



The Comparison of the Photocatalytic Performance Shown by TiO₂ and TiO₂/WO₃ Composites— A Parametric and Kinetic Study

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Kinetic and mechanistic related approaches for mostly titania were intensively studied in the literature. However, combined modelling and kinetic studies are few. Therefore, the present work focuses on modelling the dependence of the degradation kinetics of two model compounds (salicylic acid—SA and methyl orange—MO) on Evonik Aeroxide P25, hydrothermally prepared hierarchical TiO_2 and P25/WO₃ nanostars, obtained also by hydrothermal crystallization. The obtained individual semiconductors and the composites were characterized using XRD, DRS, SEM, while the photocatalytic degradation of the model pollutants were carried out varying the catalyst load, the initial pollutant concentration and incident light intensity. It was found that the degradation kinetics were independent from the hierarchical nature of the material, while significant dependencies of the degradation efficiency was found from the previously mentioned investigation parameters. All these parametric interdependences were successfully studied and a kinetic model was proposed for both bare TiO₂ and TiO₂/WO₃ composite systems.

Keywords: Kinetic Modelling, Composite Materials, Salicylic Acid, Methyl Orange, Degradation.

1. INTRODUCTION

The applicability of TiO_2 and in rare cases TiO_2 based composite photocatalysts achieved the everyday usage level, being applied in mobile air and water cleaner devices, self-cleaning paints, etc.¹ This enlarged applicability spectrum requires a careful study of the applicability circumstances and post-usage impact. One of the main concerns can be the degradation products of different pollutants on the photocatalysts.

Important research was dedicated to uncovering the mechanism of the charge generation,² the charge transfer³ and the degradation kinetics on TiO_2 based photocatalysts.^{4,5} Mostly, the degradation by-product is not directly CO_2 , water and other simple compounds,

but more complex organic molecules.⁶ In several cases the obtained degradation intermediate (issue valid in case of many other advanced oxidation processes) could be more toxic than the original molecule,⁷ therefore its elimination/minimization from the degradation mechanism is mandatory. Furthermore, not just the starting compound, but also other facts such as the application conditions should be considered. In classic photocatalytic experiments, these are the light intensity, geometry of the reactor, the concentration of the photocatalysts as well.⁸

Light intensity, is a more trivial parameter considered in the case of photocatalytic reactions. No differences were observed concerning the observations found in the literature, namely, that as the incident light intensity increases, so does the degradation rate of the pollutant, which of course at a specific light intensity value it can reach a threshold, as recombination becomes a dominant factor.^{9–11}

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The catalyst loading is a more debated parameter of the photocatalytic reactions, as for different model pollutants, different optimal catalyst loading values were optimal. That is why in some cases even extremely high 4 g \cdot L⁻¹ (case of reactive orange 4¹²), and extremely low 0.3 g \cdot L⁻¹ (case of reactive red¹³) values were found as optimal ones. The concentration of the pollutant is likewise a trivial, but nevertheless very important, as photocatalytic reactions are considered as showing mostly pseudo-first order kinetics.¹⁴

The most investigated material in the currently mentioned terms is TiO_2^{15-18} in suspension or in some cases fixed on a substrate (e.g., as films).¹⁹ In some studies ZnO,²⁰ while the newer generations of photocatalysts or composite photocatalyst related kinetic studies are rare, therefore represents a black spot in the knowledge of photocatalysis.

When the targeted molecule is considered it was found that several model pollutants were investigated in the terms of their degradation kinetics, such as phenol,^{21,22} phenol derivates,^{15,23} and sometimes more complex molecules as well, such as bisphenol.²⁴ However, photocatalytic investigations are mostly carried out using specific dyes. There were attempts to elucidate the kinetics of their degradation,^{5,25} but all these studies considered titania as the applied photocatalyst. Furthermore, few of them give details about possible intermediate formation mechanism and kinetics.

As it can be seen above there are some blank knowledge regions of this research field, the most important one being the scarce research data available concerning composite type of photocatalysts. Therefore a two stage research was proposed in the current work, which considers TiO_2/WO_3 composite materials and salicylic acid (a compound well-known kinetically²⁶) or methyl orange as model pollutants (also a well-known compound in photocatalytic activity testing).

