

Scientific paper

Visible-light-induced Photocatalytic Degradation of Herbicide Mecoprop in Aqueous Suspension of TiO₂

Biljana Abramović*, Daniela Šojić and Vesna Anderluh

Department of Chemistry, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3,
21000 Novi Sad, Republic of Serbia

Corresponding author: E-mail: abramovic@ih.ns.ac.yu

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Abstract

The visible-light-induced degradation reaction of *RS-2-(4-chloro-*o*-tolylxy)propionic acid* (mecoprop) was investigated in aqueous suspension of TiO₂ Degussa P25. Diffuse reflectance spectra showed that mecoprop adsorbed on TiO₂ powder induced visible-light absorption ($\lambda > 400$ nm). Formation of charge-transfer complexes was confirmed by recording FTIR spectra. The efficiency of TiO₂ as a photocatalyst with artificial visible light was compared to sunlight and UV light, as well as direct photolysis with visible-light, sunlight and UV light. The rate of mecoprop decomposition, in the presence of visible light, is $0.86 \mu\text{mol dm}^{-3} \text{min}^{-1}$, which is about four times higher in comparison to direct photolysis. The effect of catalyst loading was investigated as well, and it was found that even at 8 mg cm^{-3} TiO₂ the efficiency of photocatalytic degradation increases, which is significantly higher than when UV radiation is used. This difference in the effect of catalyst loading is probably a consequence of a different photodegradation mechanism under visible and UV illumination, i.e. that surface complexation between mecoprop and TiO₂ is a reasonable explanation for the visible light reactivity. Besides, the addition of 2-methyl-2-propanol, a common $\cdot\text{OH}$ radical scavenger, did not considerably affect the photocatalytic degradation of mecoprop under visible irradiation, which indicates that $\cdot\text{OH}$ radicals are not involved.

Keywords: Visible light irradiation, charge-transfer complexes, photocatalyst, photodegradation, TiO₂, mecoprop.

1. Introduction

Because of their stability, many pesticides, after use in agrotechnical measures reach surface and wastewaters by leaching, polluting them in that way. Besides, the absorption through the root system can be the cause of pesticide accumulation in plants, which, through the food chain, can endanger the living world. Because of that, it is beneficial to have at disposal a method which would enable complete pesticide elimination from contaminated waters. Photocatalytic degradation, with TiO₂ as semiconductor and near UV radiation, was proven to be a very efficient process, since it enables complete mineralization of the initial compound, as well as its intermediates.^{1–3} Besides, TiO₂ is chemically and biologically stable, non-soluble in water, acidic and basic media, non-toxic, low-priced and has a high oxidation capability. Photocatalysis by TiO₂ is the result of the interaction of electrons and holes generated in an activated solid with the surrounding medium. Activation is the consequence of light absorption. Thus, electron–hole pairs are formed in the solid par-

ticle that can recombine or participate in reductive and oxidative reactions that lead to the decomposition of contaminants. In aqueous solution, the holes at the TiO₂ surface are scavenged by surface hydroxyl groups and water molecules to generate $\cdot\text{OH}$ radicals. The resulting $\cdot\text{OH}$ radical, being a very strong oxidizing agent (standard redox potential $+2.8 \text{ V}$)⁴, can oxidize all organic compounds to the mineral end-products, i.e. CO₂ and H₂O. However, because of its large band gap of 3.2 eV, only the small UV fraction of solar light, about 3–4%, can be utilized.

