Title: Facile method to immobilize ZnO particles on glass spheres for the photocatalytic treatment of tannery wastewater

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Abstract: In order to apply the photocatalytic processes on a real scale for the treatment of industrial wastewaters, the use of slurry reactors employing suspended photocatalysts is not suitable due to the need for an uncomfortable and expensive separation phase of photocatalyst. To overcome this disadvantage, the photocatalyst particles must be immobilized on a transparent support: our work proposes, for this reason, a simple and cost effective method for the deposition of ZnO photocatalyst on glass spheres in order to formulate a structured photocatalyst effective in the treatment of aqueous solutions containing various organic dyes, commonly used in the tannery industries and in the treatment of a real wastewater at high COD content (11 g/L) coming from the refining unit of the tanning process. In particular, ZnO was immobilized on glass spheres (ZnO/GS) with a simple dip coating method, starting from zinc acetate aqueous solution, without using complexing agent and strong basic compounds. The optimization of ZnO amount on glass spheres was evaluated employing Acid Blue 7 dye, as model pollutant. In particular, it was found that best performances in terms of discoloration and mineralization of the target dye were obtained using the photocatalyst with a ZnO loading equal to 0.19 wt% (ZnO_ac1), prepared through only one dip-coating step. Moreover, the ZnO_ac1 photocatalyst can be easily separated from the reaction mixture, maintaining excellent photocatalytic activity and durability even after several reuse cycles. Finally, ZnO_ac1 showed a high photocatalytic activity in the treatment of the real wastewater, obtaining a COD removal equal to 70% after 180 minutes of UV light irradiation.

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Dear Editor,

I kindly ask you to consider for possible publication in "**Journal of Colloid and Interface Science**", our research paper entitled:

Facile method to immobilize ZnO particles on glass spheres for the photocatalytic treatment of tannery wastewater

The manuscript matches the aims and scope of the journal because it is an original and novel in relation to some fields relevant for the journal. Specifically, ZnO photocatalyst was successfully immobilized on glass spheres by a facile method based on dip-coating technique, starting from an aqueous solution of zinc acetate, without using complexing agent and strong basic compounds. The experimental results demonstrate that the preparation method allows to obtain a highly active structured catalyst for the treatment of tannery wastewater, that could be applicable on a real scale, since it is easily removable at the end of the purification process and readily available for several cycles of treatment.

Therefore, the results presented in the manuscript are an encouraging step forward in the possible application of heterogeneous photocatalytic technology in the elimination of hazard environmental pollutants especially for the degradation of bio-recalcitrant organic contaminants. The present paper has not published previously - also not in any other language- and it is not under consideration for publication elsewhere; its publication is approved by all authors.
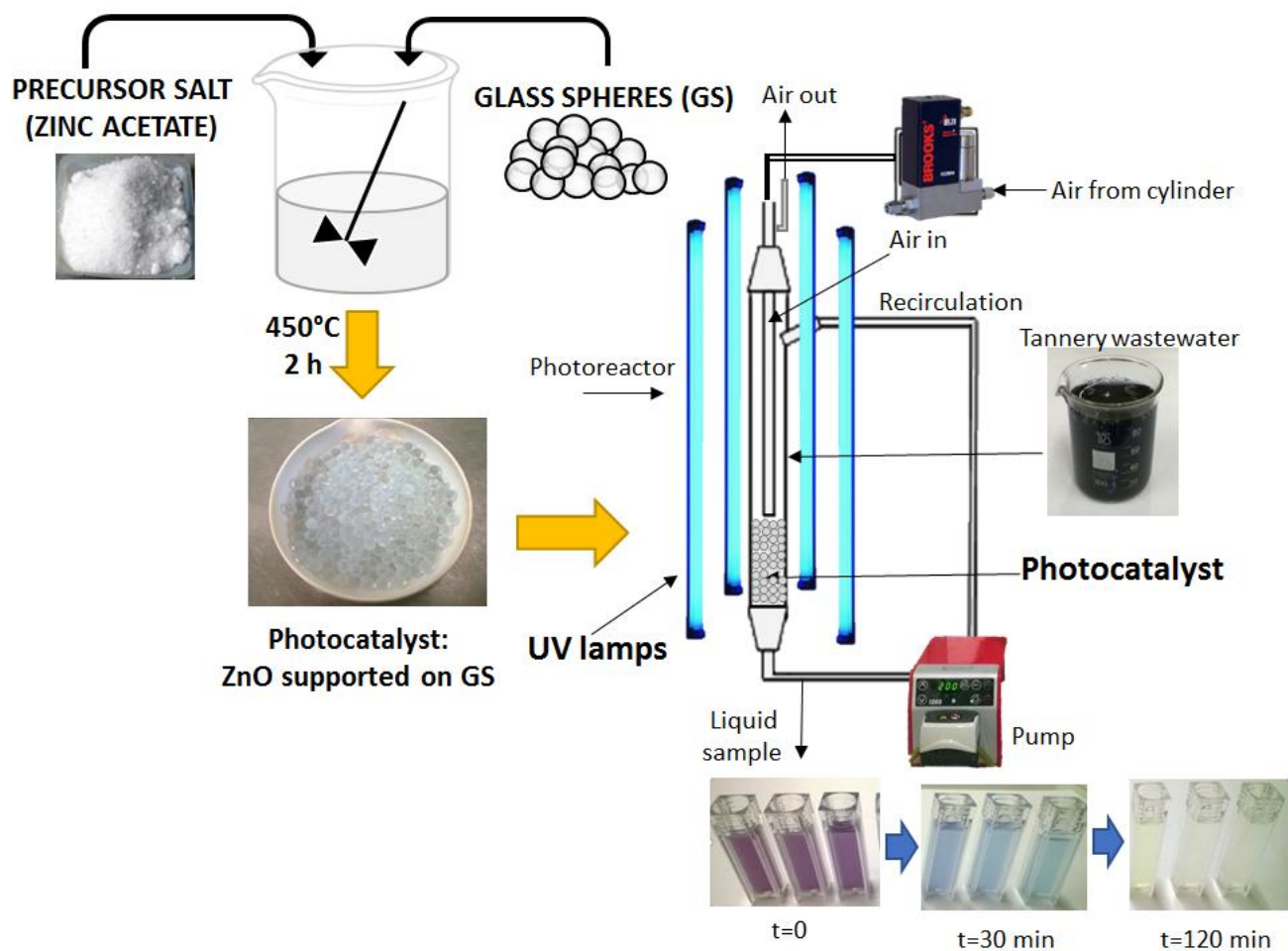
Sincerely,

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*3: Graphical Abstract

Facile method to immobilize ZnO particles on glass spheres for the photocatalytic treatment of tannery wastewater

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Abstract

In order to apply the photocatalytic processes on a real scale for the treatment of industrial wastewaters, the use of slurry reactors employing suspended photocatalysts is not suitable due to the need for an uncomfortable and expensive separation phase of photocatalyst. To overcome this disadvantage, the photocatalyst particles must be immobilized on a transparent support: our work proposes, for this reason, a simple and cost effective method for the deposition of ZnO photocatalyst on glass spheres in order to formulate a structured photocatalyst effective in the treatment of aqueous solutions containing various organic dyes, commonly used in the tannery industries and in the treatment of a real wastewater at high COD content (11 g/L) coming from the refining unit of the tanning process. In particular, ZnO was immobilized on glass spheres (ZnO/GS) with a simple dip coating method, starting from zinc acetate aqueous solution, without using complexing agent and strong basic compounds. The optimization of ZnO amount on glass spheres was evaluated employing Acid Blue 7 dye, as model pollutant. In particular, it was found that best performances in terms of discoloration and mineralization of the target dye were obtained using the photocatalyst with a ZnO loading equal to 0.19 wt% (ZnO_ac1), prepared through only one dip-coating step. Moreover, the ZnO_ac1 photocatalyst can be easily separated from the reaction mixture, maintaining excellent photocatalytic activity and durability even after several reuse cycles. Finally, ZnO_ac1 showed a high photocatalytic activity in the treatment of the real wastewater, obtaining a COD removal equal to 70% after 180 minutes of UV light irradiation.

