

Photocatalytic Degradation of Malachite Green Dyes With TiO₂/WO₃ Composite

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Abstract

This study summarizes briefly the sources of Malachite green contamination and the wide range of its toxic effects. The photodegradation of this cationic triphenylmethane dye by TiO₂ and TiO₂/WO₃ composite is examined under different experimental conditions. Two types of salts - oxalate and hydrochloride were studied and unexpectedly different kinetics of degradation was observed in the presence of TiO₂ or TiO₂/WO₃ as photocatalysts. The behavior of the hydrochloride dye is almost identical in the presence of both catalysts TiO₂ or TiO₂/WO₃, showing equal rates of degradation. However for the oxalate form the TiO₂/WO₃ composite is significantly more efficient than pure TiO₂. Even more, the apparent rate constant of degradation for oxalate is higher than that obtained for hydrochloride with the same composite TiO₂/WO₃. It is suggested that initial adsorption of the dye on the surface of the catalyst plays important role and explains the different photocatalytic performance of TiO₂/WO₃ composite powder. Most probably the sorption of Malachite green oxalate is favored by the C₂O₄²⁻ ions, this way providing direct photooxidation of the dye. It is also established by UV-VIS comparative analysis that during the proposed photopurification of the pollutants the formation of the colorless carcinogenic Leuco malachite green is negligible.

Keywords: water purification, photocatalysis, malachite green oxalate, composite powders

1. Introduction

Textile dyes are one of the most notorious contaminants in aquatic environment due to their huge industrial production, slow biodegradation and toxicity. About 700 000 tons of dyes are annually produced world-wide. Approximately 15% of the synthesized coloring agents are lost in waste waters during manufacturing or processing [1]. The triphenylmethane dye malachite green (MG) originally used as dyeing agent in the textile industry, was introduced in aquaculture in 1933 [2] and found extensive use in the fish industry all over the world due to its efficiency and low cost [2–5]. Fish farms have been using MG as a topical treatment by bath or flush

methods so it can be absorbed systemically and produce internal effects. This dye has become one of the most debated and controversial compounds in connection to its reported toxic effects [2–6]. Available mainly as oxalate or hydrochloride salt MG can be reduced to its colorless carcinogenic form Leuco malachite green (LMG). In water solution LMG is stable only at $\text{pH} < 2$ or $\text{pH} > 11.6$. The reaction is well-known and LMG is used as pH indicator. However MG used in fish treatment is reduced to LMG and accumulates in the fish tissues. It is stored primarily in serum, liver, kidney, muscle and skin of various experimental animals [2]. It is reported also that the rat, mouse, monkey and human intestinal microflora and several cultures of anaerobic bacteria play important role for the metabolic activation of the triphenylmethane dye to a potential carcinogen [6]. Therefore in the European Union and USA the MG usage in aquaculture is banned, in Germany a tolerance of 0.01 mg/kg for the sum of MG and LMG in edible fish is established. Despite that ban, the dye is still being used in many countries until exploring proper alternative for eventual complete MG replacement. MG is also used as coloring agent for silk, paper, wool, leather, cotton, jute and acrylic industries. On the other hand, there is a serious need of methods [7–11] and ways to remove the excess of MG left in large ponds after treatment [2].

In the last 10 years TiO_2 photocatalysis has been successfully used for different environmental applications such as photodegradation of organic contaminants. TiO_2 is a quite suitable non-toxic, physicochemically stable low-cost material [1,12].

This work presents the photocatalytic oxidation of MG using composite TiO_2/WO_3 photocatalyst, aimed at improving titania photoactivity and avoiding the presence of LMG in the purified solution.

