

Solar Light-Induced Decolorization of Safranin O Using Unmodified and Gold-Modified Semiconductor Oxides

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ABSTRACT: *Unmodified and gold-modified semiconductor oxides were used for the complete decolorization of non-buffered aqueous safranin O solutions. Photocatalytic properties of commercially available ZnO and TiO₂ (anatase nanopowder) were compared with those of gold-modified ZnO (Au/ZnO). Au/ZnO was obtained from commercial ZnO powder through direct current sputter coating. ZnO-based catalysts show significantly higher decolorization power in comparison with TiO₂. Au/ZnO show slightly higher activity than unmodified ZnO. Decolorization of safranin O using Au/ZnO was additionally tested in different types of mineral water. The decolorization efficiency in mineral waters was negatively correlated with the dry residue content (180 °C) and in all cases was less than in distilled water. The inhibiting effect of hydrogen carbonate was additionally investigated.*

KEYWORDS: *Zinc oxide; Titanium dioxide; Modification with gold; Decolorization; Safranin.*

INTRODUCTION

Dyes are vital chemicals for several industries. According to some estimates, more than 15% of all industrial water pollution arises from textile dyeing and treatment. The discharge of these colored compounds in the environment causes considerable visual pollution and represents a serious environmental and health hazard. Dyes usually show high stability under sunlight and resistance to microbial attack and temperature, therefore the large majority of these compounds are not degradable in wastewater treatment plants using conventional methods. The research of powerful and practical treatments to decolorize and degrade dyeing wastewaters to decrease their environmental impact has attracted increasing interest over the last decades. Physico-chemical, chemical and electrochemical methods, Advanced Oxidation Processes (AOPs), microbiological

treatments and enzymatic decomposition are the most important among these technologies [1-3].

AOPs, which are based on the in-situ generation of highly active chemical oxidants such as the hydroxyl radical, represent important technologies for acceleration the non-selective oxidation and degradation of a variety of hardly degradable organic contaminants in wastewater which cannot be eliminated by biological treatments [2, 4].

The application of metal oxide semiconductors in the AOPs has gained wide interest in the treatment of dye wastewater thanks to their good degradation efficiency, low toxicity and physical and chemical properties [2, 5]. On the other hand, the photocatalytic efficiency of semiconductor oxides is limited by the fast recombination of the photogenerated charge carriers [6, 7]. Deposition of noble metals on the oxide surface helps to prevent

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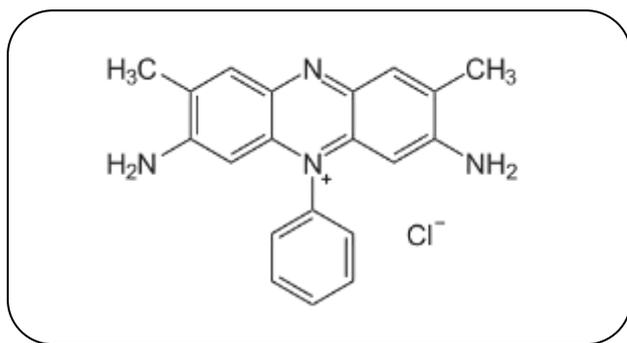


Fig. 1: Structural formula of safranin O.

the recombination of the electron-hole pairs and led to the increase of its photocatalytic activity [8-10]. Recently, the noble metal-modified ZnOs are widely used in the photocatalytic removal of different dyes [3, 11-32]. These catalysts are practically always made in solution using different synthetic pathways. There are only few examples about the use of sputter coating for obtaining such catalysts for degradation of organic dyes [3, 20, 22]. To best of my knowledge, there are no papers dealing with gold-modified ZnO obtained by a sputtering technique for the photocatalytic degradation of safranin O dye (Fig. 1).

In this work a gold-modified ZnO (Au/ZnO) prepared by sputter coating and commercially available unmodified ZnO and TiO₂ (anatase nanopowder) was applied for photocatalytic decolorization of safranin O. The photocatalytic decolorization was compared with photolytic one. The most efficient catalyst (Au/ZnO) was tested in different types of mineral water also. The effect of hydrogen carbonate on decolorization efficiency was additionally investigated.

EXPERIMENTAL SECTION

Chemicals and solutions

A solution of safranin O (Sigma-Aldrich) was prepared by dissolving the dye in double distilled or mineral water ($C_{\text{dye}} = 2.72 \times 10^{-5}$ mol/dm³, $A_{515 \text{ nm}} = 1.00$). TiO₂ nanopowder (Sigma-Aldrich, anatase, <25 nm, 99.7% trace metals basis) and ZnO powder (Kemika, p.a., min. 99%) were used as received. Au/ZnO was prepared according to the procedure described below. To remove the excess dissolved carbon dioxide the carbonated mineral waters were mixed for 3 hours before experiments using a magnetic stirrer.