Keywords: ZnO, glass spheres, structured catalyst, dip-coating, tannery wastewater

1. Introduction

The tannery industry is one of the most productive sectors for the economies of countries whose industrialization is proceeding rapidly, such as China, Turkey, Brazil, Pakistan, Bangladesh and India [1]. The tanning of leather is one of the most environmentally impacting processes due to the huge consumption of water resources and chemicals. Tannery wastewater typically is dark brown coloured waste, having high chemical oxygen demand (COD), biological oxygen demand (BOD), chromium (III) and phenolics [1-4]. In particular, the organic pollution is imputable to the residues of leather, fatty substances and organic dyes. So, these wastewaters are intensely coloured and have a quite penetrating smell [1]. Many studies have been carried out on the harmfulness of substances commonly present in wastewater of the tanning industry [5]. The effect on the ecosystem is also attributed to the intense coloration of wastewater that, by inhibiting the penetration of sunlight, reduces the activity of photosynthesis of aquatic flora and therefore the water oxygenation making the water environment inhospitable for most forms of life [1, 5]. As a consequence, the wastewaters treatment becomes compulsory, in order to reduce the pollution load. Its conventional methods generally include physical-mechanical pre-treatments followed by chemical and biological steps for the removal of organic matter. However, these traditional processes generate significant amounts of sludge and in particular they are not able to remove bio-recalcitrant compounds such as the organic dyes used in the tannery industries [5]. For this reason, the search of new technologies for wastewater treatment is moving towards innovative processes that allow the removal of these hardly biodegradable substances. In particular, advanced oxidation processes (AOPs) have attracted an increasing interest, relying on the ability to produce reactive species, such as hydroxyl radicals (HO•) [6-9]. Among the AOPs, heterogeneous photocatalysis has been intensively studied because of its ability to degrade the pollutants into nontoxic molecules without forming any kind of sludge; at the same time semiconductors (such as TiO_2 and ZnO) have been widely investigated for this purpose [10-16]. Although TiO_2 is the most used photocatalyst, in recent years ZnO performances in the photocatalytic removal of environmental pollutants have gained more attention. It is reported

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that the reaction mechanisms of photocatalytic degradation on ZnO are similar to that on TiO$_2$ [17-19]. However, it was shown that ZnO was more effective than TiO$_2$ [17, 20-22]. Some research papers have evidenced the effectiveness of ZnO in the photocatalytic removal of several organic dyes [21-24]. On the other hand, the use of photocatalysts in powder form implies their separation after the treatment process[25]. Therefore photocatalytic slurry reactors are not suitable for large scale applications of photocatalytic systems: this drawback has revealed the necessity to immobilize the photocatalyst on a transparent support [26]. As far as this feature concerns both the geometry of the support and the characteristics of the light source deserve more attention in order to ensure high process efficiency. In particular, the thickness of the supported photocatalyst should be small enough to ensure a low photon scattering; at the same time, it is necessary to use an appropriate light source to avoid poor photocatalyst excitation or a fast recombination of the photogenerated electrons-holes pair with the consequent decrease in photocatalytic activity [27]. In recent years, inert materials, such as glass, polyethylene fibers, cement, silica gel, quartz fibers, glass fibers, glass beads, ceramics, cellulose membranes, polymeric and zeolite have been used as support for ZnO [28]. There are several ZnO deposition techniques, such as the chemical vapour deposition from metallorganic compounds [29], sol gel processes [30], laser deposition [31], thermal oxidation [30, 32] or chemical bath deposition [33] . However, the search for a simple, effective and economical method for the deposition of ZnO on a transparent support is nowadays an interesting challenge. There are different studies about the deposition techniques of ZnO films on a support using aqueous solutions of precursor salts [32, 34, 35]. Literature data reported that, among the precursor salts, the use of zinc acetate guaranteed a uniform precipitation with deposition of a thin and transparent film, particularly suitable for photocatalysis [35]. However, the most studied methods report the use of complexing agent, such as ethylenediamine [33] and the adjustment of solution pH containing the precursor salt by using strong basic compounds, such as NaOH [36]. Therefore, these preparation methods are expensive and time consuming, due to their sophistication. For this reason, the aim of our work is to propose a simple and cost-effective method for the deposition of ZnO photocatalyst

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on glass spheres (ZnO/GS), in order to formulate an effective structured photocatalyst in the treatment of aqueous solutions containing different organic dyes (commonly used in the tannery industries) and in the depollution of a real wastewater coming from an Italian tannery industry.

2. Experimental

2.1 Materials and methods

The used support for the deposition of ZnO was pyrex spheres (Microglass Heim), with a diameter of 5 mm. For the preparation of the structured photocatalyst, a solution of zinc dihydrate acetate provided by Sigma-Aldrich (99%) was used. In this work Acid blue 7 (Globalchem), Red RTN (TFL), Yellow 4GL (TFL), Acid Black 210 (Globalchem) and Luganil Orange GGC (BASF), commonly used in leather dyeing processes, were chosen as model pollutants. Moreover, a real wastewater sample taken from the refining unit of a tanning industry located in Campania (Italy) was also used in photocatalytic tests. This real wastewater sample had a very dark colour, similar to purple, with density and viscosity comparable to water. The pH was around 6.5 with a COD of about 11 g/L.

2.2 Stuctured photocatalysts preparation

The pyrex glass spheres were pre-treated by washing with bi-distilled water and then calcined at 450°C for 2 h. The immobilization of ZnO on glass spheres has been performed through dip-coating technique. In particular, in a beaker, placed on a magnetic stirring plate set at a temperature of 80 °C, 10 g of zinc acetate were solubilized in 60 ml of bi-distilled water. In the obtained solution, 100 g of glass spheres were immersed and maintained under stirring condition for 30 min. The spheres were then separated from the solution and calcined at 450°C for 2 h in static air. The dip-coating and calcination processes were repeated for three times for finding the best ZnO amount

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immobilized on the glass spheres surface. For comparison, ZnO in powder form (ZnO_ac) was obtained by thermal treatment of zinc dihydrate acetate in static air at 450°C for 2 h.

All prepared samples are reported in Table 1. In order to remove the excess of ZnO particles not immobilized on glass surface, several cycles in an ultrasonic bath (CEIA-CP104) were effected until to reach a ZnO stable loading. The ZnO amount immobilized on glass spheres has been measured using precision balance (Mettler Toledo).

Table 1

2.3 Characterization techniques

The prepared photocatalysts were characterized from a chemical-phisical point of view utilizing several techniques. X ray diffraction measurements (XRD) were carried out using an X-ray micro diffractometer Rigaku D-max-RAPID, using Cu-Kα radiation. Raman spectra were obtained at room temperature with a Dispersive Micro Raman (Invia, Renishaw) equipped with 514 nm laser in the range of 100-2500 cm^{-1} Raman shift. Scanning electron microscopy (SEM) (Assing, mod. LEO 420) was used to characterize the morphology of ZnO/GS.

2.4 Photocatalytic activity test

Photocatalytic activity tests were carried out using a pyrex cylindrical photoreactor (I.D=3 cm) equipped with a peristaltic pump (Watson Marlow) for the continuous mixing of the aqueous solution. In particular, the recirculated liquid flow rate was in the range 34-130 mL/min. Moreover, an air distributor device is used for ensuring the oxygen presence inside the solution (air flow rate=140 Ncm^{3}/min).

Four UV lamps (Philips TL 8W / 08 F8 T5 / BLB, nominal power of 8W and emission peak at 365 nm) were used as light sources and they have been positioned around the external surface of the reactor. The photon flux at reactor external surface, obtained through actinometrical technique using a spectro-radiometer (StellarNet Inc), was 25 mW/cm^2 [37]. The amount of structured catalyst was 50 g. The volume of the treated aqueous solution was 60 mL. Before the irradiation with UV light, the system was left in dark for 2 h until reaching adsorption-desorption equilibrium of the pollutants on the photocatalyst surface. In order to find the optimal loading of ZnO on glass spheres, photocatalytic tests were carried out using the Acid blue 7 dye. The effectiveness of the optimized photocatalyst was then evaluated in the degradation of additional organic dyes (Red RTN, Yellow 4GL, Acid Black 210 and Luganil Orange GGC).