In general, pure TiO₂ with its large band gap is inactive under visible light illumination, which limits the practical application of TiO₂ photocatalyst. Therefore, pure TiO₂ has been modified by various ways such as impurity doping and dye sensitization to obtain visible light reactivity.⁵ Some more recent studies, however, reported that pure TiO₂ showed visible light photocatalytic reactivity, although the compound alone being degraded does not absorb visible light at all.^{6–10} Li et al.⁶ ascribed the visible light reactivity to the formation of surface complexes of H₂O₂/TiO₂ that absorb visible light. Cho et al.⁷ reported

that a complex formation between the nonionic surfactant having polyoxyethylene groups (Brij) and TiO₂ surface exhibited visible light activity for the reduction of CCl₄ and Cr(VI) and observed a broad absorption band (320–500 nm) in the Brij/TiO₂ solution. Agrios et al.^{8,9} and Kim and Choi¹⁰ also observed that homologous series of chlorophenols and phenolic compounds formed a charge-transfer complex on TiO₂. However, since most of TiO₂ photocatalytic reactions have been studied under UV irradiation, visible light reactivity of TiO₂, which occurs as a consequence of the surface complex formation mechanism appears to be largely unrecognized. There should be more examples of such surface complexation that has visible light activity.

It is for this reason that we have decided to investigate in this paper the efficiency of TiO₂ as a photocatalyst in degradation of herbicide *RS-2-(4-chloro-*o*-tolyl-oxy)propionic acid* (mecoprop) as a model-compound using artificial visible-light ($\lambda > 400$ nm). This pesticide was chosen because, as reported in literature, it is the most often found pesticide in drinking water.¹¹ Charge-transfer complex was characterized using reflectance and FTIR spectroscopy. The efficiency of TiO₂ as photocatalyst using artificial visible-light was compared with sunlight and UV light, as well as direct photolysis with visible-light, sunlight and UV light. In illumination experiments, the amount of reaction induced by irradiation was quantified by spectrophotometry.

2. Experimental

The herbicide mecoprop (98% purity), was obtained from the Chemical Factory “Kruševac”, Serbia and Montenegro. The commercial product was purified by conventional recrystallization method from water–ethanol (1:1, v/v) solution. Other chemicals were used without further purification. The purity of purified mecoprop was controlled and confirmed by ¹H NMR spectrometry (Bruker AC-250). For all experiments, the initial concentration (2.7 mmol dm⁻³) of mecoprop solution was prepared in doubly-distilled water as solvent. In the experiments in which the influence of catalyst loading was investigated, the initial mecoprop concentration was 0.9 mmol dm⁻³.

TiO₂, Degussa P25 (75% anatase and 25% rutile, specific area of 50 ± 15 m² g⁻¹, mean particle diameter 20 nm, non-porous) was used as catalyst. The UV/Vis reflection spectra of the catalyst were measured using a UV/Vis spectrophotometer Perkin-Elmer λ -45 referenced to BaSO₄. All experiments in the presence of the catalyst were carried out using a 2 mg cm⁻³ suspension of TiO₂, except in the case when the influence of catalyst loading on photodegradation of mecoprop was investigated, where the concentration range was of 0.5–16 mg cm⁻³.

Photocatalytic reaction was carried out in a cell (sample volume 20.0 cm³, continuously purged with O₂)

made of Pyrex glass with a plain window on which the light beam was focused, equipped with a magnetic stirring bar and a water circulating jacket. Aqueous suspensions of TiO₂ containing mecoprop were sonicated for 15 min before illumination, to make the TiO₂ particles uniform. The suspension thus obtained was thermostated at 40 ± 1 °C in a stream of O₂ and then irradiated. Irradiation in the visible range was performed using a 50 W halogen lamp (Philips). The Vis wavelength was selected through a 400 nm cut-off filter. Irradiation in the UV range was performed using a 125 W medium-pressure mercury lamp (Philips, HPL-N) (emission band in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm) as a second radiation source, using an appropriate concave mirror. Direct photolysis experiments were performed under the same conditions as photocatalytic degradation, but without the addition of catalyst. During irradiation the mixture was stirred at a constant speed. These experiments were also carried out at daylight (23 ± 1 °C) and in the dark, in the presence and absence of catalyst during autumn, winter and spring months 2005/06.