2. Experimental

2.1. Materials

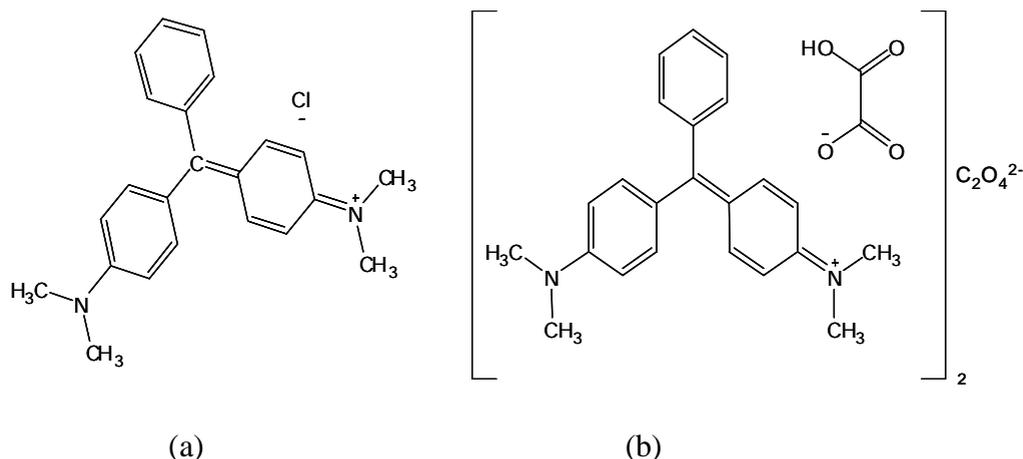
The oxides TiO_2 KRONOS 1001 Anatase from KRONOS and WO_3 from Fluka were used as catalysts and also for the composite TiO_2/WO_3 preparation. The initial charge for the composite was prepared from thoroughly homogenized TiO_2 and WO_3 powders of a 5% WO_3 content, as found to be optimal in a previous investigation [13]. As mixing media a small quantity of ethanol was added to assure better contact between both oxides. Then the mixture was thermally treated for 2 hours at 200°C and stirred well in a glass mortar after complete drying to obtain fine powder.

The characteristics of two types of malachite green salts used: malachite green oxalate (MGOx) and malachite green hydrochloride (MGH) are presented in Table 1 and structural formulas in Scheme 1.

Table 1. Characteristic data of the organic dye forms used in the experiments

Malachite green salts:	MGH (supplied from Merck)	MGOx (supplied from Sigma-Aldrich)
Empirical formula:	$C_{23}H_{26}N_2O \cdot 2HCl$	$C_{48}H_{50}N_4O_4 \cdot 2C_2H_2O_4$
Molar mass:	383 g/mol	927 g/mol
Absorption maximum (in water):	618 nm	618 nm
Minimum dye content:	85%	90%

The solution of LMG for analysis was prepared from $1 \cdot 10^{-5}$ mol L^{-1} MG solution, used as initial in the photocatalytic experiments. The pH of the LMG solution was adjusted to 12 by addition of NaOH (Merck) solution to provide complete transformation of the total MG content in the solution to LMG.



Scheme 1. Structural formulas of Malachite Green Oxalate (a) and Malachite Green Hydrochloride (b)

2.2. Instrumentation

The UV-VIS absorbance spectra were measured on Jenway (320-1000 nm) and UnicamUV500 (200-1000 nm) spectrophotometers. The pH was measured on a 211 Hanna instruments pH meter.

2.3. Photocatalytic experiments

The experiments were performed in a cylindrical glass reactor [14,15]. The source of radiation was 18 Watt fluorescent BLB UV-A lamp emitting mainly in the region of 340-360 nm. The lamp is positioned at 9 cm above the reactor so the UV-light enters the slurry across the interface with air. The initial dye concentration was $1 \cdot 10^{-5}$ mol L^{-1} . The volume of the water

suspensions was 250 ml. The catalyst loading was 1 g L^{-1} . The suspensions were first stirred in the dark for 30 min to reach sorption/desorption equilibrium of the dye. After that the UV illumination was started to carry out the photocatalysis. Aliquot samples of 6 ml were taken at determined time intervals (lamp switched off), first centrifuged and then filtered through $0.22 \mu\text{m}$ membrane filters for complete removal of the catalyst. The dye concentration in each aliquot was determined at the maximum of absorbance by spectrophotometry. pH was also determined for each aliquot. The pH during the adsorption of the dye varied in the range 4.6–5.2 and during the photocatalytic activity test pH varied in the range 5.2–6.2. The temperature was $23 \pm 2^\circ\text{C}$ during the experiments.

Stirring (300 rpm) and air bubbling (30 l h^{-1}) of the suspension were kept constant along the experiments to assure oxygen saturation, uniform access of UV light and constant transfer rate of the pollutants to the catalyst.

