Photocatalytic activity of synthesized nanosized TiO$_2$ towards the degradation of herbicide mecoprop

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Abstract

The kinetics and possible mechanism of the photocatalytic degradation of herbicide mecoprop, in UV illuminated aqueous colloids of synthesized nanosized TiO$_2$ were investigated. The rate of degradation was studied by ^{1}H NMR, UV spectrometry, as well as by potentiometric titrimetric determination of generated chloride. The catalyst dosage and effects of other kinetic factors on the photocatalytic degradation, such as initial substrate concentration, temperature and type of TiO$_2$ were investigated as well. The degradation rates were found to be strongly influenced by the above parameters. It was found that photocatalytic efficiency is lower and that a smaller number of observed organic intermediates (only 4-chloro-2-methylphenol and acetic acid) was detected than those observed in the presence of TiO$_2$ (Degussa P-25). Kinetics of the degradation were also monitored for direct photolysis, as well as for solar degradation in the presence and in the absence of TiO$_2$.
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1. Introduction

Among the different approaches to pesticide elimination from wastewaters, heterogeneous photocatalysis using semiconductor particles under band gap irradiation has been frequently investigated [1–4]. In recent years, the scientific community has shown a great concern for the possible adverse effects that the presence of these pesticides in water and food may have on human health and the equilibrium of the ecosystem, such as carcinogenesis, neurotoxicity, effects on reproduction, and cell development effects, particularly in the early stages of life. It is pertinent to mention here that biodegradation, which is the major mechanism used in wastewater treatment, is inefficient for complete detoxication. For that reason, photochemical oxidation processes have been applied for the treatment of wastewaters con-

taminated with organic materials such as hydrocarbons, haloaromatics, phenols, halogenated biphenyls, surfactants, textile dyes, pesticides, and so on, which have been successfully mineralized in TiO$_2$ slurries. In the last few years, the investigations have been focused on properties of nanosized semiconductors [5]. These ultrafine semiconductors with extremely small and well defined diameters, which influence their optical and electronical properties, enable a researcher to employ experimental conditions to ensure that, on the average, less than one electron–hole pair is formed per semiconductor cluster during each light pulse [6]. These particles have a potential application in the area of photoelectrochemistry, microelectronics, thin film coatings, photocatalysis, etc. [5].

In this study, herbicide mecoprop (*RS*-2-(4-chloro-*o*-tolyloxy)propionic acid, C$_{10}$H$_{11}$ClO$_3$) was chosen as a model compound of a photodegradable organic waste substance in water because of its worldwide use for the selective control of many annual and some perennial weeds. It is

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absorbed by leaves with translocation to roots. Soil metabolism studies indicate that mecoprop is persistent in the soil. Duration of residual activity in soil is about 2 months [7] and it may be translocated to the foliar portions of agriculture crop, where it is partially or totally metabolized. Because of its partial solubility in water (3.4×10^{-3} mol dm^{-3} at 25 °C) it can penetrate to deep soil strata and reach the groundwater. As reported in the literature, this is the most often found herbicide in drinking water [8]. The aim of this work was to study the efficiency of nanosized TiO$_2$ synthesized in our laboratory towards the photocatalytic degradation of mecoprop present in water. After characterization of the synthesized TiO$_2$ by X-ray diffraction and BET-surface area method, the present photocatalytic degradation study involved the application of potentiometric titrations, as well as ^{1}H NMR and UV spectrometry. The proposed degradation mechanism was compared to that for degradation in the presence of TiO$_2$ (Degussa P-25) [9]. Kinetics of photocatalytic degradation were compared to kinetics of direct photolysis, as well as to kinetics under solar irradiation in the presence and in the absence of TiO$_2$.

2. Experimental

2.1. Chemicals and solutions

The herbicide mecoprop (98% purity), was obtained from the Chemical Factory "Župa" Kruševac, Serbia and Montenegro. The commercial product was purified by conventional recrystallization method from water−ethanol (1:1) solution. All other chemicals were used without further purification. In all experiments, doubly-distilled water was used except for ^{1}H NMR measurements where D$_2$O (Merck, 99.8% purity) was applied as solvent. For the investigation on the effect of the initial substrate concentration, a stock solution (2.7 mmol dm^{-3}) of mecoprop was prepared, and further diluted to prepare the lower concentration solutions.

The nanosized TiO$_2$ (mean particle diameter 4 nm) was synthesized at the Institute of Nuclear Sciences, Vinča, Belgrade, Serbia and Montenegro by controlled hydrolysis of titanium(IV) chloride (Fluka, p.a.) [10]. The solution of TiCl$_4$, cooled to −20 °C, was added dropwise to water at 0 °C and kept at this temperature for several hours. The solution contained ~0.1 mol dm^{-3} TiO$_2$ at pH 1.7. Adjustment of pH was made by dialysis against water at 4 °C, until pH 3. This step is important in elimination of low-weight titanium hydroxide aggregates, which are present at pH 1.7. At pH 3, the concentration of low-weight aggregates is 5% of total concentration of Ti(IV) [10]. The final concentration of TiO$_2$ was determined spectrophotometrically, from concentration of the peroxide complex obtained after dissolving the nanoparticles in concentrated H$_2$SO$_4$. This solution was appropriately diluted to obtain a solution of lower TiO$_2$ content (2 mg cm^{-3}). For the investigation of intermediate

formation and degradation by ^{1}H NMR spectrometry, it was necessary to prepare a solution of TiO$_2$ in deuterium oxide. To that purpose, a more concentrated solution of TiO$_2$ nanoparticles was prepared in distilled water (0.278 mol dm^{-3}), which was further diluted with deuterium oxide to mass concentration of 2 mg cm^{-3}.