To do a detailed reaction mechanism related study, which is assumed to be feasible, a large amount of experimental data is needed. To minimize somewhat the amount of experimental work, without deteriorating the validity of the mechanism, different modelling approaches, which are based on kinetic and mechanistic investigations, can be applied.

2. EXPERIMENTAL SECTION

The materials applied in the experiments were used as received, without further purification commercially available TiO₂ (Evonik Aeroxide P25, 89% anatase, 11% rutile) as reference catalyst, titanium tetrachloride (TiCl₄ 99.9% Aldrich) as precursor, thiourea (H_2NCSNH_2 , 98%, Aldrich), sodium-dodecyl sulfate (SDS, $CH_3(CH_2)_{11}$)OSO₃ 99%, Aldrich), hydrochloric acid HCl 37% (Sigma-Aldrich, Germany), for the degradation tests and for the synthesis we used deionized water. The organic compound used for photodegradation was salicylic acid,

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99.5% purity (Sinteza, Oradea). Ammonium metatungstate hydrate (AMT) ((NH₄)₆H₂W₁₂O₄₀ · xH₂O, Sigma Aldrich, 99.99%) and hydrochloric acid (HCl, Merck, 37%, 12 M), were used for the synthesis of WO₃ micro-crystallites. In the case of tungsten trioxide, the used reference catalyst was commercial tungsten(VI) oxide (WO₃, Sigma Aldrich, 99.9%). For the determination of the photocatalytic activity aqueous solution of methyl orange (C₁₄H₁₄N₃NaO₃S, Sigma Aldrich) was used.

2.1. Synthesis of TiO₂

The synthesis method of this material was already described in our previous publication,²⁷ however a shorter overview was provided here. In the first instance, SDS (5.3 g) was dissolved in distilled water and mixed with 7 g of thiourea. Simultaneously the titanium dioxide precursor TiCl₄ was added drop-wise in 11 mL HCl_{cc} (37%). After complete solubilization of the capping agents, the mixture containing the precursor was added dropwise to the aqueous solution under vigorous stirring. During the addition of the precursor a light gelation occurred. The molar ratio applied during the synthesis was: $TiCl_4$:SDS:thiourea:HCl:H₂O = 1:2:10:11:300. The solution was immediately transferred into a sealed, Tefloncoated autoclave, and was further heated at 180 °C for 24 h. The obtained white precipitate was washed several times with distilled water until no H₂S was noticed and the organic impurities were completely removed. The product was dried in an oven at 70 °C for 12 h under airflow. The sample will be denoted as TiO₂-HT.

2.2. Synthesis of WO₃ Nanostars

The synthesis method of this material was already described in our previous publication,²⁸ however a shorter overview was provided here. 0.768 g AMT and 0.525 mL 37% HCl was dissolved in 12.5 mL of distilled water. The solution was stirred for 15 min., then hydrothermally treated at 180 °C for 4 h and a green colloidal suspension was obtained. The obtained products were collected by centrifugation at 1600 rpm for 15 min., and were washed with distilled water. After centrifugation, the products were dried for 6 h at 70 °C, and then they were annealed at 500 °C for 30 min. and a yellowish powder was obtained. The sample will be identified later as WO₃-AMT; the AMT abbreviation comes from the molecular formula of ammonium metatungstate hydrate.

2.3. Preparation of the WO₃/TiO₂ Nanocomposites

The chosen WO₃ and TiO₂ was used for the preparation of the nanocomposites. In each case 24 wt.% WO₃ and 76 wt.% TiO₂ (Evonik Aeroxide P25) was the ratio of the components.^{28, 29} The nanocomposites were prepared *via* mechanical mixing in an agate mortar for 3×5 min. and the samples were denoted as follows: WO₃ name + TiO₂ name. Evonik Aeroxide TiO₂ will be referred as P25 later, while the commercial WO_3 , WO_3 -COM. The commercial tungsten trioxide was used as reference due to its property that it wasn't synthesized via hydrothermal treatment and it does not contain shape tailored WO_3 nanoand microcrystals.