2.5 Analytical measurements

Liquid samples were taken from the reactor at different times and analysed with a Thermo Fisher Evolution 201 UV-Vis spectrophotometer to determine the change in dyes concentration through the measurement of the absorbance at λ = 638, 515, 415, 572 and 446 nm for Acid blue 7, Red RTN, Yellow 4GL, Acid Black 210 and Luganil Orange GGC, respectively.

The TOC of aqueous samples was measured by the high temperature combustion method on a catalyst (Pt-Al$_2$O$_3$) in a tubular flow microreactor operated at 680 °C [38, 39].

For the real wastewater, the photocatalytic activity has been evaluated by monitoring the COD during the irradiation time. The COD measurement has been performed according to a standard method [40].

3. Results and Discussion

3.1 Photocatalysts characterization

3.1.1 X-ray diffraction (XRD)

XRD measurement results for the ZnO/GS are shown in Figure 1.

Figure 1

No signals are detectable for uncoated pyrex spheres due to the amorphous structure of the glass [25]. On the contrary, for ZnO_ac1, ZnO_ac2, ZnO_ac3 samples, it is possible to observe peaks located at 2θ 31.72°, 34.38°, 36.25°, 47.56° and 56.65°, respectively corresponding to the (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) planes of ZnO with hexagonal wurtzite crystal structure [41]. Moreover, no diffraction peaks of other impurities were detected, underlining that the substance deposited on the glass substrate only belongs to ZnO [42]. The average crystallite sizes of ZnO immobilized on glass spheres were calculated using the peak at 2θ ~ 36° through the Debye–Sherrer's equation (Table 1). The obtained values for all the structured photocatalysts were the same as unsupported ZnO, as previously observed in literature [35].

These last results evidenced that ZnO deposition on glass spheres using zinc acetate avoids alteration of crystallographic characteristics of ZnO, as evidenced by the unchanged size of the crystallites even after more dip-coating steps.

3.1.2 Raman

The prepared structured photocatalysts were also analyzed by Raman spectroscopy and the results are reported in Figure 2 in comparison with unsupported ZnO (ZnO_ac).

Figure 2

The glass support did not evidence Raman signals, whereas all the ZnO/GS samples showed bands related to bulk zinc oxide [43]. These bands became better defined and more intense by increasing the ZnO amount deposited on glass spheres. The Raman peaks at around 437 cm^{-1} and 580cm^{-1} were assigned to ZnO E_2 (high) and A_1 longitudinal optical (LO) modes, respectively. The relatively higher intensity of the E_2 (high) mode as compared to the other signals indicates that the ZnO particles immobilized on glass spheres have a hexagonal wurtzite phase with good crystallinity [44] in agreement with XRD results (Figure 1). The peak E_1(LO) positioned at about 584 cm^{-1} is ascribable to the formation of some defects, such as an absence of oxygen, interstitial Zn, and the free carrier lack [43]. The weak intensity of this peak may suggest a relatively low density of defects in ZnO crystals [43, 44].

3.1.3   SEM images results

The surface morphology of ZnO/GS samples is studied by SEM microscopy and the obtained results are presented in Figure 3. The SEM images of the surface of the support shows only the presence of some surface cracking, due to the roughness of the glass induced by the thermal pre-treatment of the support (Figure 3 a).

Figure 3

After the first dip-coating step (ZnO_ac1), it was possible to observe the presence of an almost continuous ZnO film, despite some visible cracks and a small fraction of glass surface not covered by ZnO particles (Figure 3 b).

The second dip-coating step (ZnO_ac2) induced the formation of ZnO aggregates with different size and without homogeneous distribution (Figure 3 c).

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The third dip-coating step (ZnO_ac3) generated aggregates larger than 2 microns, and the smaller ZnO particles are completely covered and visible only in certain areas (Figure 3 d).

3.2 Photocatalytic activity results

3.2.1 Influence of ZnO amount on glass spheres

In order to define the best amount of ZnO deposited on glass spheres, Acid blue 7 has been chosen as model dye. The comparison between the photocatalytic activity in terms of discoloration and mineralization is reported in Figure 4 and 5, respectively.

In the case of the test with the support, a very slight discoloration is noticed during the irradiation time (Figure 4). However, there isn't variation in the TOC value for this sample (Figure 5). This result demonstrate that Acid blue 7 dye has only a slight photolysis effect, confirming that it is suitable as reference dye.

Figure 4

Figure 5

During the photocatalytic tests, it was possible to observe a progressive decrease of Acid blue 7 concentration (Figure 4), achieving a discoloration of about 95, 80 and 68 % with the ZnO_ac1, ZnO_ac2 and ZnO_ac3 samples, respectively after 60 min of irradiation time. In particular the best performances in terms of discoloration and mineralization of the dye were obtained with the ZnO_ac1 photocatalyst. In fact, with this sample, the complete discoloration of Acid blue 7 was achieved after 120 min of irradiation time (Figure 4) and the dye mineralization was about 91% after 240 min of irradiation time (Figure 5). However, the performances of ZnO_ac2 photocatalyst are better than ZnO_ac3, due to a worsening of the ZnO surface distribution on glass spheres as the number of dip-coating steps increases (as observed from SEM images). This means that the amount

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of photocatalyst added after the second dip-coating step covers the lower ZnO layers deposited previously on the spheres, with a consequent inhibition of photocatalytic activity [26]. From these results, it is evident that the optimal content of ZnO on glass spheres was equal to 0.196 wt% and it is reached after only one dip-coating step. Consequently ZnO_ac1 structured photocatalyst was chosen to inverstigate the influence of operating conditions.

3.2.1 *Recyclability of ZnO_ac1 photocatalyst*

The recyclability of catalysts is one of the most important parameters to be investigated for a photocatalyst formulation [26, 45, 46]. Especially with regard to ZnO based photocatalysts, this aspect is crucial, because literature studies report photosensitivity and photocorrosion phenomena of ZnO in aqueous solution under UV irradiation, which causes a significant reduction in photocatalytic efficiency [47-49]. For this reason, with the purpose to evaluate the stability of the formulated ZnO_ac1 photocatalyst, recycle experiments under UV light irradiation were performed for five cycles with the same sample and experimental conditions (Figures 6 and 7).

Figure 6

Figure 7

The results demonstrated that there was the complete discoloration (Figure 6) after 120 min of irradiation time for all the cycles with a TOC removal of about 90% (Figure 7) after 240 min of irradiation time. These results confirm that the photocatalytic activity of ZnO_ac1 was nearly unchanged indicating that there was no photocorrosion phenomena of ZnO and demonstrating its stability after several reuse cycles too.

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3.2.2   Photocatalytic tests at different liquid flow rate

In order to understand any effects of kinetic limitation due to transport phenomena, several tests with ZnO_ac1 photocatalyst were carried out by changing the flow rate of recirculated fluid. The tested flow rates are 35, 65, 95 and 130 mL/min. The Acid blue 7 concentration was 50 mg/L for all the photocatalytic tests.

The obtained results in terms of discoloration and mineralization during the irradiation time are shown in the Figure 8 and 9, respectively.

Figure 8

Figure 9

Both the discoloration (Figure 8) and mineralization (Figure 9) did not change with the increase of recirculated liquid flow rate. These last results clearly evidenced that no limitation to the mass transfer of Acid blue 7 dye from the liquid phase to the photoactive surface took place, confirming that the overall Acid blue 7 photocatalytic degradation rate is controlled by kinetics [50].

3.2.3   Influence of the initial dye concentration

The effect of initial Acid blue 7 concentrations on the photocatalytic activity of ZnO_ac1 was studied in the range 12.5-100 mg/L at recirculated liquid flow rate of 130 mL/min. Figure10 and 11 show the Acid blue 7 discoloration and mineralization behavior, respectively.