2.2. Photodegradation procedure

The photochemical cell (sample volume 20.0 cm^{3}) was made of Pyrex glass with a plain window (on which the light beam was focused), with a magnetic stirring bar, a water circulating jacket, and two openings: for O$_2$ stream and taking of ^{1}H NMR or UV sample (or for combined glass electrode). Colloids of TiO$_2$ containing mecoprop (2.7 mmol dm^{-3}) were sonicated for 10 min before illumination. The illumination process was carried out at 40 ± 1 °C. Colloids were illuminated with a 125 W mercury lamp (Philips, HPL-N) (emission bands in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm) using an appropriate concave mirror. These experiments were also carried out by using solar light instead of the lamp during autumn months. In order to investigate spontaneous decomposition of the substrate, one solution was exposed to daily sunlight at 23 ± 1 °C, while the other was left protected from the sunlight at the same temperature. Direct photolysis experiments were carried out under the same conditions, as well as photocatalytic degradation, but with no TiO$_2$ added.

2.3. Analytical procedure

The purity of purified mecoprop was controlled and confirmed by ^{1}H NMR spectrometry (Bruker AC-250).

The synthesized nanosized TiO$_2$ was characterized by BET method (Micromeritics Instrument Corporation ASP 2000.V1.03) and by X-ray diffraction (XRD, Philips PW 1710).

Concentration changes of chloride generated during the degradation were monitored by potentiometric titration, with the aid of a silver electrode coupled via a suitable salt bridge to a saturated calomel electrode (Radiometer) and connected to a pH-meter (Radiometer PHM 62). The standard solution of silver nitrate (0.05 mol dm^{-3}, standardized against a 0.005 mol dm^{-3} standard solution of NaCl) was added discontinuously by a Radiometer ABU12 automatic piston burette. After transferring of the entire illuminated sample (20 cm^{3}) to a 50 cm^{3} beaker, the solution was mildly heated to reduce its volume to 10 cm^{3}, and after the addition of 10 cm^{3} of acetone to the reaction vessel, the reaction mixture was titrated with the standard silver nitrate solution. The titration end-point was determined from the derivative titration curve.

For spectrophotometric determinations during the herbicide degradation, aliquots of 0.25 cm^{3} of the reaction mixture were taken at regular time intervals and diluted to

10.00 cm^3. The solutions containing TiO$_2$ were filtered to separate the TiO$_2$ particles and their spectra were recorded on a spectrophotometer (Specord UV–vis, Jena, Carl-Zeiss) in the wavelength range from 200 to 340 nm.

Samples for quantitative ^{1}H NMR measurements (0.5 cm^3) after filtration were evaporated to dryness. Complete kinetic analysis was performed on the basis of several repeated measurements. After that, the ^{1}H NMR spectral profiles of only the parent compound were monitored on a Bruker DRX-500 instrument dissolving the evaporated samples in 0.5 cm^3 of D$_2$O with addition of sodium salt of 3-trimethylsilyl-1-propane sulfonic acid (DSS) as internal standard. The percentage of degradation was calculated on the basis of comparing the integrated surface value of the herbicide and the standard signals present in spectra. Besides that, solutions of mecoprop were prepared in D$_2$O (2.7 mmol dm^{-3}) and in the course of photodegradation, 0.6 cm^3 samples were taken for qualitative and quantitative ^{1}H NMR analysis of intermediates (Bruker AC-250).

Changes in the pH during the direct photolytic degradation were monitored continuously by potentiometry using a combined glass electrode (Iskra) connected to a recorder (Goerz Electro, type Servogor SbRE 647,9) via a pH-meter (Iskra MA 5706), as well as by antimony electrode coupled to a saturated calomel electrode (Radiometer) via a potassium nitrate electrolytic bridge and connected to a pH-meter (Radiometer PHM 62).

3. Results and discussion

During the oxidation of organic compounds over TiO$_2$, the semiconductor particles are subjected to band gap excitation (light of wavelengths $\lambda < 400$ nm) which results in charge separation occurring in each of these particles. One can thus utilize these charge carriers for oxidation and reduction on the same particle. In aqueous solution, the holes at the TiO$_2$ surface are scavenged by surface hydroxyl groups and water molecules to generate $^\bullet$OH radicals which then oxidize the dissolved organics to CO$_2$, H$_2$O and corresponding inorganic ions. One of the disadvantages of such a system is the undesired electron–hole recombination within each particle, which is extremely efficient in the absence of a proper electron acceptor or donor representing the major energy-wasting step, thus, limiting the achievable quantum yield. This is usually overcome by scavenging electrons with a sacrificial electron acceptor such as dissolved oxygen so that the holes can participate in the oxidation of organics. Although a number of possible decomposition pathways can be envisioned, the formation and subsequent reactions of hydroxyl radicals, which are a very strong oxidizing agent (standard redox potential 2.8 V), are generally accepted as the predominant degradation pathways of organic substrates in oxygenated aqueous solutions.