Blank experiments with the pure dye solutions, illuminated with UV light for 2 hours, were conducted prior to the photocatalytic experiments. No significant discoloration of the solutions was observed indicating that the direct photolysis of the dyes is negligible.

3. Results and discussion

The kinetics of photodegradation of MGH and MGOx in the presence of the photocatalysts TiO_2 , WO_3 and TiO_2/WO_3 composite are shown in Figs. 1 and 2, respectively. The photodegradation of MHG in the presence of oxalate anions (oxalate added as $2 \cdot 10^{-5} \text{ mol L}^{-1} \text{ K}_2\text{C}_2\text{O}_4$) is also presented in Fig. 1. As might be expected the WO_3 itself has no photocatalytic action for both MG salts investigated. The well known photocatalytic action of TiO_2 is clearly expressed especially in case of MGH where complete degradation is achieved in 35 minutes, compared to 50 minutes in case of MGOx. This effect should be expected, taking in account the different structure and characteristic data of the used forms of MG (Table 1, Scheme 1).

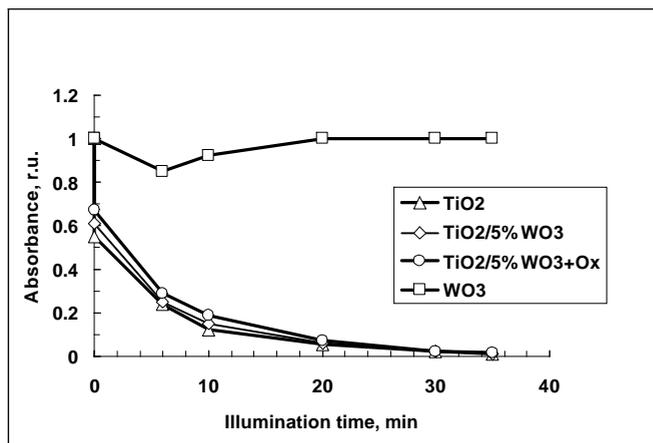


Fig. 1. Photopurification of 1.10^{-5} mol L $^{-1}$ MGH aqueous solutions under UV irradiation with the different catalyst samples.

The efficiency of MGH degradation in the presence of TiO₂/WO₃ composite is almost identical as in the presence of pure TiO₂, as can be seen in Fig. 1. However, remarkable increase in the photocatalytic activity of this composite is observed for MGOx in comparison to the pure TiO₂ (Fig. 2). The process of complete photodegradation of MGOx with the composite lasts less than 25 min in comparison with 50 min for pure TiO₂.

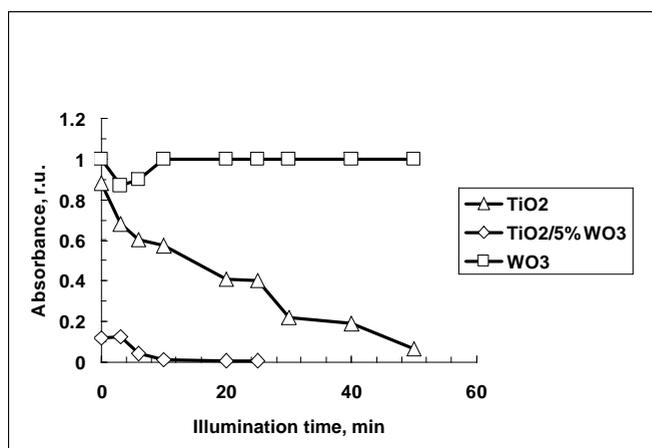


Fig. 2. Photopurification of 1.10^{-5} mol L $^{-1}$ MGOx aqueous solutions under UV irradiation with the different catalyst samples.

In order to clarify the role of the oxalate anions for the observed increased efficiency of MGOx degradation, series of experiments were performed with MGH and addition of oxalate anions as K₂C₂O₄ in the concentration range 1.5×10^{-5} mol L $^{-1}$ selected as equal to that of the dye concentration (1:1.5 molar ratio MG:C₂O₄²⁻ in MGOx). As seen from Fig. 1 the simple presence of the oxalate anions in the solution does not cause any change in the efficiency of the processes of sorption and photodegradation of MGH with TiO₂/WO₃ in comparison with pure TiO₂.