2.4. Methods and Instrumentation

Crystalline phases and particle size were determined by X-ray diffractometry (XRD, Shimadzu 6000) using Cu-K α radiation ($\lambda = 1.5406$ Å) equipped with a graphite monochromator. The crystallites average size was calculated using the Scherrer equation.³⁰

A JASCO-V650 spectrophotometer with an integration sphere (ILV-724) was used to measure the DRS spectra of the samples (250–800 nm). To obtain the band-gap energy values, the well-known Kubelka-Munk approach was applied.³¹

The microstructure of the samples was analyzed by the field-emission scanning electron microscopy (SEM), (FEI Quanta 3D FEG) operating at 20 kV. Samples for SEM measurements were attached to a carbon adhesive pad which was fixed to an aluminum stub.

The photocatalytic tests were performed under UV irradiation in a photoreactor (continuous air flow, continuous stirring. 6×6 W UV black-light lamps, $\lambda_{max} = 365$ nm, thermostated at 25 °C). The suspension containing the photocatalyst and the pollutant (initial concentrations applied of salicylic acid (SA) and methyl orange (MO) were C_{0.SA} C_{0.MO}, the concentration of the applied photocatalysts were $C_{cat} = 0.5$, 1.0, 1.5 and 2.0 g · L⁻¹, total volume of the suspension $V_{susp} = 170$ mL) was continuously purged with air, assuring a constant dissolved oxygen concentration during the whole experiment. Prior to the degradation experiments the used suspension was kept in the dark for 10 min. to establish the adsorption/desorption equilibrium. The kinetic modelling of the reaction system was carried using Matlab R2016a.

The concentration of SA was followed by UV-Vis spectrophotometry with an Analytic Jena Specord 250+ spectrometer, where the samples' spectra were registered in the 250–350 nm interval, while in the case of MO this range was from 250–800 nm. Furthermore, SA was followed by High Pressure Liquid Chromatography (HPLC), (Agilent 1100 series), using an ODS column (length 25 cm, an ODS column is filled with a packing of octadecyldimethylsilyl groups). An acceptable detection of the SA and its intermediates was achieved within 10 minutes using a water: methanol eluent (90:10) pumped at a rate of 0.7 cm³ · min⁻¹, using three different detection wavelengths 210, 250 and 298 nm.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Characterization

As already mentioned, the present paper will focus on several reaction kinetic issues directly related to TiO_2

and WO₃. Therefore, the characterization of the used materials was mandatory.

The XRD patterns of the used photocatalysts are shown in Figure 1. The reference photocatalyst was Evonik Aeroxide P25 (TiO₂-P25, $D_{\text{anatase}} = 25 \text{ nm}$, $D_{\text{rutile}} = 50 \text{ nm}$), which consisted from 89 wt.% of anatase and 11 wt.% of rutile. TiO₂ (TiO₂-HT, $D_{\text{anatase}} = 14.2 \text{ nm}$ obtained in Section 2.1 contained just anatase. Both WO₃s used (WO₃-COM, $D_{\text{WO}_3-\text{COM}} = 25 \text{ nm}$ and WO₃-AMT, $D_{\text{WO}_3-\text{AMT}} = 60 \text{ nm}$) were crystalline and contained only the monoclinic crystal phase of WO₃.

The optical properties of the semiconductors were evaluated using DRS (Fig. 2). As it was expected, both TiO₂s band-gap energy values were in the UV range (3.12 eV TiO₂-P25 and 3.21 eV or TiO₂-HT). TiO₂-P25 showed a small visible light absorption shoulder, due to its small rutile content. Monoclinic WO₃ showed an enhanced visible light absorption in case of both samples (2.61 eV WO₃-COM and 2.25 eV or WO₃-AMT). However, a major difference was observable in their DRS spectrum. The WO₂-COM sample showed a usual absorption edge in the visible light as generally expected in many cases when WO3 was measured. However, when WO3-AMT was analyzed, an inflection point was detected at 475 nm pointing out possible hierarchical structures, which may cause this interesting behavior. The composites' DRS spectra was also registered, which showed the individual peculiarities of the bare oxides' spectra, while the measured band-gap values were between the two oxides' band



Figure 1. The XRD patterns of the used nanomaterials.



Figure 2. DRS spectra of the used semiconductors.

gap energy (3.02 eV-TiO₂-P25/WO₃-AMT, 2.94 eV-TiO₂-P25/WO₃-COM).