A typical XRD spectrum of the nanosized TiO$_2$ particles is presented in Fig. 1. The XRD peaks corresponding to 101,
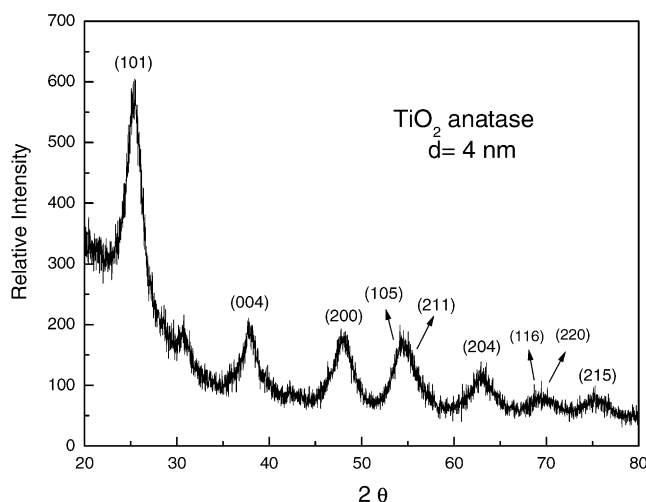

Fig. 1. Difractogram of synthesized nanosized TiO$_2$.

004, 200, 105, 211, 204, 116, 220, 215 planes indicate that TiO$_2$ is in an anatase crystal phase. The peaks are relatively broad due to the small crystalline dimensions. The Scherrer diffraction formula was used to estimate the crystalline size (d):

$$d = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the X-ray wavelength (0.1541 nm), β is the peak angular width and θ is diffraction angle of the peak. The crystalline size was found to be 4 nm.

The surface area of the synthesized TiO$_2$ determined by the BET method was found to be 300 m^2 g^{-1}, and is higher than the surface areas of TiO$_2$ (Millennium PC50, PC100, PC105, PC500) [11]. Its absorption spectrum [10] includes all emission bands of the used radiation source.

Results obtained by studying the photocatalytic decomposition of the various compounds with chlorine show that the complete degradation gives carbon dioxide, water, and hydrochloric acid (if no other heteroatoms are present in the parent compound except Cl). For this reason, we decided to follow the photooxidation of mecoprop by potentiometric titrations of chloride produced as a function of illumination time. The literature data [9,12] show that the photodecomposition of the aromatic ring with chlorine as substituent takes place simultaneously with the HCl evolution, thus the increase in the concentration of released chloride can be used to calculate the rate of mecoprop aromatic ring decomposition. For this reason, the influence of catalyst dosage, initial substrate concentration, as well as temperature on the photodecomposition efficiency were investigated in this way.

The photodegradation of 0.9 mmol dm^{-3} mecoprop in the oxygenated aqueous colloids was examined in the TiO$_2$ concentration range of 1–4 mg cm^{-3} with the aim to optimize the catalyst dosage during the irradiation process. The effect of increasing catalyst dosage on the photodegradation
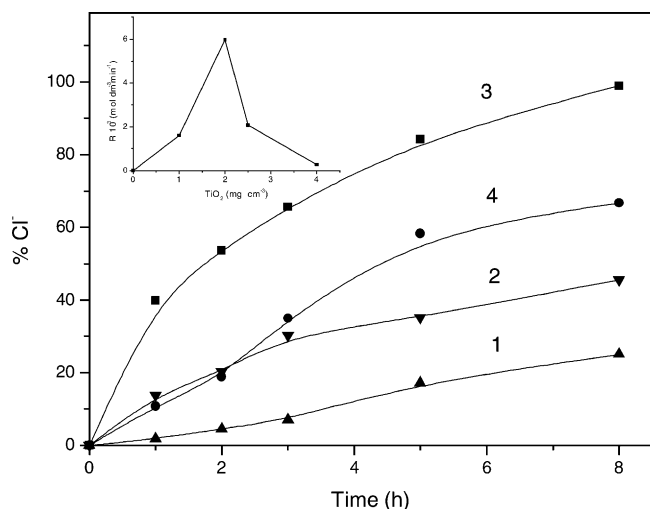
Fig. 2. Kinetics of chloride generation from mecoprop (0.9 mmol dm^{-3}) in the presence of different TiO$_2$ concentrations (mg cm^{-3}): (1) 4.0; (2) 2.5; (3) 2.0; and (4) 1.0. The insert represents the effect of TiO$_2$ content on mecoprop rate degradation determined for the first 60 min of irradiation.