For spectrophotometric determination during the degradation of the mecoprop aliquots of 0.25 cm³ of reaction mixture were taken at regular time intervals and diluted to 10.00 cm³ with doubly distilled water. In the experiments in which the influence of catalyst loading was investigated, 0.25 cm³ aliquots were taken and diluted to 5.00 cm³ with doubly distilled water. After irradiation, the suspensions containing TiO₂ were filtered through a Millipore (Millex-GV, 0.22 μ m) membrane to separate the TiO₂ particles and their spectra were recorded on a spectrophotometer (Secomam anthelie Advanced 2) in the wavelength range from 200 to 400 nm. Kinetics of the degradation was monitored at 229 nm.

FTIR spectra were recorded using a Thermo Nicolet Nexus 670 spectrophotometer in the 1000–4000 cm⁻¹ region with 4 cm⁻¹ resolution and 100 scans. For analysis, 20 cm³ of mecoprop solution (2.7 mmol dm⁻³) containing 2 mg cm⁻³ of appropriate catalyst was stirred for 4 h in the dark. During this time, the mecoprop was adsorbed on TiO₂ particles. The residue obtained after decantation was dried at 60 °C. Spectra were recorded on pellets consisting of a mixture of samples and KBr to achieve better cohesion of the sample.

The initial values for the kinetic curves were corrected for the value of the adsorbed mecoprop on the catalyst.

3. Results and Discussion

To investigate the possibility of use of TiO₂ as a photocatalyst in the visible light region, the appropriate reflectance spectra were recorded. Figure 1 illustrates the light reflection properties of TiO₂ (curve 2) and TiO₂ after treating with mecoprop (curve 1). As can be seen, a certain degree of light absorption by the TiO₂ powder in the

visible light region indicates that this catalyst should be photocatalytically active in the visible light region, although significantly less than in the case of experiments in which UV illumination would be used. This is attributed to the presence of the rutile form of TiO_2 .¹² Namely, TiO_2 Degussa P25 beside 75% of anatase form (band gap of 3.2 eV, i.e. wavelength 385 nm), also contains 25% of rutile form, which corresponds to the band gap of 3.0 eV, i.e. wavelength of 410 nm. Besides that, when TiO_2 is treated with mecoprop a red shift occurred in which a tailing absorbance in the visible region (400–500 nm) was observed (curve 1) compared with the spectrum of sole TiO_2 powder (curve 2), indicating the formation of a charge-transfer complex between TiO_2 and mecoprop, causing an even higher degradation efficiency in the presence of TiO_2 and visible light. Agrios et al.^{8,9} have accomplished similar results. They also observed that 2,4,5-trichlorophenol formed a charge-transfer complex on TiO_2 which was activated by light wavelengths as long as 520 nm. These authors have also found that in case of pure anatase TiO_2 , the spectra of anatase and anatase/2,4,5-trichlorophenol are identical which led them to the conclusion that in this case formation of a charge-transfer complex does not occur. They also conclude that the charge-transfer complex formation was highly favored with TiO_2 Degussa P25 that has mixed phases of anatase and rutile and that the complexation on pure-phase anatase or rutile was significantly reduced. At this point, it should certainly be mentioned that Kim and Choi¹⁰, however, have found that pure anatase enables visible-light-induced photocatalytic degradation forming a surface complex with the compound.

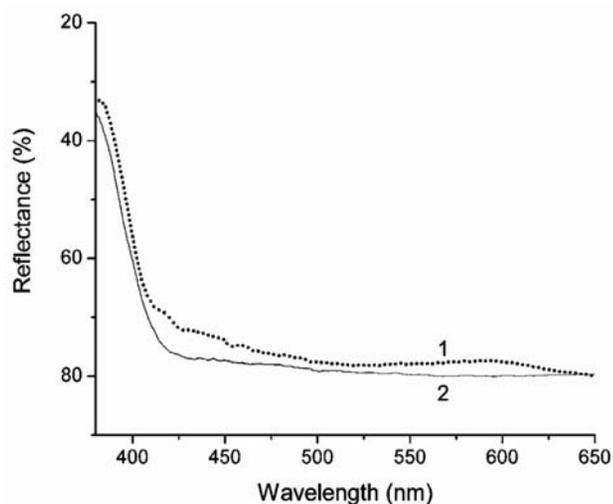


Figure 1. Reflectance spectra of: (1) TiO_2 -mecoprop; (2) TiO_2

To confirm the assumption of intermediate complex formation between mecoprop and TiO_2 , appropriate FTIR spectra were recorded. Figure 2 shows the FTIR spectrum of the TiO_2 Degussa P25. It shows a broad band centered