The morphology of the obtained photocatalysts was both hierarchical as it is shown in Figure 3. The secondary crystals were in the micrometric range for WO₃-AMT (4 μ m, homogenous size distribution) and few hundreds of nanometers for TiO₂-HT (750–900 nm). The individual primary crystallite size values were calculated as it was shown in the beginning of this section. This structural organization may lead to enhanced charge separation mechanism as already discussed in our previous publication²⁷ and may result an interesting kinetic behavior during the degradation of different model pollutants.

3.2. The Photocatalytic Activity of the Obtained Nanomaterials

3.2.1. The Photocatalytic Performance of TiO₂-HT and TiO₂-P25

The photoactivity of these materials was tested on a model pollutant, which degrades by direct hole oxidation and 'OH attack.³² Also, it is known that SA forms surface complexes with TiO₂, which sometimes can confer a yellow color to the catalyst, while permitting the well-known photosensitization mechanism.³³ Therefore, it was interesting to investigate whether secondary shape controlling can intervene in the degradation mechanism of this model pollutant, because it is known that this simple morphological feature may have a serious impact on the general efficiency of titania photocatalysts.²⁷ The first approach was to use different initial concentrations of SA, considering the existence of the well-known chemisorption of this compound.

As it can be seen in Figure 4 different removal efficiency values were obtained, as expected. Additionally, the degradation curves' shape was quite different suggesting different degradation mechanisms or different rate determining steps. Similar results can be found in the literature, such as the case 4-nitrophenol.¹⁵ In that work it was found that, the degradation reaction mostly occurs on the surface, however other works, such the one published by Ollis and coworkers,³⁴ show that a smaller fraction of the photocatalytic reactions occurs in the liquid phase, despite the strong adsorption of the model compound. This observation may be important later. The variation of the photocatalyst concentration showed the expected results, namely, that there is an optimum value which was $\approx 1 \text{ g} \cdot \text{L}^{-1}$.



Figure 3. SEM micrographs of the obtained samples (TiO₂-HT and WO₃-AMT).

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Figure 4. Degradation curves of SA on TiO_2 -HT, when different degradation parameters were varied (the initial concentration of SA, the applied light intensity and suspension concentration).

Lower catalyst concentration may favor efficient illumination, but the amount of catalyst is not sufficient to achieve high degradation rates. Suspension concentration values higher than $1 \text{ g} \cdot \text{L}^{-1}$ are sufficient to achieve high degradation yield, but caused a serious inhibition factor in illumination efficiency.

As, the light intensity was varied, first it was expected that the shape of the degradation curves will be the same, while the slope of these curves will be in direct relationship with the applied light intensity. While the second hypothesis was partially confirmed (Fig. 4), the first one not, pointing out an interesting phenomenon. The shape of the degradation curves may change when the intermediate profiles change during the degradation process. Therefore, the following strategy was applied: the degradation curves obtained from the spectrophotometric measurements were fitted considering a kinetic model. If the proposed model does not fit the chosen degradation curves, then supplementary HPLC measurements should be carried out. Indeed, as expected the model was showed several errors when spectrophotometric data was the only data taken in consideration. Therefore, it was mandatory to consider hydroxylated intermediates as previously suggested.³⁴

That is why the 3 intermediates were considered (3,5dihydroxybenzoic acid, another dihydroxybenzoic acidnot identified and catechol) and the kinetic equations detailed subsequently were applied, in accordance with the Langmuir-Hinshelwood kinetics.

It is generally accepted that the Langmuir-Hinshelwood equation describes the kinetics of a photocatalytic oxidation system.^{35, 36} The reaction rate R_t of the pollutant S_t at any time t during the irradiation will be given by R_t

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(Eq. (1)). Also, stable intermediates are generated.

$$R_{t} = -\frac{dS}{dt} = \frac{K_{ads} \cdot S_{t} \cdot k}{1 + K_{ads} \cdot S_{t} + \sum_{j=1}^{n} (K_{(I)} \cdot I_{t})_{j}}$$
(1)

 I_j is the *j*th stable reaction intermediate generated during the degradation of pollutant to CO₂; *k*—reaction rate constant [mol·L⁻¹·min⁻¹]; R_t —initial reaction rate [mol·L⁻¹·min⁻¹].