Fig. 3. Effect of the initial mecoprop concentrations (mmol dm^{-3}) on the kinetics of chloride evolution in the presence of synthesized nanosized TiO$_2$ (2 mg cm^{-3}): (1) 2.70; (2) 1.35; and (3) 0.90.

rate of mecoprop is shown in Fig. 2. As it has previously been mentioned, this effect was studied by determination of chloride eliminated during photodegradation by potentiometric titrations at different illumination times. It is evident that the concentration of TiO$_2$ nanoparticles has a pronounced effect on the degradation rate. Up to about 2 mg cm^{-3} of TiO$_2$ nanoparticles, the degradation rate increases simultaneously with increasing the concentration of TiO$_2$. Further increase of TiO$_2$ concentration resulted in decrease of degradation rate. Some authors [13] have reported similar results with TiO$_2$ (Degussa P-25). Namely, they found that the photocatalytic rate constants are proportional to the mass of catalyst at low dosages. The observed effect of increasing degradation rate of mecoprop to a certain value can be ascribed to the increase in the number of photons being absorbed by semiconductor, reaching to a maximum for higher catalyst dosages, corresponding to a full absorption of the incident light flux [14]. Theoretically, increasing catalyst loading above the optimal value becomes inconsequential as all available light is already utilized. The value of this maximum depends on the design of the photoreactor and the geometry of the incident radiant flux [14–16]. At high TiO$_2$ concentrations, particles aggregate, reducing the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface is decreased. The increase in opacity and light scattering by the particles may be the other reasons for the decrease in the degradation rate [17]. The optimal catalyst loading found experimentally in this study, was around 2 mg cm^{-3}.

Generally, as the oxidation proceeds, less and less of the surface of the TiO$_2$ particle is covered, as the pollutant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing illumination time. It has been
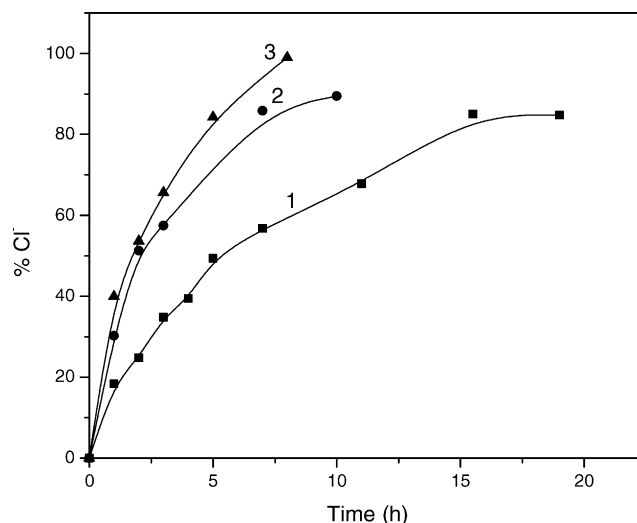
agreed, with minor variation, that the expression for the rate of photomineralization of organic substrates in the presence of irradiated TiO$_2$ follows the Langmuir–Hinshelwood (L–H) kinetic model. In order to confirm that this is the case in our experimental conditions, we investigated the influence of substrate concentration on the photocatalytic efficiency during the degradation of mecoprop (Fig. 3). It is evident that the initial concentration has a pronounced effect on the degradation efficiency. Namely, at the same irradiation time, the percentage of chloride released related to the initial amount of mecoprop is smaller if the initial mecoprop concentration is higher. It can also be seen that the adsorption of chloride released is higher if the initial substrate concentration is higher (Fig. 3, curves 1 and 2). For this reason, the maximum values of evolved chloride for higher initial concentrations (2.7 and 1.35 mmol dm^{-3}), although the curve plateaus, do not correspond to the stoichiometric quantity of mecoprop.

On the basis of the results shown in Fig. 3, a linear regression fit (by the least squares method with simple weighting) to the curves ln c(substrate) versus t(irrad.) were obtained for all the three initial mecoprop concentrations, indicating that Eq. (1), which is a form of reduced Langmuir–Hinshelwood equation, can be used as a good approximation over the range of examined initial concentrations,

$$\ln\left(\frac{c_0}{c}\right) = k_r K t = k_{ap} t \tag{1}$$

where k_r is the reaction rate constant, K is the equilibrium adsorption constant and k_{ap} is the apparent first-order reaction constant ($k_{ap} = k_r K$). From the slopes of these plots, we calculated the k_{ap} values (Table 1). It can be seen that the k_{ap} values decrease with increasing mecoprop concentrations, indicating thus that the reaction is not a simple first-order one but is combined [1]. The resulting apparent first-order

Table 1
Values of k_{ap} obtained for different initial concentrations of mecoprop

c_0 (mmol dm^{-3})	$k_{ap}10^3$ (min^{-1})	r
0.90	4.90	0.9946
1.35	4.50	0.9982
2.70	1.83	0.9864

r, Linear regression coefficient.

reaction constant has been used in all subsequent plots to calculate the photocatalytic efficiency.