Figure 10

Figure 11

In particular, the complete discoloration of the dye has been achieved in 240 min of irradiation time for all the tested Acid blue 7 concentrations. The same results were obtained for the mineralization (Figure 11). In fact, for all the tested initial concentrations, a similar TOC removal (in the range 87-93%) was obtained after 240 min of irradiation time. However, From Figure 10 and 11, it can be noted that, for irradiation times lower than 240 min, the photocatalytic activities slightly decreased only when the initial dye concentration in solution was equal to 100 mg/L. This may be explained by the fact that the photonic flow was mitigated when the Acid blue 7 concentration in solution was increased from 50 up to 100 mg/L, hence the absorption of photons by ZnO immobilized on glass spheres decreased, and consequently the photocatalytic reaction rate is reduced [38, 51].

3.2.4   *Efficiency of ZnO_ac1 in the removal of different tannery dyes*

In order to verify the efficiency of ZnO_ac1 structured photocatalyst in the removal of tannery dyes different from the Acid blue 7, additional photocatalytic experiments were carried out on aqueous solutions containing the dyes described in the section 2.1 at initial concentration of 50 mg/L. The results in terms of discoloration and mineralization are shown in Figure 12 and 13, respectively.

Figure 12

Figure 13

As it was possible to observe, the optimized ZnO_ac1 photocatalyst was effective in the removal of all the tested dyes. In particular, for Acid Black 210 and Yellow 4GL dyes similar discoloration degree (87%) and TOC removal (about 45% for Yellow 4GL and 47 % for Acid Black 210) were achieved after 240 min of irradiation. While, at the same irradiation time, in the case of Luganil Orange GGC, the structured photocatalyst evidenced discoloration (98%) and TOC removal

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performances (72%) higher than the other analysed dyes. Finally, ZnO_ac1 photocatalyst showed a slight lower photocatalytic activity in the degradation of Red RTN dye.

With regard to the comparison with literature about the degradation of organic dyes, it must be considered that the most studied ZnO based photocatalysts are tested in powder form [52-55] making their use very difficult from a practical point of view. Thus, ZnO immobilized on glass spheres could be considered a promising structured photocatalyst for wastewater purification processes, without needing to recovery the catalyst from the treated solution. Several studied reported also the immobilization of ZnO particles on different macroscopic glass supports, such as glass plates [56] and spiral-shaped glass [57]. These photocatalysts were tested mainly in the photocatalytic degradation of textile dyes, whereas no specific paper devoted to the photocatalytic removal of tannery dyes using ZnO based structured photocatalysts has been still published.

3.2.5   *Photocatalytic test on real wastewater*

The effectiveness of the optimized ZnO_ac1 structured photocatalyst was finally evaluated in the treatment of a real wastewater sample coming from the refining unit of the tanning process. The results are shown in Figure 14 in terms of COD behavior as a function of run time. In dark conditions, the decrease of COD was equal to about 5%. After the dark period, UV lamps were turned on and the photocatalytic degradation process started, determining a progressive decrease of COD, achieving a removal of about 70 % after 180 min of irradiation time.

Figure 14

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4. Conclusions

The results of this study showed that ZnO photocatalyst was successfully immobilized on glass spheres (ZnO/GS) by a facile method based on dip-coating technique, starting from an aqueous solution of zinc acetate, without using complexing agent and strong basic compounds. The amount of the ZnO on glass spheres increased with the number of dip-coating steps and varied from 0.19 wt% (one dip-coating step) up to 0.35 wt% (three dip-coating steps). The structure of ZnO/GS photocatalysts were characterized by different techniques. In particular, Raman analysis and XRD patterns of ZnO/GS samples evidenced that the immobilized ZnO exhibited crystalline structure very similar to that of the unsupported one, evidencing that ZnO deposition on glass spheres using zinc acetate avoids alteration of crystallographic characteristics of the semiconductor, even after more dip-coating steps. The efficiency of structured photocatalysts was evaluated in the discoloration and mineralization of recalcitrant contaminants like tannery dyes under UV light irradiation. The best photocatalytic performances were obtained with the ZnO/GS photocatalyst with a ZnO loading equal to 0.19 wt% (ZnO_ac1). This optimized photocatalyst showed a very good performance, after several reuse cycles too. Moreover ZnO_ac1 photocatalyst was effective in the depollution of a real wastewater at high COD (11 g/L) coming from the refining unit of the tanning process, reaching 70 % of COD removal in 180 min of irradiation time.

These results demonstrate that the preparation method (used for the immobilization of ZnO on glass spheres) allows to obtain a highly active structured catalyst for the treatment of tannery wastewater, that could be applicable on a real scale, since it is easily removable at the end of the purification process and readily available for several cycles of treatment.

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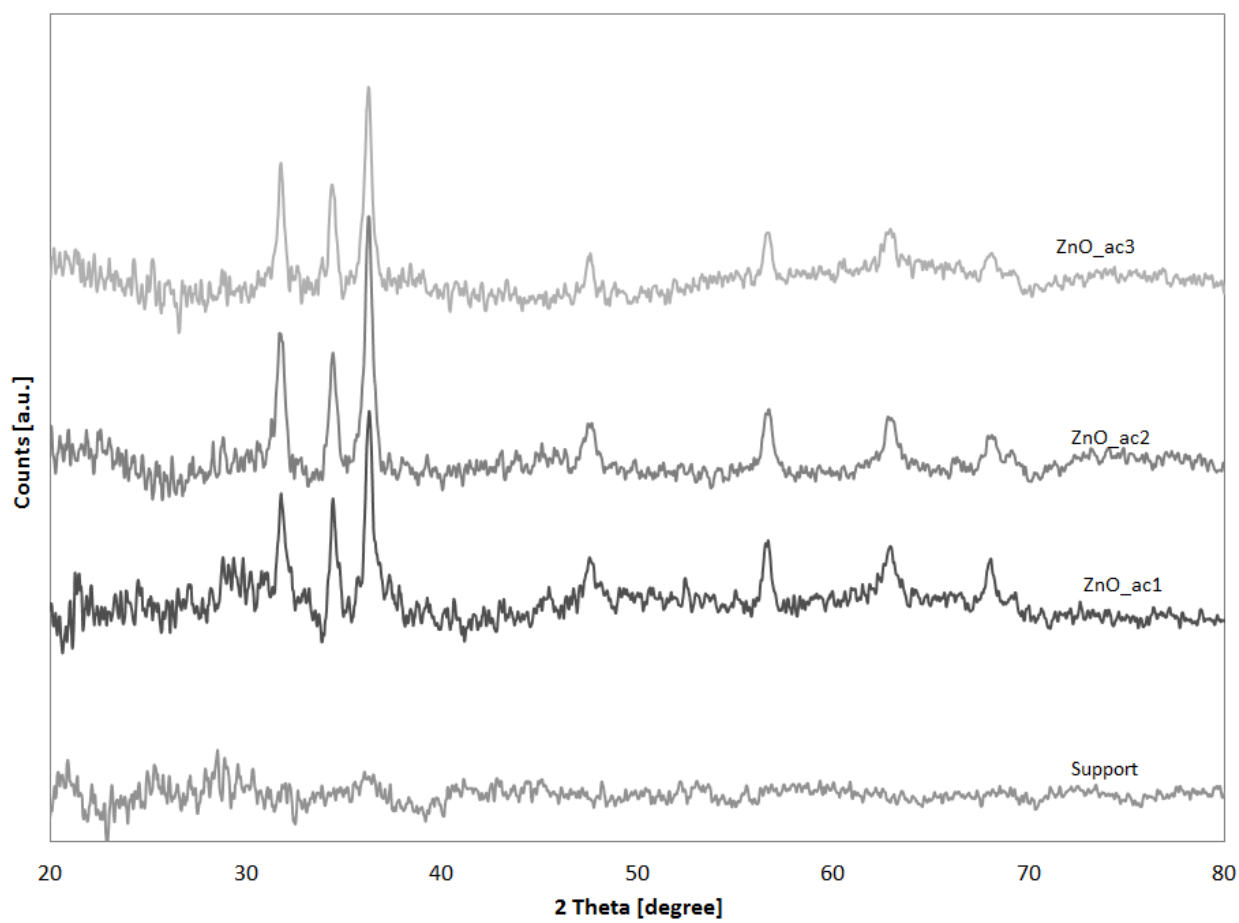
5: Figures