Preparation of Au/ZnO

The gold-modified ZnO catalyst was prepared from pure ZnO powder by direct current sputtering using a BAL-TEC SCD-005 (Bal-Tec) sputter coater. A thin layer of ZnO powder (500 mg) was put in a 5 cm diameter Petri-dish and sputtered with gold in 4 consecutive steps. The watch-glass covered dish was intensively shaken between sputtering steps. The sputtering parameters were as follows: working time, 4×90 s; used current, 30 mA; working distance, 50 mm) [3].

Photodegradation

Identical borosilicate glass beakers (IsoLab, 013.01.101) containing 25.00 cm³ of crystal violet solution with or without catalyst were subjected to natural solar irradiation in consecutive sunny summer days. All catalyst-containing solutions were mixed during the experiments to minimize sedimentation. All experiments were done in duplicate. When the time of degradation was higher than the daily available insolation time, the samples were put into the dark before the next insolation session (next day).

Visual decolorization monitoring

During the investigation of the effect of catalyst amount, mineral water type and hydrogen carbonate concentration on decolorization efficiency the decolorization of the samples was monitored visually (the time for the total decolorization was determined and mutually compared using the relative scale taking 100% for the most efficient system). Kinetic investigations were done by spectrophotometry according to the procedure described below.

Spectrophotometry

Spectrophotometric investigations were performed on a Jenway 6300 single-beam visible spectrophotometer (Jenway, United Kingdom) using quartz cuvettes with 1.00 cm path length. The samples for the analysis were filtered through appropriate membrane filters. The degradation of safranin O was monitored at 515 nm.

RESULTS AND DISCUSSION

Effect of catalyst concentration

One of the most important steps in catalytic process optimization is the determination of the optimal catalyst

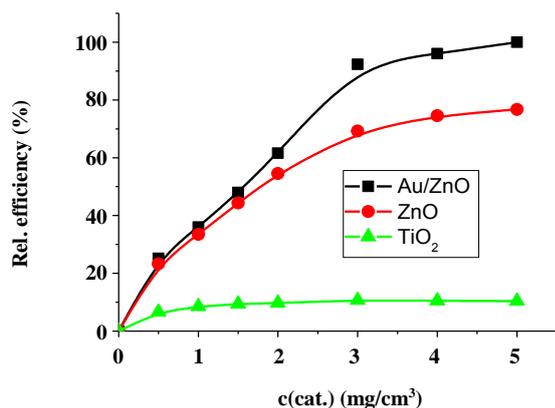


Fig. 2: Effect of catalyst concentration on decolorization efficiency.

point of view. In this phase, a visual monitoring was applied concentration, both from the chemical and economical for the determination of the time of total decolorization for all investigated catalytic systems at seven different concentration levels in 0.5–5.0 mg/cm³ range. It is clearly visible that ZnO-based catalysts show higher decolorization efficiency in comparison with TiO₂ at all concentrations (Fig. 2). At the same time, it is also clear that in the case of ZnO-based systems the catalyst concentration has a more pronounced effect on the decolorization rate than in the case of TiO₂. In the case of ZnO-based systems, the decolorization efficiency rose in the whole investigated range, with moderate changes over 3 mg/cm³ level. The ZnO and Au/ZnO practically did not show significant differences in efficiency at lower concentrations, while the difference was pronounced at higher ones (≥ 1.5 mg/cm³), where Au/ZnO was much more efficient. In the case of TiO₂, the efficiency increased to 1.0 mg/cm³ level and remained unchanged at higher ones. Taking in account that higher catalyst concentration (≥ 1.0 mg/cm³) in case of TiO₂ did not result in higher efficiency and also the economic side of view, which do not justify the use of high catalyst concentrations, especially in case of noble metal-modified ones, further comparisons were done at 1.0 mg/cm³ level.

Decolorization kinetics

Decolorization kinetics of all investigated systems was monitored spectrophotometrically (Fig. 3). The photolytic degradation was also monitored under the same conditions. Generally, the efficiency of ZnO-based

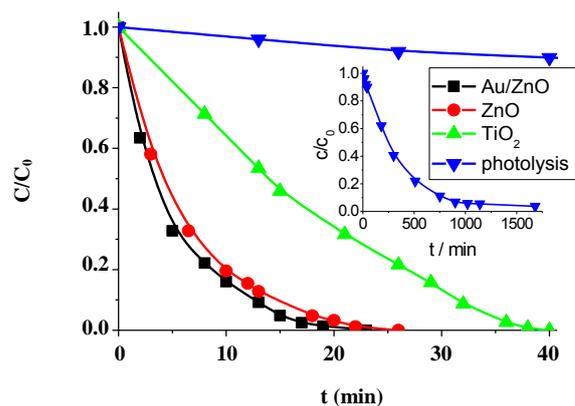


Fig. 3: Kinetics of safranin O decolorization using different procedures; $c_{cat} = 1.00$ mg/cm³.

catalysts was undoubtedly higher in comparison with TiO₂. Although ZnO showed quite high activity, the gold-modified catalyst slightly surpassed its efficiency. The photolytic degradation was the slowest from the investigated ones. The half-life of safranin O was just 3.3 and 4.2 min for Au/ZnO and ZnO, respectively. In the case of TiO₂, the half-life was 13.9 min. The photolytic half-life was 249.6 min. More than 95% of safranin O was decolorized after 15.1, 18.1, 34.5 and 1286.7 min for Au/ZnO, ZnO, TiO₂ and photolysis, respectively.