The usually low temperature dependence of photocatalytic degradation rate is reflected by the low activation energy compared with an ordinary thermal reaction. As reported in literature [18,19], the values of the overall apparent activation energy of photocatalytic oxidation of different substrates are in the range from 5 to 28.4 kJ mol^{-1}. In the case of application of thick titanium dioxide films for semiconductor photocatalysis, activation energy is ca. 2.5 kJ mol^{-1} [19]. Fig. 4 represents the effect of temperature on mecoprop degradation rate. The dependance of photodecomposition rate of mecoprop on temperature was also investigated by potentiometric titration of produced chloride. The Arrhenius plot yielded a straight line from which the calculated overall apparent activation energy was 53.79 kJ mol^{-1}. Obviously, this value is higher than that obtained for photocatalytic degradation of other compounds using TiO$_2$ Degussa P-25, but it is acceptable if it is taken into account that at our experimental conditions, the efficiency of photocatalytic degradation is very small. On the basis of these results, 40 °C was used as working temperature during further experiments. For TiO$_2$ photocatalyst, irradiation is the primary source of electron−hole pair generation at ambient temperature as the band gap energy is too high to be overcome by thermal activation. Therefore,
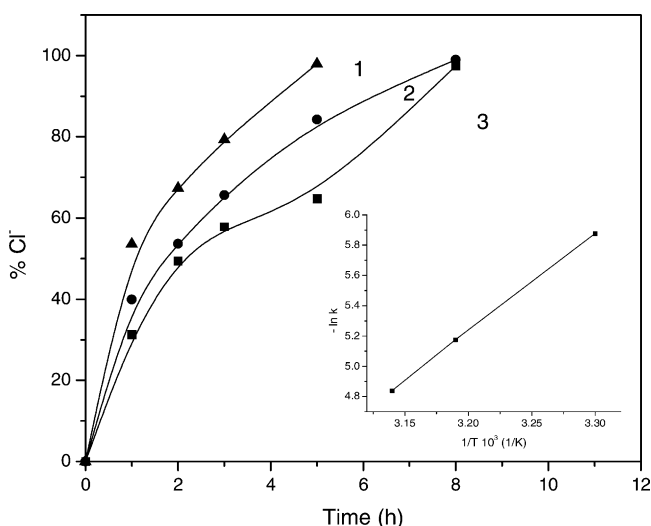

Fig. 4. Effect of temperature (°C) on mecoprop degradation rate (0.9 mmol dm^{-3}) in the presence of nanosized TiO$_2$ (2 mg cm^{-3}): (1) 45; (2) 40; and (3) 30. The insert represents the Arrhenius plot of, $-\ln k$ against $1/T$.
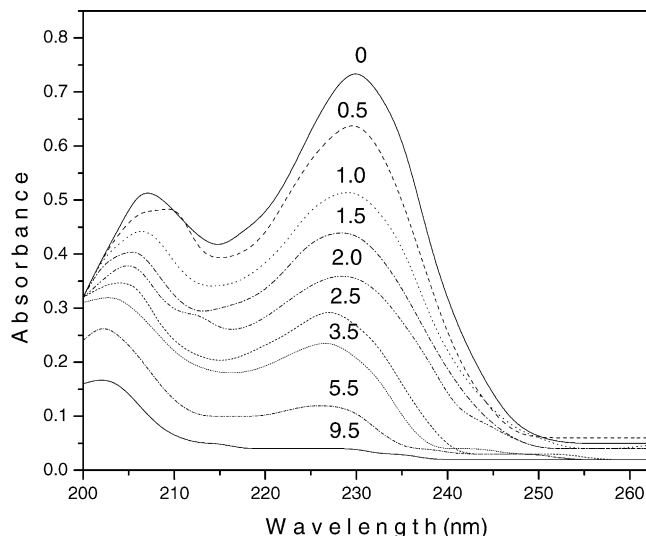

Fig. 5. UV spectral profiles during the mecoprop (2.7 mmol dm^{-3}) photodegradation by using synthesized nanosized TiO$_2$ (2 mg cm^{-3}). The numbers on each line represent the illumination time in hours.

the increase in the rate constant was most likely due to the increasing collision frequency of molecules in solution, which increases with increasing temperature.

The observed evolution of the UV spectra of mecoprop under illumination in the presence of synthesized TiO$_2$ is shown in Fig. 5. The spectrum of the investigated substrate shows two absorption maxima. The kinetics of aromatic ring degradation were monitored at the higher wavelength. The profile of this maximum changes with illumination time indicating that at this wavelength region in addition to the initial substrate, some of the intermediates formed during the photocatalytic degradation probably also absorb. The change of the absorption maximum profile can also be ascribed to the change of pH value in acidic direction, which is a result of chloride formation due to the aromatic ring degradation [20]. Because of the indicated change in the pH, neutralization of charged TiO$_2$ occurs causing aggregation with increasing irradiation time. As is obvious from the results shown in Fig. 5, the degradation of mecoprop does not automatically result in the complete mineralization of this molecule. In Fig. 6, curve 1 represents the kinetic curve for the degradation of the initial compound as well as of the intermediates, monitored by the changes of the aromatic ring concentration in the presence of the synthesized TiO$_2$. In fact, the degradation of the parent compound and immediately formed aromatic intermediates occurs simultaneously but at different rates. As can be seen, the slope of this curve changes after 2 h. The steeper part of the curve can be ascribed to the degradation of the initial compound, which dominates up to 2 h of illumination, with the apparent reaction rate constant $k_{ap} = 0.0058$ min^{-1}, $r = 0.9996$. The less steep part of the kinetic curve (Fig. 6, curve 1) can be ascribed to the degradation of the aromatic intermediates ($k_{ap} = 0.0022$ min^{-1}, $r = 0.9994$). In the case of the herbicide mecoprop degradation in the presence of TiO$_2$
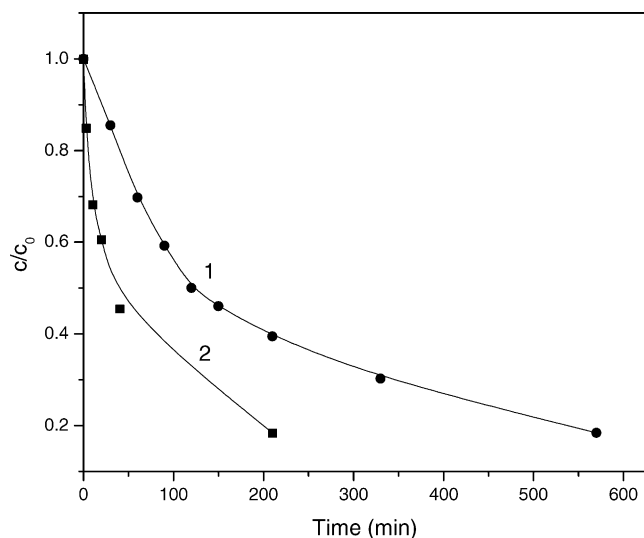
Fig. 6. Kinetics of the mecoprop (2.7 mmol dm^{-3}) degradation monitored by spectrophotometry in the presence of TiO$_2$ (2 mg cm^{-3}): (1) synthesized in this work; and (2) Degussa P-25.