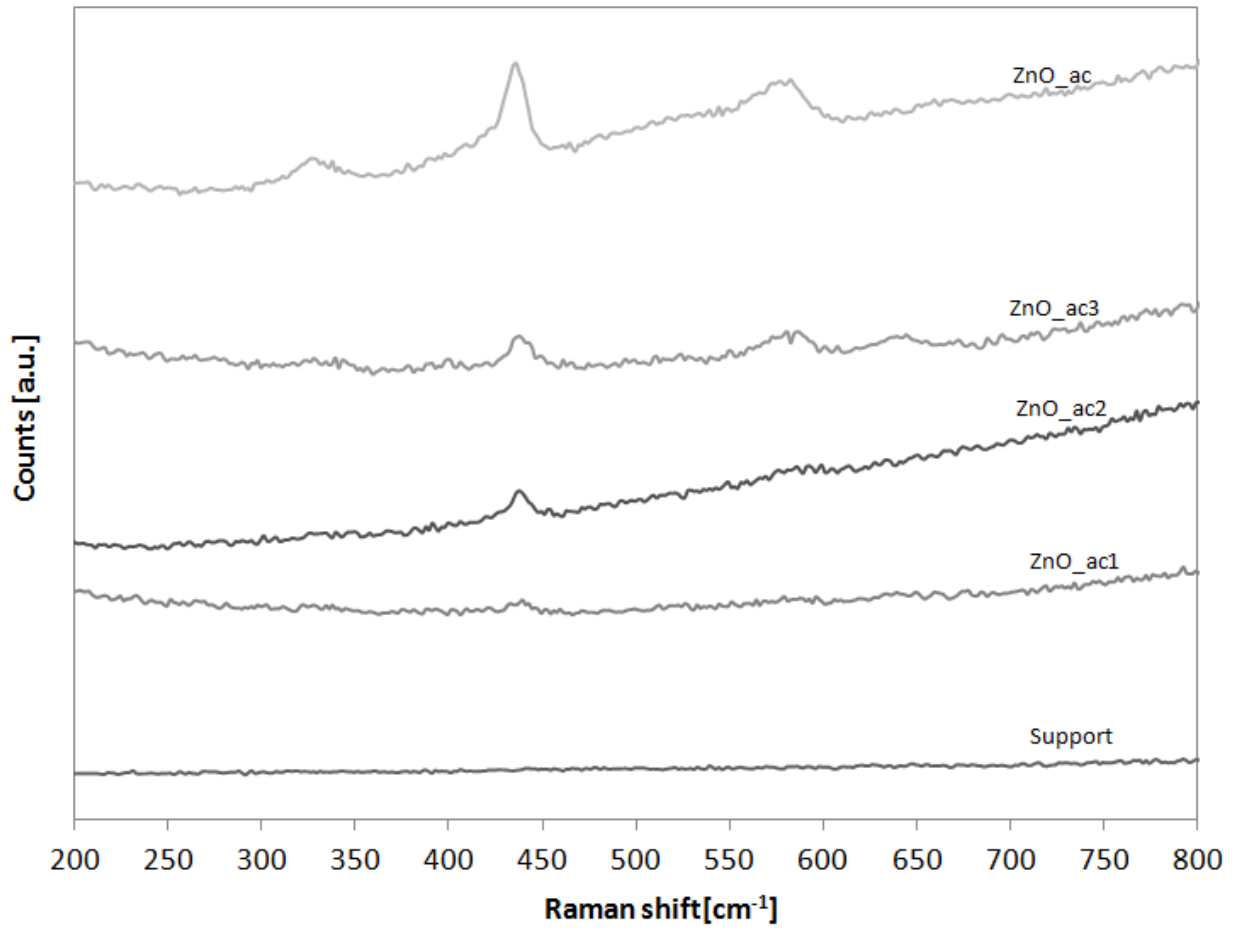**Figure 1**: XRD spectra

Figure 2: *Raman spectra.*

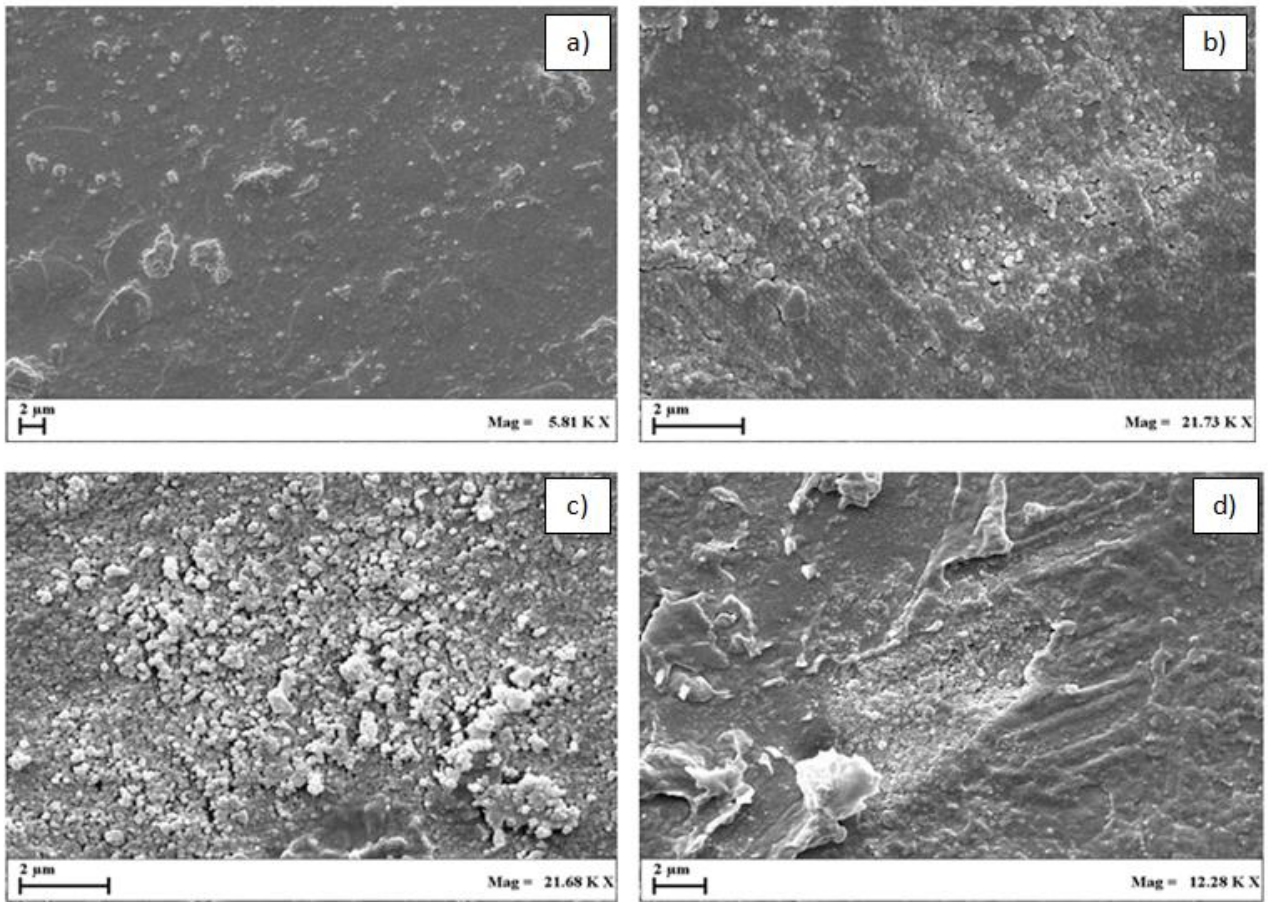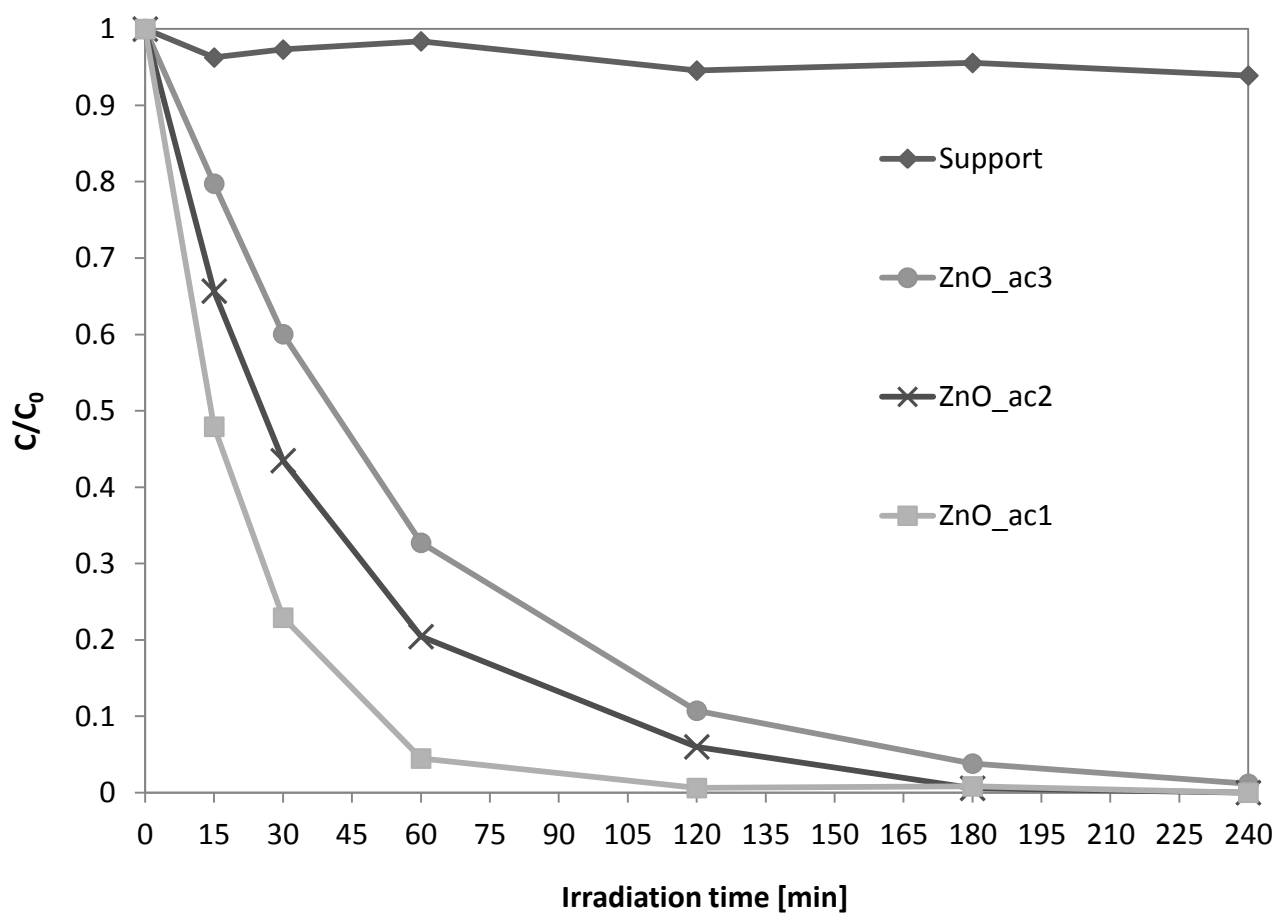*Figure 3*. SEM images: a) support, b) ZnO_ac1, c) ZnO_ac2, d) ZnO_ac3.