For TiO₂-HT catalyst, the ratio of k_j/k_{-j} (formation/consumption reaction rate constant) was obtained from the experimental data, considering the ratio of the maximum intermediate concentration and the concentration of SA at that time. The consumption reaction rate constant k_{-j} was obtained from the experimental data. The formation reaction rate constant k_j did not provide relevant data graphically, while k_j was determined from the ratio of k_j/k_{-j} . Our predictive kinetic model (Eqs. (2–5)) based on the L-H kinetics for SA and its intermediates can be described with the equations showed below. Using these equations, it was possible to calculate the concentration of SA and I_j during the photocatalytic experiment.

$$\frac{dS}{dt} = \frac{-K_S \cdot S_t \cdot k}{1 + (K_s \cdot S_t + K_I \cdot ([I_1]_t + [I_2]_t + [I_3]_t))} \quad \bigcirc^{\mathsf{OH}}$$
(2)

$$\frac{dI_1}{dt} = \frac{K_I \cdot (k_1 \cdot S_t - k_{-1} \cdot [I_1]_t)_{2,115,51}}{1 + (K_s \cdot S_t + K_I \cdot ([I_1]_t + [I_2]_t \oplus [I_3]_t))_{11}} \underbrace{(\mathcal{O}(H)_{11} \otimes \mathcal{O}(H)_{11}}_{\text{Delivation}}$$

$$\frac{dI_2}{dt} = \frac{K_I \cdot (k_2 \cdot S_t - k_{-2} \cdot [I_2]_t)}{1 + (K_s \cdot S_t + K_I \cdot ([I_1]_t + [I_2]_t + [I_3]_t))}$$
(4)

$$\frac{dI_{3}}{dt} = \frac{K_{I} \cdot (k_{3} \cdot S_{t} - k_{-3} \cdot [I_{3}]_{t})}{1 + (K_{s} \cdot S_{t} + K_{I} \cdot ([I_{1}]_{t} + [I_{2}]_{t} + [I_{3}]_{t}))} \xrightarrow{HO}_{OH} (5)$$

where, K_s and K_I are adsorption constants, $k_{1,2,3}$ formation reaction rate constants and $k_{-1,-2,-3}$ consumption reaction rate constants. Two very important aspects should be emphasized here. First, if the spectrophotometric data are corrected using the HPLC measurements the degradation curve will take a new form, as shown in Figure 5.

Therefore, the degradation rate constant of SA was independent from the applied light intensity (when $\ln(C/C_0)$ vs. time was represented graphically), while the main reason for it was the different formation and consumption rate constant of the obtained degradation intermediates, as it is shown in Figure 6. This also means that these light intensity values are still sufficient to promote the degradation of SA (same degradation efficiency), but changes in the light intensity values. This could suggest a degradation pathway switching:

• When, the applied light intensity is high the chosen semiconductor generates higher amount of charge carrier pairs, which can produce a higher amount of 'OH radicals

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and degradation occurs in the liquid phase, not permitting a coverage of the surface by SA molecules.

• At lower light intensity values the generated 'OH radical amount is surely lower; therefore, the degradation must occur also by an alternate route, which could be direct oxidation by photogenerated holes.

• If the above situation occurs, then the surface must be covered with SA. This could be true, as the compounds generated by the hydroxyl radical route are accumulating in the liquid, pointing out the lack of "space" on the catalysts surface.

• This also means that in the case of pollutants with good adsorption an investigation concerning the light intensity may give hints about reaction kinetics and intermediates' generation.

The same observations were made when Evonik Aeroxide P25 was used, so it seems that the observed degradation kinetics for SA is not secondary morphological dependent. Even if Evonik Aeroxide P25 was more efficient, the kinetic trends and observations made were the same and will be not listed separately. Therefore, in the next step just P25 was used together with WO₃. The chosen pollutant will be this time MO, to eliminate surface sensitization and increased adsorption/chemisorption of SA and to demonstrate the general validity of the studied degradation parameters.