(Degussa P-25), the complex degradation process was faster (Fig. 6, curve 2) and the parts pertaining to the aromatic ring degradation of the initial substrate and the intermediates could be observed as well. It can be seen that while the initial mecoprop concentration of 2.7 mmol dm^{-3} is mostly degraded within 120 min of illumination when synthesized nanosized TiO$_2$ is used as the photocatalyst (Fig. 6, curve 1), a significant portion of the intermediates has been transformed for the equivalent time in the presence of TiO$_2$ (Degussa P-25) (Fig. 6, curve 2).

If the time necessary for reaching maximum chloride concentration value upon illumination of a 2.7 mmol dm^{-3} solution of mecoprop (about 15 h) (Fig. 3, curve 1), is compared to the time necessary for the same percentage of aromatic intermediates degradation for the solution of the same initial concentration (Fig. 6, curve 1), it can be seen that the time required for chloride elimination is longer, which is probably a consequence of chloride adsorption on the semiconductor surface.

The photoassisted oxidative degradation of mecoprop in the presence of synthesized TiO$_2$ in this work was also followed by recording temporal ^{1}H NMR spectra (Fig. 7). The ^{1}H NMR signals (D$_2$O, δ (ppm)) of the parent compound were: 1.55 (3H, d, $J = 6.7$ Hz, CH$_3$) (a); 2.21 (3H, s, CH$_3$) (b); 6.72 (1H, d, $J = 8.9$ Hz, arom. H) (e); 7.13 (1H, dd, arom. H) (d) and 7.22 (1H, d, $J = 2.4$ Hz, arom. H) (f). The signal of methine proton was overlapped by HDO signal from D$_2$O. Since, in this case, the spectra of illuminated and evaporated samples (subsequently dissolved in D$_2$O) were recorded, only the signals of the parent compound could be observed, with the exception of the signal at 1.34 ppm which probably belongs to an aliphatic intermediate containing the CH$_3$–CH structural unit in its structure (α-hydroxyl-propionic acid). The possibility of α-hydroxyl-propionic acid formation has been explained earlier [9]. As can be seen from Fig. 7, the ^{1}H NMR signals decreased during illumination and almost completely disappeared after 4 h. The kinetic data obtained by area measurement of the ^{1}H NMR signal belonging to CH$_3$ group (b) (Fig. 7) during photooxidative decomposition of mecoprop are shown in Fig. 8 for two different photocatalysts: synthesized TiO$_2$ (curve 2) and TiO$_2$ (Degussa P-25) (curve 1). While it is observed that the mecoprop degradation proceeds much more rapidly in the presence of TiO$_2$ (Degussa P-25), the reaction rate is found to decrease with prolonged irradiation in the presence of
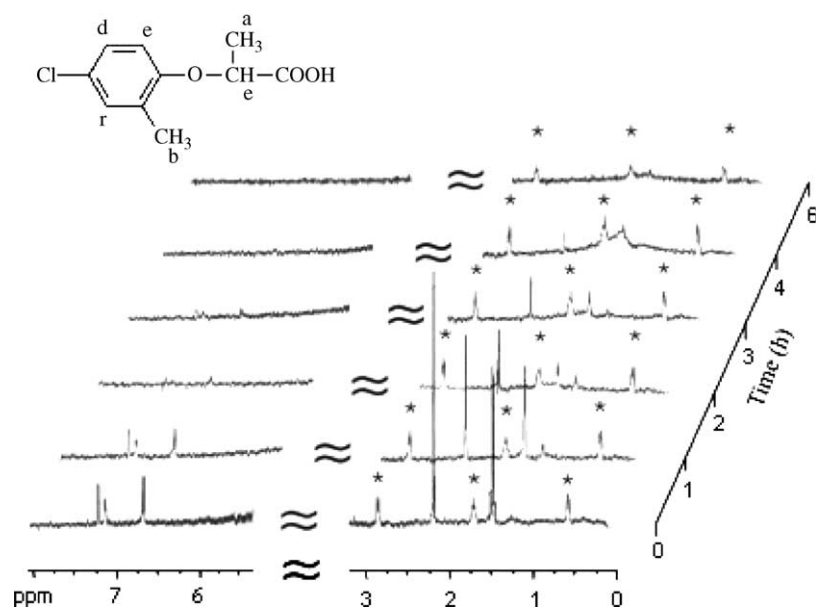