Figure 4. *Influence of the amount of ZnO deposited on glass spheres in the photocatalytic Acid blue 7 discoloration; initial dye concentration: 50 mg/L; liquid flow rate: 130 ml/min.*
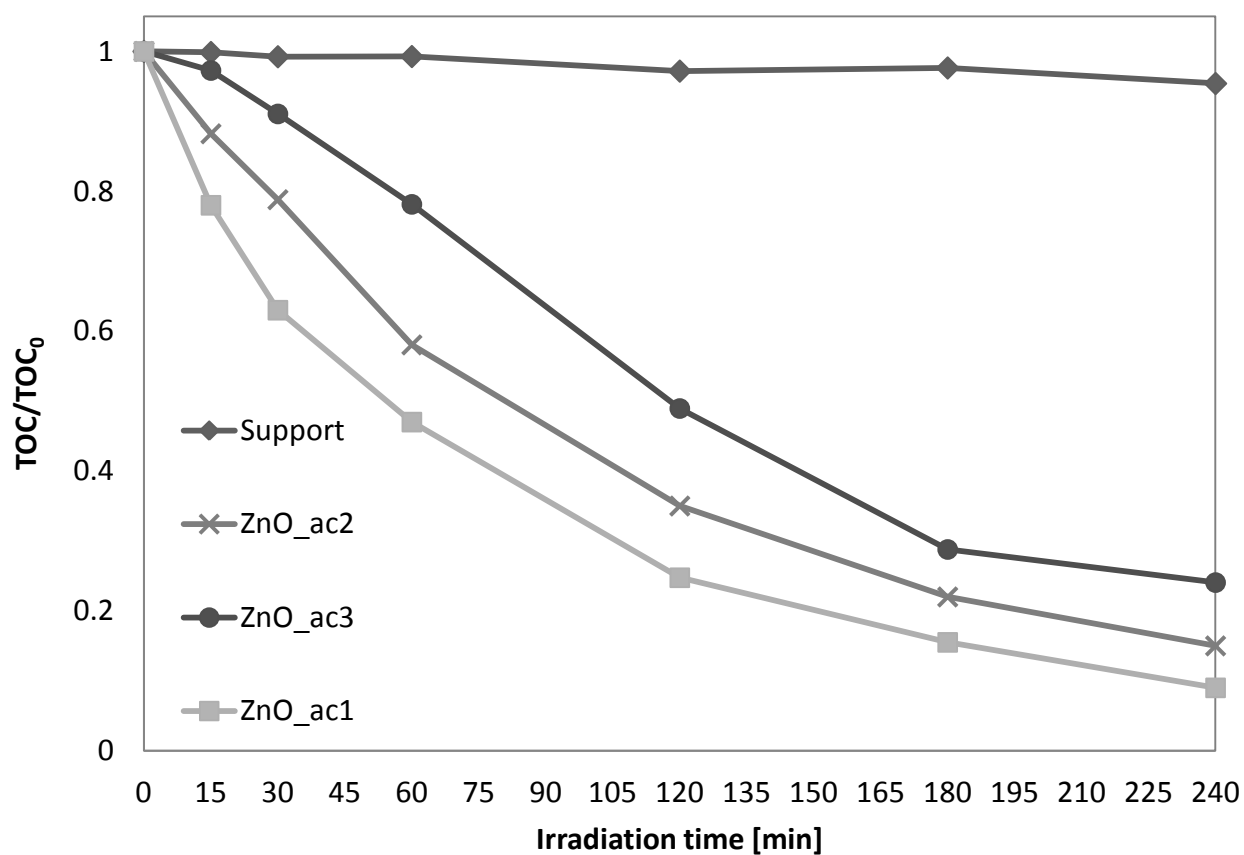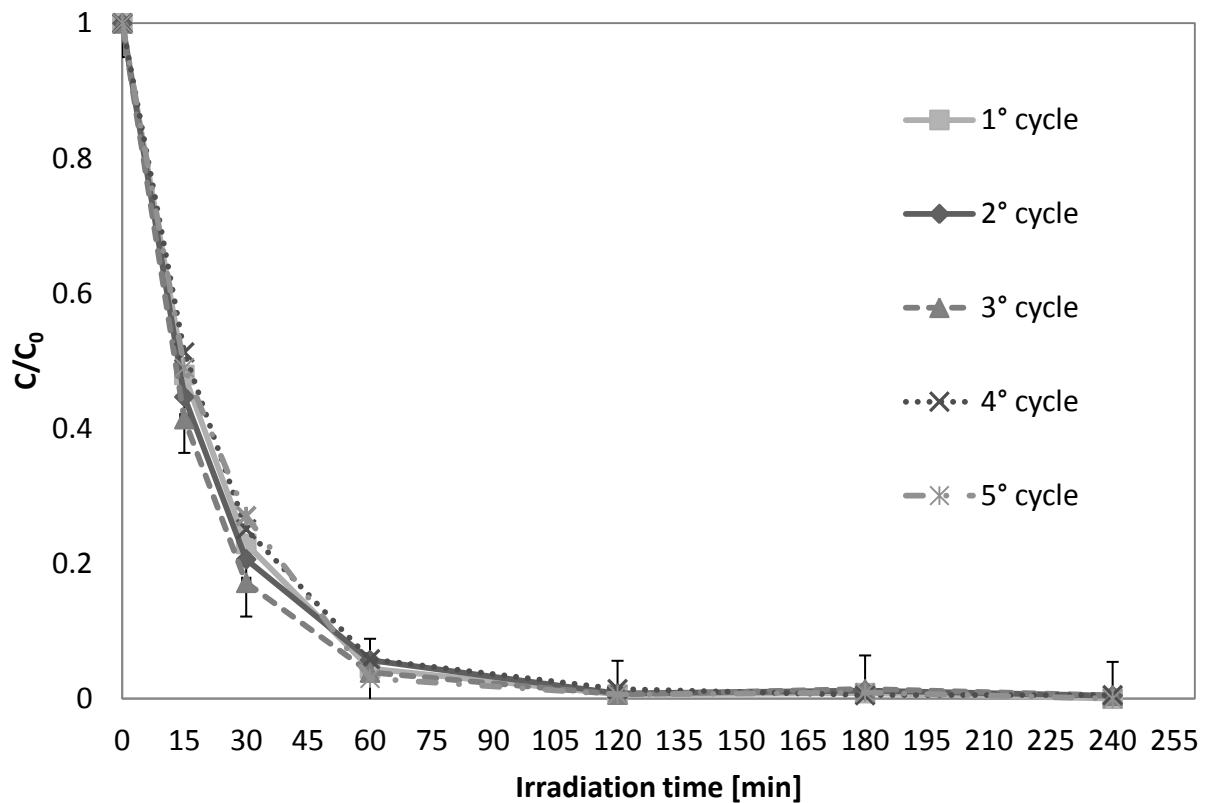
Figure 5. Influence of the amount of ZnO deposited on the glass spheres in the photocatalytic Acid blue 7 mineralization; initial dye concentration: 50 mg/L; liquid flow rate: 130 ml/min.