As next step the degree of equilibrium sorption ($D_s\%$) and the rate constants of photodegradation (k) are calculated according to the equations 1 and 2 and the results obtained are depicted in Table 2. The degree of sorption is calculated by the equation:

$$D_s \% = \frac{A_0 - A_{EQ}}{A_0} \times 100, \quad (1)$$

where A_0 is the absorbance at λ_{\max} of the initial dye solution and A_{EQ} is the absorbance at λ_{\max} of the dye suspension after 30 minutes contact (stirring) with the catalyst sample without illumination. The apparent rate constants are determined by the equation:

$$C = C_{in} \cdot e^{-kt}, \quad (2)$$

where C is the concentration of the dye solution at the moment t , C_{in} – the initial dye concentration and t – time of UV illumination in minutes.

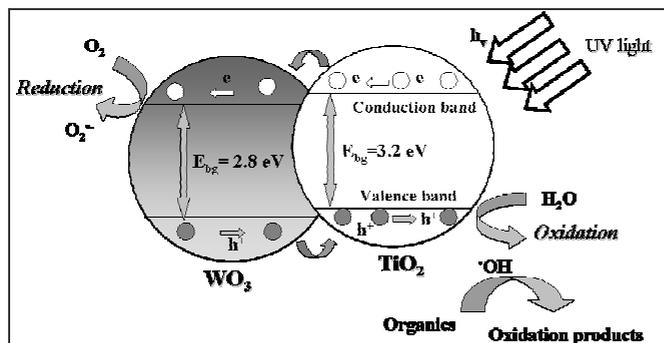
Table 2. Sorption (after 30 minutes in the dark) and apparent rate constants of photocatalysis with the different suspensions

Pollutant	MGH			MGOx	
	TiO ₂	TiO ₂ /5% WO ₃	TiO ₂ /5%W O ₃ /Ox	TiO ₂	TiO ₂ /5%W O ₃
Catalysts sample	TiO ₂	TiO ₂ /5% WO ₃	TiO ₂ /5%W O ₃ /Ox	TiO ₂	TiO ₂ /5%W O ₃
Sorption (D_s), %	45.05±0.53	38.73±0.52	32.62±0.51	12.78±0.52	91.79±0.54
Rate constant (k), min ⁻¹	0.212±0.00	0.187±0.00	0.166±0.00	0.055±0.00	0.442±0.00
	6	7	6	7	7

As can be seen, the highest degree of sorption and the highest rate constant value (Table 2) are achieved in case of MGOx degradation with TiO₂/WO₃, despite of its higher molecular mass and dye content (Table 1). Unexpectedly this effect is not observed in case of MGH even in the presence of oxalate anions. In general it is accepted that dyes photodegradation with TiO₂ is due to indirect oxidation of the organics provided by the ·OH radicals formed. In case of coupled semiconductor photocatalyst, e.g., composite TiO₂/WO₃, the mechanism of the process should follow the mechanism presented at Scheme 2. The expected advantage of the used mixed catalysts is the avoidance of the main losses of electrons and holes due to recombination, as a result of better charge separation.

The latter leads to the conclusion, that avoiding recombination is not the only reason for the observed effect of fast photodegradation of MGOx in the presence of composite photocatalyst. Most probably, the process of initial dye sorption should be also taken into account in this case. The surface of TiO₂ is positively charged. The surface of the mixed catalyst TiO₂/WO₃ is even

more positively charged in comparison to pure TiO_2 , due to the charge separation during the preparation procedure (Scheme 2).



Scheme 2. UV induced oxidation of organic pollutants on TiO_2/WO_3 catalyst

On the other hand, the negatively charged oxalate ions of MGOx (Scheme 1) can be more effectively attracted to the surface of the mixed catalyst. This is in good correlation with the highest degree of sorption calculated for MGOx at the end of the dark period (Table 2). Moreover, it might be assumed that the $\text{C}_2\text{O}_4^{2-}$ ion is playing the role of a “bridge” for direct oxidation of the two connected chromophore groups of the dye during the photocatalysis. This suggestion could be supported by the literature data stating that oxalate ion is a well recognized complex-forming ligand and acts as sacrificial electron donor [16], thus supporting the direct oxidation of the dye.