at 3435 cm^{-1} , ascribed to basic hydroxyl groups, whereas a band at 1635 cm^{-1} corresponds to adsorbed molecular water.^{13,14} Peaks can also be observed in the $3000\text{--}2800\text{ cm}^{-1}$ range (CH_2 , CH_3 stretching mode) that are most likely due to the presence of some organic impurities.

Figure 3 presents FTIR spectra of mecoprop (curve 1), the difference between spectra of mecoprop adsorbed on TiO_2 samples and spectra of the TiO_2 Degussa P25 (curve 2), mecoprop adsorbed on TiO_2 samples (curve 3), and the TiO_2 Degussa P25 (curve 4). It is clearly visible that during herbicide adsorption on the catalyst surface, a band due to $\nu(\text{C}=\text{O})$ at 1704 cm^{-1} disappears, while a band at 1722 cm^{-1} appears with much lower intensities than those from free mecoprop. It can also be seen that the peak at 1635 cm^{-1} is significantly wider (curve 3) in comparison to the one in case of sole TiO_2 (curve 4). Subtraction of these two spectra results in a band at 1588 cm^{-1} . Besides that, a new band showing a considerable intensity appears at 1405 cm^{-1} . These two bands are attributed to symmetric and asymmetric vibrations of the formed of *RS*-2-(4-chloro-*o*-tolylloxy)propionate species. Other authors have obtained similar results by studying interactions of different acids with TiO_2 .^{15,16}

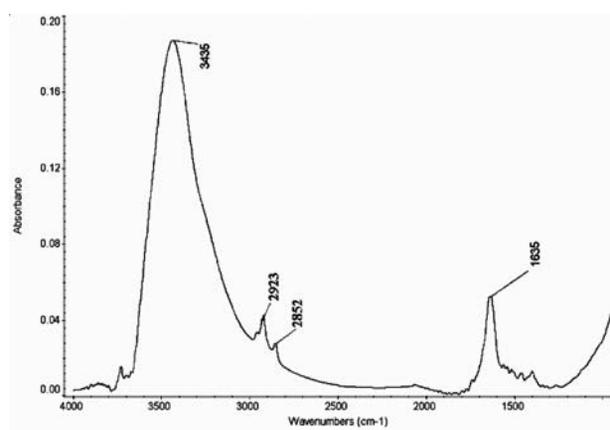


Figure 2. FTIR spectra of TiO_2

To explore the visible photocatalytic activity of TiO_2 , the kinetic of degradation of mecoprop by artificial visible light (Figure 4, curve 3) was compared to that by UV light (Figure 4, curve 4). The kinetic curves presented in Figure 4 were obtained by spectrophotometric monitoring of mecoprop aromatic moiety degradation. As could have been expected from the previous discussion, mecoprop degradation by visible light could have been expected (curve 3). Certainly, upon comparing photocatalytic activity of TiO_2 in the presence of UV and visible radiation, it can be said that the rate of mecoprop degradation is about 11 times higher in the first case, which could have been expected. Namely, the rate of mecoprop degradation in the presence of visible light is $0.86\text{ }\mu\text{mol dm}^{-3}\text{ min}^{-1}$, while under UV illumination it is $9.7\text{ }\mu\text{mol dm}^{-3}\text{ min}^{-1}$.