Figure 6. *Evaluation of Acid blue 7 discoloration during the irradiation time on ZnO_ac1 photocatalyst for different cycles; initial dye concentration: 50 mg/L.;liquid flow rate: 130 ml/min.*
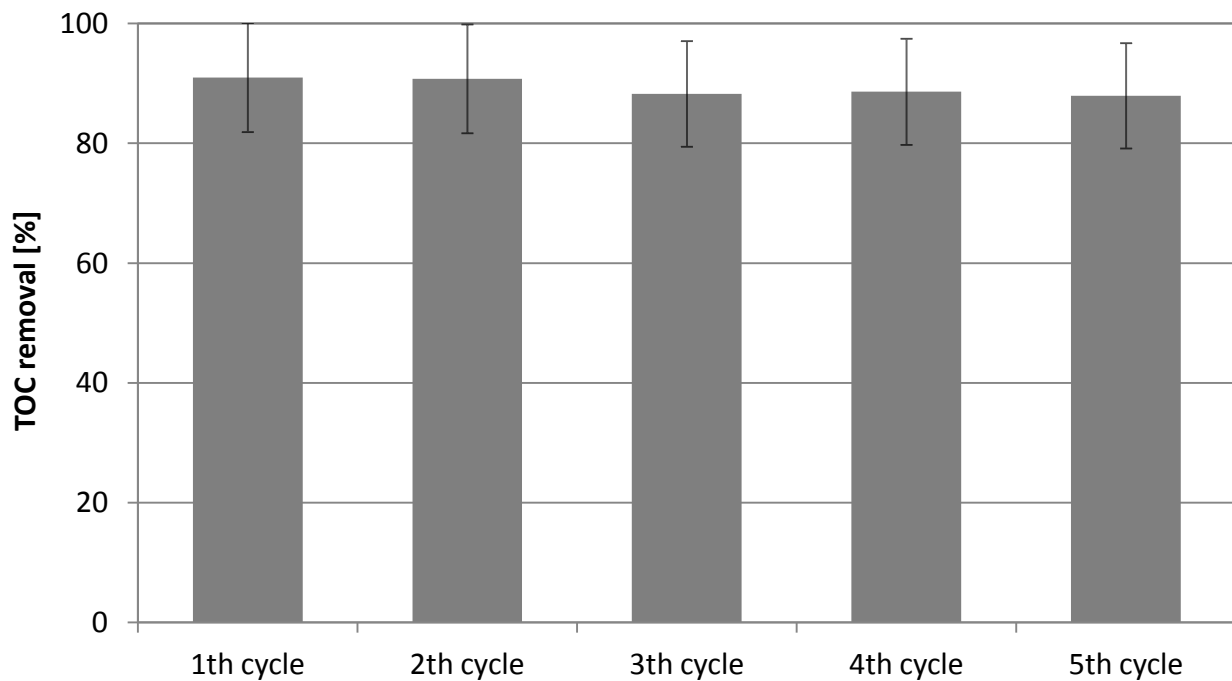
Figure 7. *Evaluation of Acid blue 7 mineralization after 240 minutes of irradiation time on ZnO_ac1 photocatalyst for different cycles; initial dye concentration: 50 mg/L ;liquid flow rate: 130 ml/min.*
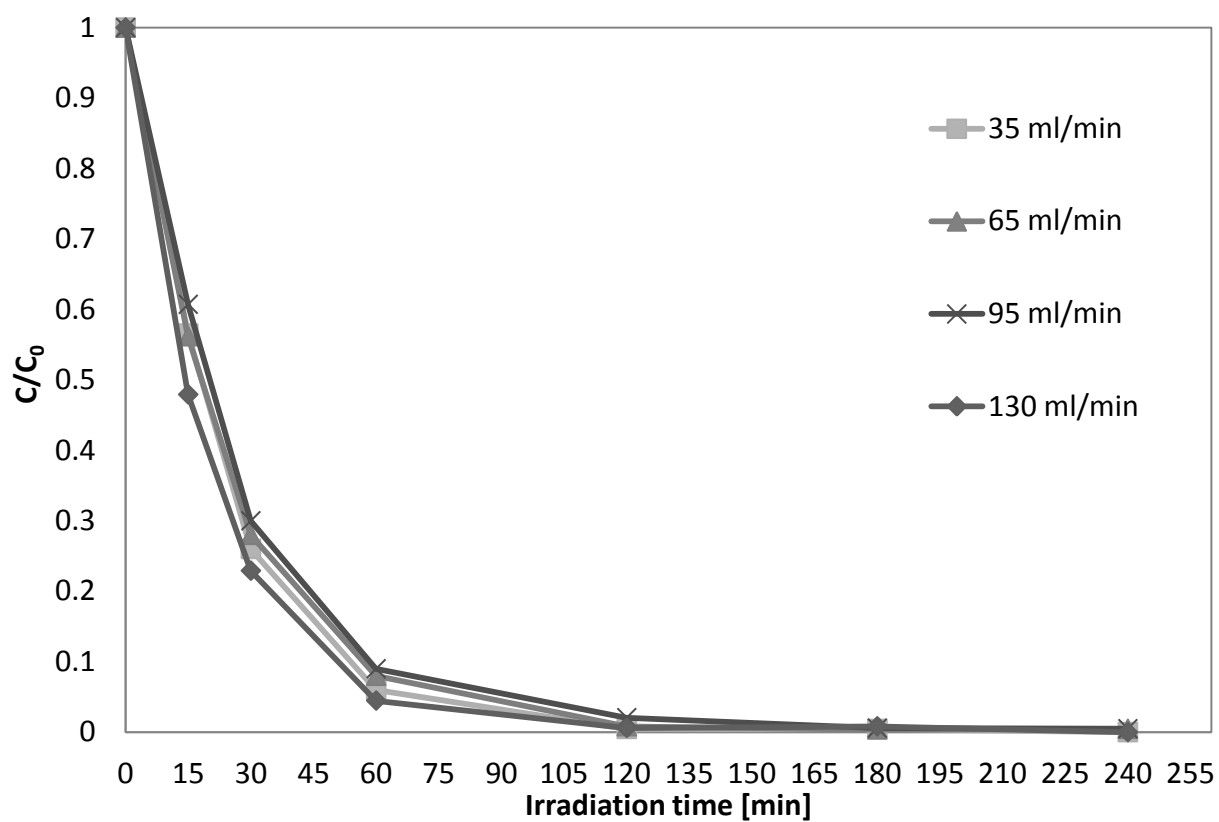