(3) by Inger WO₃ Based Composites and Giving Feedback to the Bare Photocatalysts' Shown Kinetics

WO₃ acts as a charge separator in the present case as these materials (WO₃-AMT and WO₃-COM) do not show any adsorption or photocatalytic activity towards MO.²⁸ Also, when the UV-Vis spectrum of MO was recorded, no absorption maximum shifts were observed, pointing out the fact that the degradation lead to products, which are most likely non-aromatic small organic molecules. Therefore, it was proposed to compare the behavior of TiO₂-P25, TiO₂-HT with the composite made from TiO₂-P25 and WO₃-AMT. Thus, all the obtained results will be presented considering the results from the previous section (Section 3.2.1). It should be noted that the MO degradation capacity of TiO₂-P25 and WO₃-COM was also investigated, but the results were not presented, as they showed the same trends during the parameter investigation.

In the case of MO, the first step was likewise to test the effect of the initial concentration of the dye (Fig. 7). The trend shown by the applied composite revealed the same behavior as in the case of SA, namely that with the increase of the MO concentration the achieved conversion decreased.

When the catalyst load was investigated an interesting phenomenon was observed, namely that at a smaller scale, changes in the suspension concentration did not have any significant effect in the degradation of SA (case of P25),



Figure 5. HPLC based degradation curves versus UV/Vis spectrophotometric based curves and the degradation intermediate evolution profiles, when the impact of the UV-A light intensity was evaluated.

that is why the investigations were carried out on a larger catalyst load interval when the composite's photocatalytic performance was carried out. It was found that at low catalyst load values a very low photocatalytic conversion was a suspension. achieved (Fig. 8). As TiO₂ can be bound quite efficiently by When the light intensity was the variable parameter to the surface of WO₃ as it was previously shown,²⁹ it cannot be excluded that larger agglomerations were formed diminishing thus the contact surface between solid and liquid entities.

As the catalyst load was raised, the previously mentioned effect disappeared, while further increase resulted a direct decay of the degradation efficiency that may be attributed to the WO₃ component, which normally



(Fig. 9), the linear dependence of the conversion with the light intensity was found only in the case of the composite material, due to the facts mentioned in the previous section of the paper. This means that the degradation of MO could occur just in the solution, because:

• Insignificant adsorption on the catalyst surface after the dark step of the photodegradation process.



Figure 6. Formation and degradation rate constants for the three different intermediates



Figure 7. Comparison of the effect of the initial concentration of the pollutant on TiO2-P25 and TiO2-P25/WO3-AMT composite photocatalysts' degradation efficiency.



Figure 8. Comparison of the effect of the catalyst load on TiO_2 -P25 and TiO₂-P25/WO₃-AMT composite photocatalysts' degradation efficiency.

• No shifts of the MO peak occurred during the degradation, which could mean direct oxidation to low molar weight carboxylic acids.

• Linear dependence of the degradation efficiency with the light intensity.

Considering the above mentioned facts, a kinetic model was further proposed.

From the general kinetic point of view the removal of a pollutant can be described with the following simple equations:

$$-\frac{[C]}{dt} = r \tag{6}$$

$$r = k \cdot [MO]^n \tag{7}$$

where r is the reaction rate, k is the apparent rate constant, C is the concentration of the pollutant an n is the order of the reaction. When approaching mathematical



Figure 9. Comparison of the effect of the light intensity on TiO₂-P25 and TiO₂-P25/WO₃-AMT composite photocatalysts' degradation efficiency.

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Table I. The k values obtained from the applied kinetic model where the catalyst load was modified.

Catalyst load	<i>k</i> ₁	2	k_2	2	<i>k</i> ₃	
$(g \cdot L^{-1})$	(\min^{-1})	R^2	(\min^{-1})	R^2	(\min^{-1})	R^2
0.5	0.0021	0.992	0.3863	0.993	0.0952	0.999
1	0.0096	0.992	0.8683	0.999	0.2353	0.999
1.5	0.0056	0.991	0.5961	0.959	0.1596	0.987
2	0.0041	0.969	0.4362	0.997	0.1374	0.994

modelling in heterogenous photocatalysis the Langmuir-Hinshelwood mechanism is the most used one, especially when adsorption-desorption equilibrium can be considered. According to Langmuir-Hinshelwood approach the reaction rate can be calculated from the equation below:

Hence r is the reaction rate, k_1 is the adsorption apparent rate constant, k_2 is the apparent rate constant of the pollutant degradation, C is the pollutant concentration.