Fig. 7. ^{1}H NMR spectral profiles of mecoprop (2.7 mmol dm^{-3}) during photodegradation in the presence of synthesized TiO$_2$; *signals of internal standard (DSS).
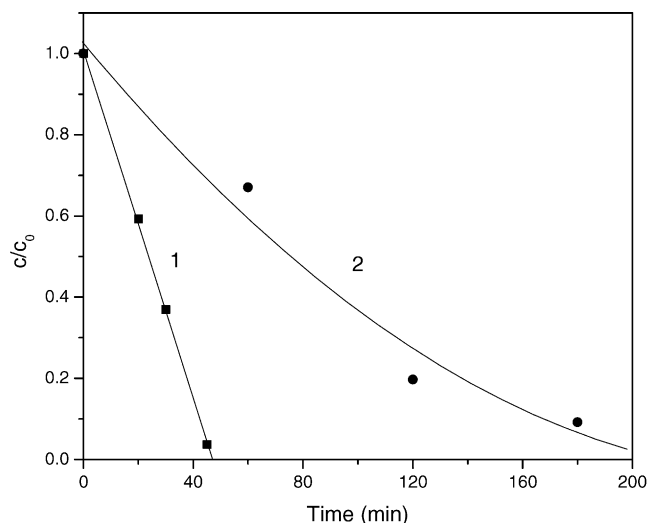
Fig. 8. Kinetics of the mecoprop (2.7 mmol dm^{-3}) photocatalytic degradation observed by ^{1}H NMR spectrometry in the presence of 2 mg cm^{-3} TiO$_2$: (1) Degussa P-25; and (2) synthesized in this work.

synthesized TiO$_2$ which can be fitted reasonably well by an exponential decay curve suggesting first-order kinetics Eq. (1). Similar results for the degradation of 3-nitrobenzenesulfonic acid were obtained by Rachel et al. [11], who observed a more efficient degradation in the presence of TiO$_2$ (Degussa P-25) than in the presence of TiO$_2$ (Millennium, type PC100, PC105 and PC500), all of which were with a higher surface area and 100% anatase. The same authors concluded that the relative efficiencies of various photocatalysts depend on the substrate used for the test. The obtained reaction rate constant pertaining solely to the degradation of the initial compound in the presence of synthesized TiO$_2$ was $k_{ap} = 0.014$ min^{-1} ($r = 0.9920$), which is about two times higher than the value obtained by UV spectrophotometry (Fig. 6, curve 1). This can be explained by the fact that the kinetics determined by UV spectrophotometry during the same degradation period are influenced by the absorption maxima of all aromatic intermediates formed simultaneously with mecoprop degradation.

Otherwise, the literature results of the photodegradation of model compounds using different kinds of TiO$_2$ photocatalysts [11,21] with different bulk and surface properties, i.e., BET-surface area, impurities, lattice mismatches or density of hydroxyl groups on the catalyst surface, indicate that the latter are apparently not responsible for the photocatalytic activity or alternatively just compensate each other. In the case of TiO$_2$ (Degussa P-25), which is clearly the most commonly used photocatalyst, there is no apparent relationship between photocatalytic activity and specific surface area. Degussa P-25 (consists of 75% anatase and 25% rutile with a specific BET-surface area of 50 ± 15 m^2 g^{-1} and a primary particle size of 21 nm) owes its high photoreactivity to a slower recombination between electrons and holes [21] whereas TiO$_2$ (Hombikat UV 100) has a high photoreactivity

due to faster interfacial electron transfer rate [21]. According to the mentioned literature data, a higher mecoprop degradation rate in the presence of Degussa P-25, in our case, can be explained not only by fact that the use of this photocatalyst guarantees longer lifetimes of the photogenerated electron–hole pairs, but also by the fact that adsorption/desorption of the substrate and reaction intermediates is slower on the surface of nanosized TiO$_2$.

For the investigation of the mecoprop degradation mechanism by ^{1}H NMR spectrometry, it was necessary to prepare the solution of the synthesized TiO$_2$ in the maximal amount of D$_2$O. As has already been stated in the experimental section, a separate, more concentrated batch of TiO$_2$ was prepared in water, which was further diluted with enough deuterium oxide to minimize the influence of water on the ^{1}H NMR signals. In this case, the efficiency of the catalyst was significantly lower. ^{1}H NMR signals could be observed even until about 16 h of illumination, while in the presence of the previously synthesized catalyst in water, without further dilution with deuterium oxide (Figs. 7 and 8), the same signal was visible until about 4 h.