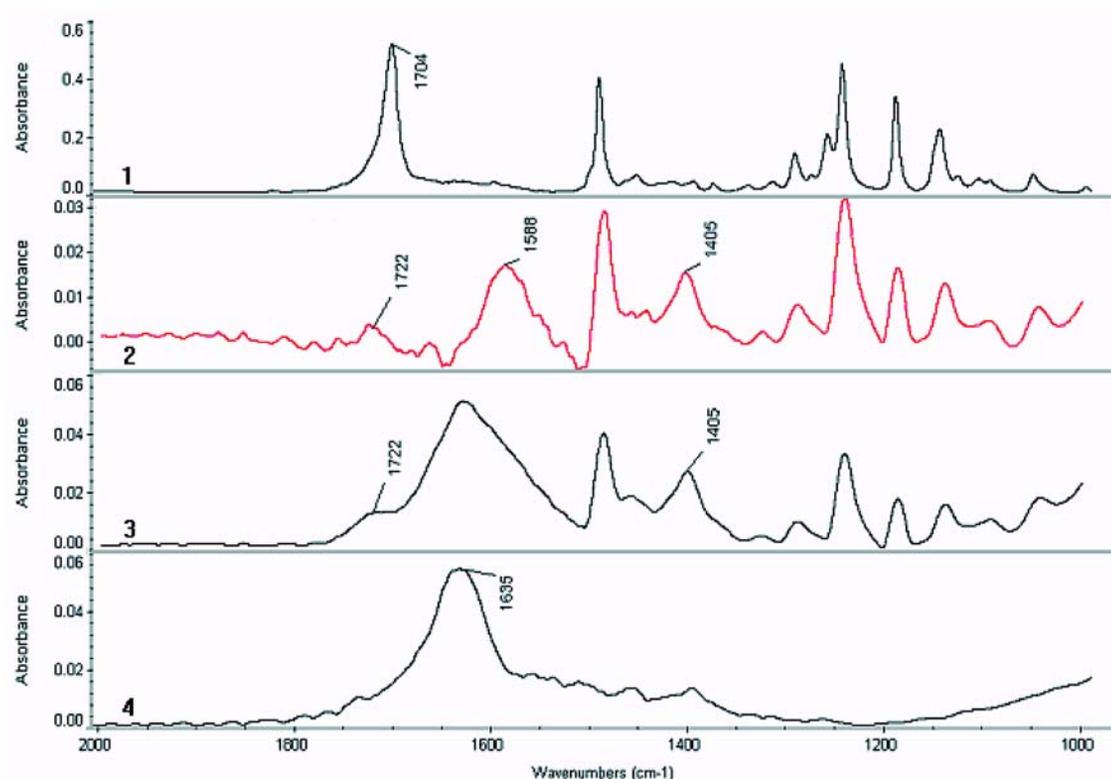


Figure 3. FTIR spectra of: (1) mecoprop alone; (2) the difference between spectra of mecoprop adsorbed on TiO_2 and TiO_2 ; (3) mecoprop adsorbed on TiO_2 ; (4) TiO_2

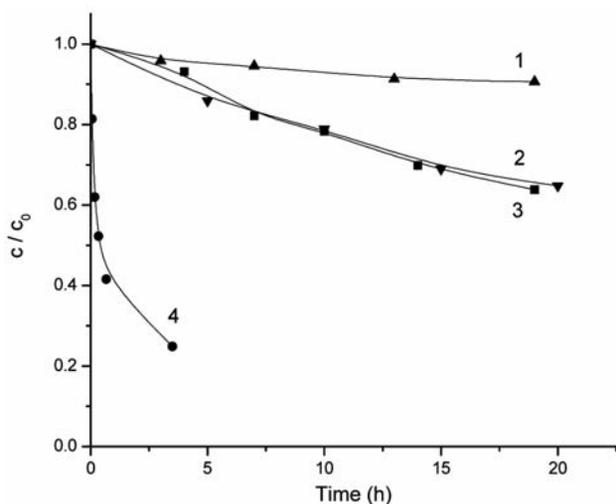


Figure 4. Kinetics of mecoprop photodegradation (2.7 mmol dm^{-3}): (1) halogen lamp, direct photolysis; (2) mercury lamp, direct photolysis; (3) halogen lamp in the presence of TiO_2 Degussa P25 (2 mg cm^{-3}); (4) mercury lamp in the presence of TiO_2 Degussa P25 (2 mg cm^{-3})

Upon comparing the rates of visible and UV photocatalytic degradation of 4-chlorophenol in the presence of Degussa P25, Kim and Choi¹⁰ have found that this ratio is even higher, i.e. that the rate of degradation in the UV region is about 26 times higher than in the visible region.