In Tables I–III the R^2 values were attributed to the respective k values, which were calculated from plotting the concentration versus the time using linear fitting in each case. The slopes of the linear fits will yield the k values. In case of k_1 , $\ln C/C_0$ (0, 10, 20 min.); in case of k_2 the concentration (30, 40, 50, 60 min.); in the case of k_3 the $C^{0.75}$ (60, 480, 100, 120 min.) values were plotted versus time. From the above statements, which were

adjusted to our case, the following equation can be used:

$$-\frac{[\mathrm{MO}]}{dt} = \frac{\{k_1 \cdot k_2 \cdot k_3 \cdot [\mathrm{MO}]^n\} \cdot [\mathrm{MO}]}{(1+k_1) \cdot [\mathrm{MO}]} \tag{9}$$

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In the equation above k_1 is the adsorption apparent rate constant, k_2 is the apparent rate constant of the MO degradation, k_3 is the apparent rate constant of the degradation

Table II. The k values obtained from the applied kinetic model where the initial concentration was modified.

Initial concentration (µM)	$k_1 \ (\min^{-1})$	R^2	$k_2 \pmod{(\min^{-1})}$	R^2	k_3 (min ⁻¹)	R^2
62.5	0.0162	0.984	0.6897	0.997	0.1836	0.991
125	0.0096	0.992	0.8683	0.999	0.2353	0.999
187.5	0.0013	0.999	0.5570	0.977	0.1780	0.998
250	0.0015	0.997	0.7294	0.999	0.0913	0.990

Table III. The k values obtained from the applied kinetic model where the light intensity was modified.

Light intensity (W)	$k_1 \ (\min^{-1})$	R^2	$k_2 \ (\min^{-1})$	R^2	k_3 (min ⁻¹)	R^2
12	0.0011	0.986	0.1487	0.993	0.0426	0.994
18	0.0031	0.988	0.3138	0.991	0.0879	0.998
24	0.0050	0.996	0.5510	0.998	0.1506	0.996
36	0.0096	0.992	0.8683	0.999	0.2353	0.999



Figure 10. The comparison of the model and the experimental data.

of the MO intermediates and n is the order of the reaction, in our case, between 0 and 1. This equation is used when k_1 and k_2 have first order kinetics (the k values were summarized in Table I).

Considering the data collected we have concluded, that in our case k_1 and k_2 show a pseudo-first order kinetics followed by a fractional order k_3 . We have implemented this in our mathematical model, hence we obtained the equation below:

$$-\frac{[\text{MO}]}{dt} = \frac{\{(k_1/2.303) \cdot k_2 \cdot k_3 \cdot [\text{MO}]^n\} \cdot [\text{MO}]}{1 + (k_1/2.303) \cdot [\text{MO}]}$$
(10)

Where [MO] is the dye concentration, k_1 is the adsorption apparent rate constant, k_2 is the apparent rate constant of the MO degradation, 2.303 is a divisor to convert the natural logarithm to a base 10 log $[\log_{10}(x) = \ln(x)/2.303]$, k_3 is the apparent rate constant of the degradation of the MO intermediates and *n* is a fractional order, between in this case the attributed reaction order for the MO intermediates is 0.75. The equation above was used for modeling

the MO degradation with WO_3 -TiO₂ composite photocatalysts. The scripts for the simulations were written and validated in Matlab 2016a, and ordinary differential equation (ode45) was used to solve these equations and the chosen model fitted acceptably the experimental data (Fig. 10).

4. CONCLUSIONS

The present work reemphasized the fact that a degradation process can be influenced severely, by just changing some of the reaction parameters, including catalyst concentration, initial concentration of the pollutants and light intensity. Not in all the cases the expected dependencies were obtained. It was found that in the case of the catalyst concentration and initial pollutant concentration the usual observations were made, while in the case of the light intensity the formed intermediates intervene in the degradation product kinetics. In each of the cases a specialized model was elaborated and applied which fitted the experimental data accordingly. However, it should be noted that by introducing the WO₃ in the system resulted the same

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behavior but with different impact intensities of the chosen parameters. Furthermore, the hierarchical nature of the oxides' crystals did not show any impact on the observed kinetics.

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