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of mecoprop through ^{1}H NMR analysis. After 2 h of illumination, a singlet signal, which can be ascribed to the methyl group of 4-chloro-2-methylphenol, was observed at 2.17 ppm. This signal reaches its maximal intensity after 16 h of illumination and then begins to decrease. It was observed that the degradation of 4-chloro-2-methylphenol is followed by formation of acetic acid which is one of the degradation intermediates already identified during the early hours of the irradiation (noted after 3 h of illumination, at 2.00 ppm). So, ^{1}H NMR analysis performed during the mecoprop photodegradation indicated that in the presence of synthesized photocatalysts only two intermediates are observed: 4-chloro-2-methylphenol and acetic acid, while on the contrary, a greater number of intermediates was observed in the presence of Degussa P-25 [9]. This is in accordance with literature data [14] where it is concluded that, smaller amounts of organic intermediates are detected in solution when the catalyst surface area is higher. Namely, with an increase in the specific area, the adsorption efficiency for the sequential intermediate products is increased. Taking into account the nature of some of the observed species and the rate of their disappearance, as well as the literature data [9,12,22–24], we proposed a similar possible pathway for photocatalytic degradation of herbicide mecoprop to the one reported earlier [9]. The difference between this pathway and the previously reported one is that no other aliphatic intermediates, except acetic acid were observed, which is probably due to either adsorption on the high semiconductor surface area or to their fast degradation.

In order to confirm the efficiency of photocatalytic degradation, the kinetics of the degradation were monitored for near UV-illumination in a stream of oxygen and in the absence of TiO$_2$ (direct photolysis). The results of these

experiments indicate that the investigated substrate (2.7 mmol dm^{-3}) also decomposes, but incompletely, even after 42.5 h of illumination. Namely, this process is significantly slower, indicating that the photochemical process is scarcely responsible for the observed fast transformation during photocatalytic degradation.

The experiments were also performed in the absence of TiO_2 in the presence and absence of sunlight. Kinetics of solar photodegradation in the presence of TiO_2 were also studied. It was observed that the substrate does not decompose spontaneously neither in the presence nor in the absence of sunlight during the 6 days for which the process was monitored. Under the conditions of solar photodegradation in the presence of synthesized TiO_2 and TiO_2(Degussa P-25), degradation of the substrate was observed, but at a much slower rate than when artificial UV light was used. It can also be noted that the rates of direct photolysis as well as solar photodegradation in the presence of TiO_2 (Degussa P-25) are practically equal, but only in the initial period.

Generally, monitoring the change in pH during a photocatalytic process gives a valuable insight into the net changes in the investigated system. Thus, the change in the pH (obtained by the use of the combined glass electrode, as well as by antimony electrode) after first five hours of direct photolysis confirms that the dominant process is simultaneous formation of less acidic intermediates in comparison to the initial compound. According to literature [25], one of these intermediates, could be 4-chloro-2-methylphenol. In this case, the reaction of chloride evolution from the initial compound and aromatic intermediates obviously does not occur in the first step. Somewhat higher pH values, observed when antimony electrode is used, are probably due to the formation of some organic hydroxyl acids (for example, α-hydroxyl-propionic acid, whose existence as an intermediate is observed during the photoinduced degradation). However, this difference is relatively small.

4. Conclusion

The objective of this study was the investigation of photocatalytic degradation of mecoprop, a model compound for herbicides, in the presence of synthesized nanosized TiO_2. The nanosized TiO_2 (mean particle diameter 4 nm) was synthesized by controlled hydrolysis of titanium(IV) chloride. Besides the catalyst dosage, effects of other kinetic factors (initial substrate concentration, temperature and type of TiO_2) on the photocatalytic degradation were investigated in this work. These effects were examined by potentiometric titrimetric determination of the released chloride. The obtained results clearly demonstrate the importance of choosing the optimum degradation parameters for obtaining high degradation rates of the model compound, which is essential for any practical application of photocatalytic oxidation processes. The studied synthesized nanosized TiO_2 was expected to be as photocatalytically efficient as one of the commercially available kinds of TiO_2 (Degussa P-25, 75% anatase), since it is 100% anatase, which is the active form of TiO_2. For this reason, as well as because of a significant difference in surface area, the efficiency of these two photocatalysts was compared. On the basis of UV spectrometric measurements, it can be concluded that complete decomposition of mecoprop, as well as the removal of the aromatic intermediates in the presence of the studied synthesized TiO_2 occurs very slowly in comparison to TiO_2 (Degussa P-25), indicating its lower efficiency. The results of ^{1}H NMR spectrometric measurements, obtained during photodegradation in the presence of synthesized TiO_2 indicate the existence of two intermediates in significant amounts: 4-chloro-2-methylphenol and acetic acid. This phenomenon can be explained by higher surface area of nanosized TiO_2, which makes it more efficient in intermediate adsorption. An aromatic ring intermediate, with chlorine as substituent, undergoes ring opening, which is followed by Cl^- ion generation. Further degradation leads to formation of acetic acid, carbon dioxide and water.

Different photochemical reactivity was observed when solutions were irradiated in sunlight or near-UV light. Under the conditions of solar photodegradation in the presence of synthesized TiO_2, it was found that the reaction rate is higher and that the degradation is more efficient than in the case of solar degradation in the absence of TiO_2 and for UV-direct photolysis.

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