However, these authors have found that this ratio is markedly different depending on the kind of TiO_2 sample. Namely, using Ishihara ST-01 the degradation rate of the said compound in the presence of visible light is only about 1.5 times lower than when UV light was used. From this they conclude that although Degussa P25 is much more active than ST-01 under UV illumination, P25 is less active than ST-01 under visible-light.

To investigate the efficiency of the catalyst in the processes of visible photodegradation, the experiments were also performed under the conditions of direct photolysis using artificial visible light (Figure 4, curve 1). As can be seen, in this case as well, mecoprop degradation takes place, although at a significantly lower rate, i.e. the rate has the value of $0.22 \mu\text{mol dm}^{-3} \text{ min}^{-1}$, which is about four times slower. However, when the efficiency of artificial visible photocatalytic degradation was compared to direct photolysis with UV radiation, it was found that the rates of degradation are very similar (Figure 4, curves 2 and 3).

Kinetics of mecoprop degradation in the presence of sunlight was studied in the presence and absence of the mentioned photocatalyst (Figure 5). It was noted that the compound does not degrade spontaneously in the presence of sunlight in a 274 day period during which the process was monitored (curve 3). Under the conditions of solar photocatalysis in the presence of TiO_2 Degussa P25 (curve 4), the mecoprop degrades, but much slower than

in the presence of artificial radiation. As can be seen, during the first 20 days photodegradation takes place at a higher rate having the value of $0.08 \mu\text{mol dm}^{-3} \text{min}^{-1}$, to continue at a significantly lower rate ($0.003 \mu\text{mol dm}^{-3} \text{min}^{-1}$) after that period. Having in mind the fact that sunlight, as has been said, contains a certain percentage of UV light, it could be expected for the mecoprop photodegradation process in the presence of TiO_2 to take place at a higher rate when a natural radiation source is used than when artificial visible light is used. However, a lower solar degradation rate is a consequence of different intensities of the said radiation sources.

To investigate the stability of mecoprop solution, its concentration was determined in the absence and presence of TiO_2 (Figure 5, curves 1 and 2) in the dark during a longer time period. It can be concluded from these results that the solution is very stable because no spontaneous mecoprop degradation occurs (curves 1 and 2) in the period of about nine months. It should be mentioned here that the kinetic curve 2 is corrected for the adsorbed value of mecoprop (3.2%) in the first 15 minutes.

The influence of catalyst loading on the photodecomposition efficiency was also investigated by the spectrophotometric method. The photodegradation of 0.9 mmol dm^{-3} mecoprop in the oxygenated aqueous suspension was examined in the TiO_2 concentration range of $0.5\text{--}16 \text{ mg cm}^{-3}$ with the aim to optimize the

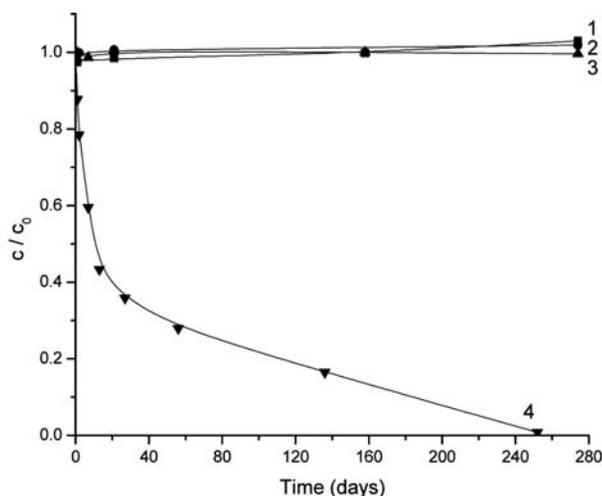


Figure 5. Kinetics of mecoprop (2.7 mmol dm^{-3}) degradation: (1) in the dark; (2) in the dark in the presence of TiO_2 (2 mg cm^{-3}); (3) solar irradiation; (4) solar irradiation in the presence of TiO_2 (2 mg cm^{-3})