As a third step of this study the possibility of eventual transformation of MGOx into LMG during the photodegradation process is investigated in the presence of both photocatalysts TiO_2 and TiO_2/WO_3 . The pH of the initial MGOx solution was raised up to $\text{pH} > 11.5$ to ensure total decolorizing and full transformation of the MGOx to its leuco form. The UV-VIS spectra of both forms are shown in Fig. 3. The peak at 260 nm corresponds and clearly shows the existence of colorless LMG form in the solution.

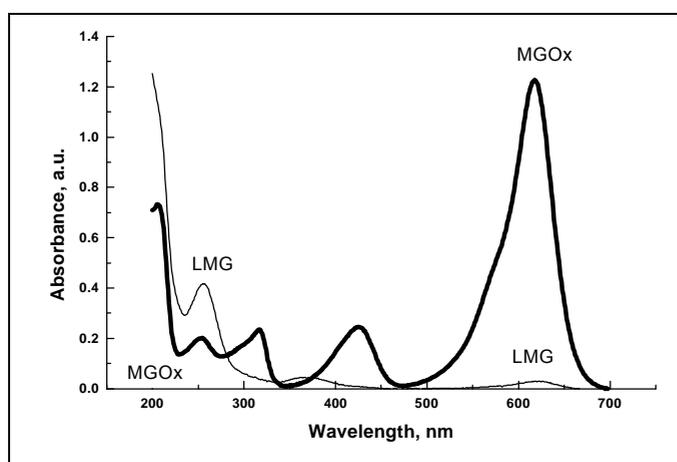


Fig. 3. Comparative UV-VIS spectra of malachite green oxalate ($\lambda_{\max} = 618$ nm) and leuco malachite green ($\lambda_{\max} = 260$ nm) solutions.

The time dependence of MGOx photooxidation with TiO_2/WO_3 is shown in Fig. 4. As seen from the figure no formation of LMG at $\lambda_{\max} = 260$ nm as a result of photodegradation process is observed.

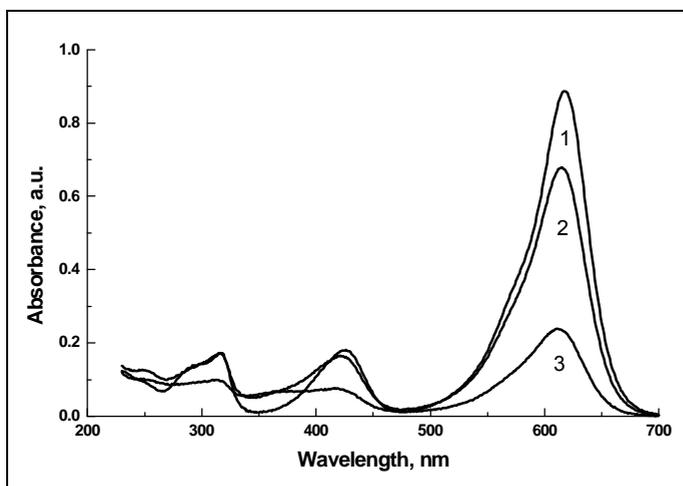


Fig. 4. Change in absorbance spectra of MGOx with the illumination time for the TiO_2/WO_3 photocatalyst. Curves 1, 2 and 3 show the absorbance spectra after 0, 10 and 30 minutes of UV irradiation of the suspension, respectively.

The presented spectra point to a shift of the characteristic absorption maximum of the dye from 618 nm to 610 nm. This shift effect is observed at UV light induced photodegradation of MGOx on TiO_2 particles [11] where N-de-methylation intermediates were separated, identified and characterized thus clarifying the mechanism of the process.

4. Conclusions

The photocatalytic degradation of malachite green in form of hydrochloride and oxalate salts in slurry using pure TiO_2 and TiO_2/WO_3 powder catalysts was studied. The obtained results reveal that in case of TiO_2 the rate of photodestruction of malachite green hydrochloride is higher than that of malachite green oxalate. The application of TiO_2/WO_3 powder catalysts twice increased the rate of degradation of MGOx. The process is accompanied by forced sorption ability during the dark period. This effect can be explained by the stronger attraction of the oxalate anion from the dye to the TiO_2/WO_3 surface, thus forming a bridge between the catalyst and the pollutant and providing direct oxidation of the dye under UV irradiation.

It is established by UV-VIS comparative analysis that during the proposed photooxidation process the formation of leuco malachite green could be neglected.

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