\ln (c_{MB}/c_{MB,0})$ in the presence of TiO₂ catalyst (\blacksquare) and without TiO₂ catalyst (\blacktriangle) after exposure to sunlight for 210 min



Fig. 9. Variation of $-\ln(c/c_0)$ (MB) in the presence of TiO₂ catalyst (\blacksquare) and without TiO₂ catalyst (\blacktriangle) for samples kept in the dark for 210 minutes

The kinetics of the degradation process was also described. In experimental study:

- has resulted a pseudo first-order kinetic model rationalized in terms of Langmuir-Hinshelwood model;

- it was determined the constant rate of reaction k, for the samples following the exposure at solar radiation in comparison with a sample kept under darkness;

- the half time was calculated for all samples.

photodegradation Linearization of the process was not possible for the entire domain, which shows that the mechanism of photodegradation is complex, and is particular for each experiment. It is necessary to analyse all factors that influence the kinetics of photodegradation of dyes to design а photocatalytic system.

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Modelarea matematică a activității fotocatalitice ale pulberilor de TiO2 obținute prin precipitare chimică

Rezumat: Lucrarea descrie modelarea matematică a activității fotocatalitice ale pulberilor de TiO_2 obținute prin precipitare utilizând ca precursor clorura de titan III. Pulberile obținute au fost caracterizate prin difracție de raze X și spectroscopie UV-Viz. Utilizând datele obținute s-au modelat proprietățile structurale și optice cu ajutorul relațiilor lui Sherrer și Tauc. Dimensiunea medie a cristalitelor a fost calculată utilizând relația lui Scherrer. Energia benzii interzise calculată cu relația lui Tauc a fost de 3.8 eV și 2.8 eV înainte și după tratament termic. Activitatea fotocatalitică a TiO_2 a fost determinată prin degradarea Albastrului de Metilen în prezența suspensiei de TiO_2 cu expunere la radiația solară. Datele experimentale au arătat faptul că procesul de fotodegradare este descris de o cinetică de ordin I raționalizată de modelul Langmuir-Hinshelwood.

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