catalyst dosage during the irradiation process. Figure 6 only presents the results up to $8 \text{ mg cm}^{-3} \text{TiO}_2$, although the plateau is reached at $12 \text{ mg cm}^{-3} \text{TiO}_2$, since at concentrations above 8 mg cm^{-3} the catalyst also disperses on the walls of the reaction vessel above the reaction solution, increasing its surface area, on one hand, and

decreasing its amount in the solution, on the other hand. For these reasons, the reaction conditions are not the same as at lower catalyst loadings, and thus the reaction rates of mecoprop degradation are not comparable. This is why the amount of 8 mg cm^{-3} can conditionally be taken as optimal. Several authors^{17–22} have investigated the optimal mass concentration of TiO_2 under UV irradiation. They have found that it varies in a wide range ($0.15\text{--}2.5 \text{ mg cm}^{-3}$) depending on the photocatalysed system, photoreactor shape and radiation source geometry. Upon comparing the results with those of the cited authors, it can be noted that the effect of catalyst loading in case of visible-light-induced photocatalytic degradation is significantly different. This is most likely due to the different photodegradation mechanism in the presence of visible and UV radiation. Obviously, at visible-light-induced photocatalytic degradation, compound-surface interaction is a critical factor in determining the visible photocatalytic degradation activity. Kim and Choi¹⁰ have obtained similar results, finding that among various commercial TiO_2 samples, Ishihara ST-01 ($340 \text{ m}^2/\text{g}$) and Hombikat UV100 ($348 \text{ m}^2/\text{g}$), that have the highest surface area, show the highest visible photocatalytic degradation activity for 4-chlorophenol.

To confirm the difference in the mecoprop degradation mechanism under visible and UV radiation, we investigated the effect of addition of 2-methyl-2-propanol, a

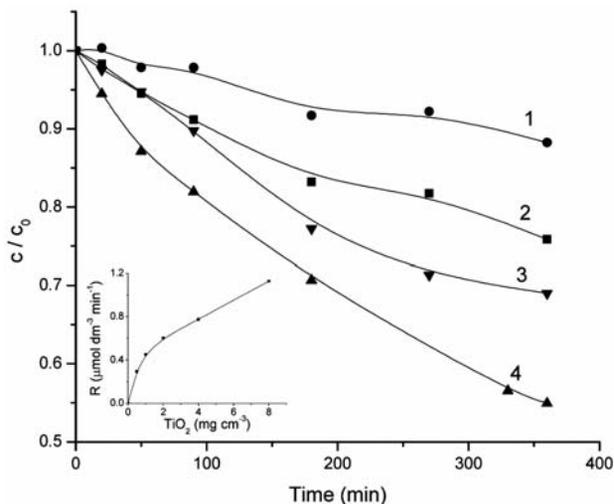


Figure 6. Kinetics of mecoprop photodegradation (0.9 mmol dm^{-3}) in the presence of different TiO_2 concentration (mg cm^{-3}): (1) 0.5; (2) 2.0; (3) 4.0; (4) 8.0. The insert represents the effect of TiO_2 loading on mecoprop degradation rate

common $\cdot\text{OH}$ radical scavenger. Namely, for degradation of mecoprop with UV illumination the presence of $\cdot\text{OH}$ radicals is required.^{22,23} Since it was found that the presence of 2-methyl-2-propanol practically does not influence the rate of photocatalytic degradation of mecoprop under visible irradiation, it was confirmed that the degradation

mechanism of the above mentioned compound under visible irradiation should be different from that under UV irradiation.