Effect of mineral water type

The efficiency of the Au/ZnO catalytic system was tested in different types of mineral water (Table 1) and was compared with the process of distilled water. It was clearly visible that the dry matter content at 180 °C (which correlates well with the hydrogen carbonate content) influences the decolorization process significantly (Fig. 4). The process was slower in waters with high dry matter (and hydrogen carbonate) content, while in slightly mineral one was fast and comparable to the process in distilled water.

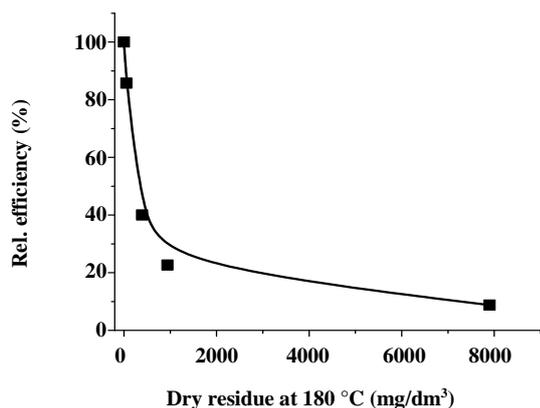
Effect of hydrogen carbonate

To prove the significant effect of hydrogen carbonate on decolorization efficiency, the degradation over Au/ZnO was studied also in model solutions containing different hydrogen carbonate concentrations (Fig. 5, upper curve). The change of the degradation efficiency with the increase of hydrogen carbonate concentration show decreasing trend like in case of mineral waters,

Table 1: Selected characteristics of the investigated mineral waters.

Water type / Selected parameters*	Hydrocarbonates (mg/dm ³)	Dry residue (at 180 °C) (mg/dm ³)
Mineral water 1	42.7	55
Mineral water 2	415	392
Mineral water 3	994.3	939
Mineral water 4	7800	7900

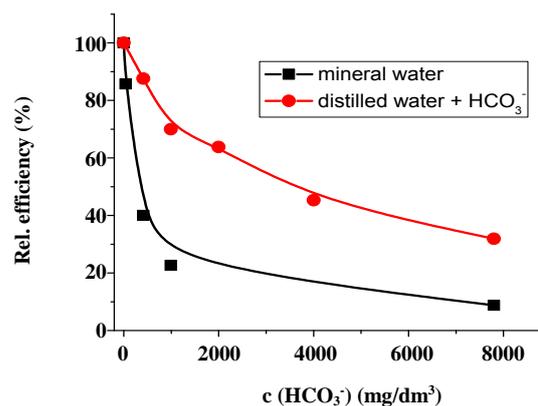
* declared amount

Fig. 4: Effect of dry residue content on decolorization efficiency over Au/ZnO; $c_{cat} = 1.00 \text{ mg/cm}^3$.

but the decrease was much lower than in mineral waters with the same hydrogen carbonate concentration. It is clear that hydrogen carbonate has a significant inhibitory effect on the decolorization in all investigated systems (Fig. 5, both curves), but the presence of further ions and possibly different pH in mineral waters has an additional negative influence on the degradation process (Fig. 5, lower curve). More complex research is needed for complete explanation of this difference.

CONCLUSIONS

Decolorization of non-buffered safranin O solutions was performed using a gold-modified ZnO prepared by sputter coating, unmodified ZnO and TiO₂ (anatase nanopowder). ZnO-based catalysts showed significantly higher decolorization efficiency in comparison with TiO₂ at all catalyst concentration levels. The efficiency of Au/ZnO was very similar to this of unmodified ZnO at lower concentrations, while surpassed its efficiency at higher ones ($\geq 1.5 \text{ mg/cm}^3$). The decolorization was additionally investigated in different mineral waters as real systems in comparison with suspension in distilled

Fig. 5: Effect of hydrogen carbonate content on decolorization efficiency over Au/ZnO; $c_{cat} = 1.00 \text{ mg/cm}^3$.

water. The dry residue content of mineral waters had a significant inhibitory effect on the decolorization efficiency of Au/ZnO. The effect of hydrogen carbonate concentration - which is strongly connected to the dry residue content - was additionally investigated. It was shown that the presence of hydrogen carbonate lowers the decolorization rate in model solutions containing different hydrogen carbonate concentrations, but this effect was much less pronounced than in mineral waters with the same hydrogen carbonate content. The presence of further ions and possibly different pH in mineral waters greatly decreased the decolorization rate.

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