It was also found that 75% of the mecoprop degrades after 12.5 hours of illumination, leading to a conclusion that there is a tendency of complete mecoprop elimination from the solution, i.e. that the mentioned compound could be degraded under visible illumination ($\lambda > 400$ nm) and TiO₂. Kim and Choi¹⁰ have obtained similar results by studying photocatalytic degradation of 4-chlorophenol. However, the same authors state that dichloroacetate could not be degraded under visible-light. Also, Agrios et al.⁸ conclude that the visible-light-induced transformation of 2,4,5-trichlorophenol on TiO₂ produced coupling products only, and no mineralization was achieved. All of this indicates that the efficiency of TiO₂ photocatalytic degradation in the presence of visible radiation greatly depends on the kind of compound.

4. Conclusion

Results clearly demonstrate that mecoprop can be degraded on TiO₂ under visible-light through the surface complexation mechanism. TiO₂ treating with mecoprop caused a red shift in which a tailing absorbance in the visible region (400–500 nm) was observed, compared to the spectrum of TiO₂ powder, indicating the formation of a charge-transfer complex between TiO₂ and mecoprop. On the basis of FTIR spectra it was found that a charge-transfer complex between TiO₂ and mecoprop is formed through carboxylate formation. The rate of degradation was studied by UV spectrometry. It was found that the rate of mecoprop degradation under visible-light is 0.86 $\mu\text{mol dm}^{-3} \text{min}^{-1}$, which is about four times faster than direct photolysis. Contrary to common expectations, under the conditions of solar photodegradation in the presence of TiO₂ Degussa P25, the mecoprop degrades, but much slower than in the presence of artificial visible light, which is a consequence of a difference in radiation intensity. However, the kinetics of mecoprop UV degradation is about 11 times faster than under artificial visible light. The influence of catalyst loading was investigated as well, with a simultaneous increase in the degradation rate with an increase in the concentration of TiO₂, which is in agreement with the fact that the visible light reactivity is apparently proportional to the surface area of TiO₂. It was found that even at 8 mg cm⁻³ TiO₂ the efficiency of photocatalytic degradation increases, which is significantly higher than when UV radiation is used. This difference in the effect of catalyst loading is probably a consequence of a different photodegradation mechanism under visible and UV illumination, which was confirmed by studying the kinetics of photocatalytic degradation in the presence of 2-methyl-2-propanol, a known [•]OH radical scavenger. It was found that its presence practically

does not affect the photocatalytic degradation of mecoprop under visible irradiation, which indicates that [•]OH radicals are not involved.

5. Acknowledgments

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Povzetek

Študirali smo fotolitski razpad *RS-2*-(4-kloro-*o*-toliloksi)propijonske kisline (mecoprop), v vodni suspenziji TiO₂ Degussa P25. Z difuzno reflektančno spektroskopijo smo ugotovili, da mecoprop adsorbiran na TiO₂, inducira absorpcijo vidne svetlobe ($\lambda > 400$ nm). Nastanek charge-transfer kompleksov smo potrdili s FTIR spektri. Primerjali smo hitrost razpada v prisotnost TiO₂ fotokatalizatorja pri uporabi umetne vidne svetlobe, sončne svetlobe in UV svetlobe, s hitrostjo direktne fotolize. Hitrost razpada mecopropa z vidno svetlobo ($0.86 \mu\text{mol dm}^{-3} \text{min}^{-1}$) s katalizatorjem je približno štirikrat višja kot pri direktni fotolizi. Določili in pojasnili smo optimalno količino TiO₂ pri različnih vrstah svetlobe. Dodatek 2-metil-2-propanola, kot lovilca $\cdot\text{OH}$ radikalov, ne vpliva znatno na hitrost fotolize z vidno svetlobo, zato sklepamo, da $\cdot\text{OH}$ radikali pri fotolizi ne sodelujejo.