Figure 8. *Influence of the liquid flow rate on the Acid blue 7 discoloration during the irradiation time on ZnO_ac1 photocatalyst; initial dye concentration: 50 mg/L.*
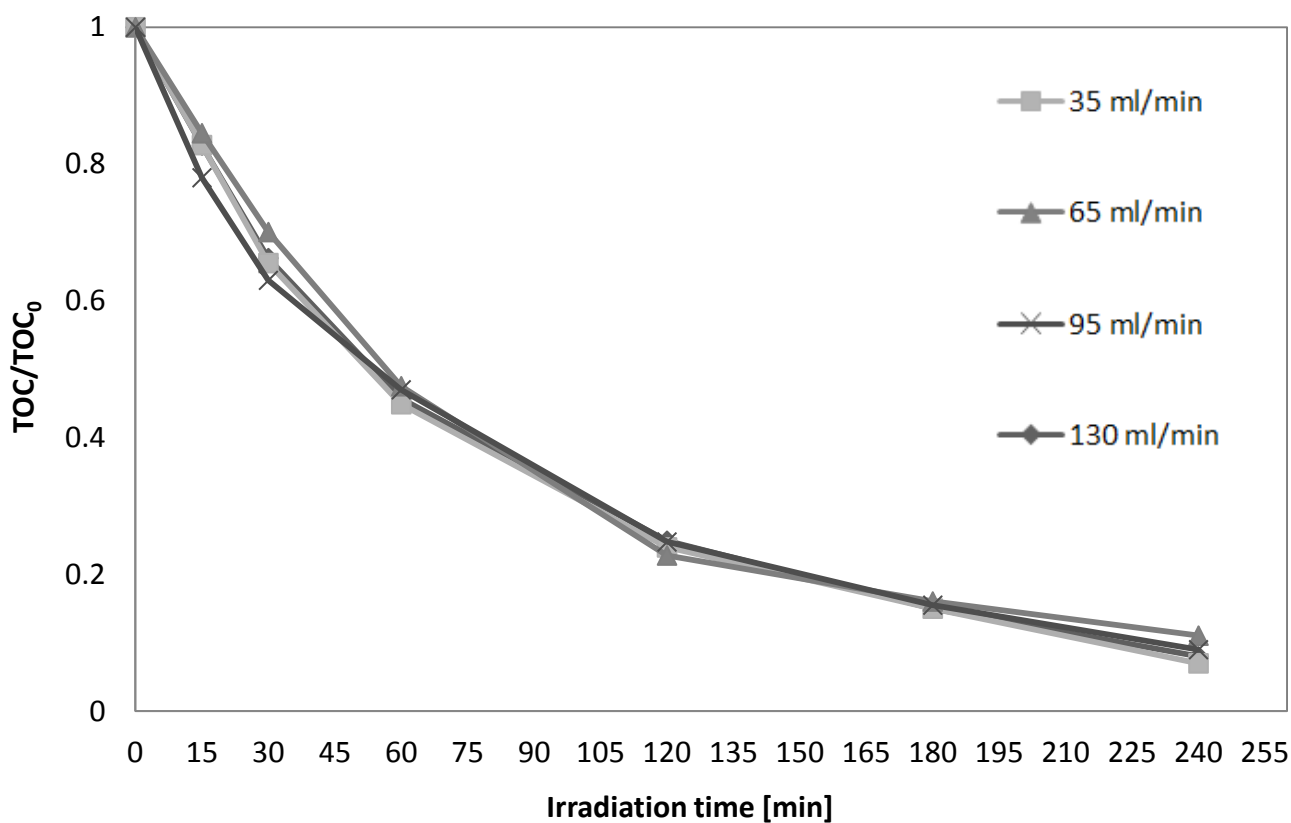
Figure 9. *Influence of the liquid flow rate on the Acid blue 7 mineralization during the irradiation time on ZnO_ac1 photocatalyst; initial dye concentration: 50 mg/L.*
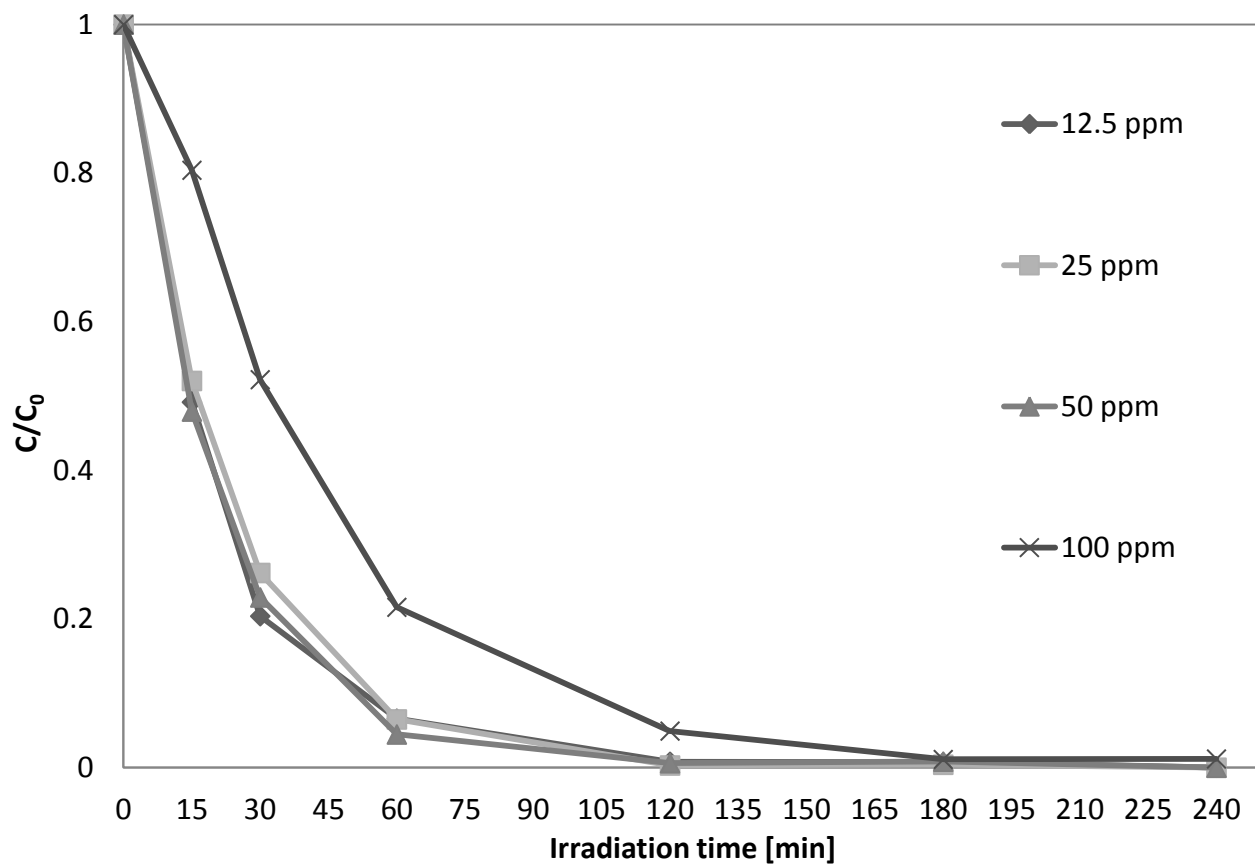
Figure 10. *Influence of the initial dye concentration on the Acid blue 7 discoloration during the irradiation time; liquid flow rate: 130 ml/min.*
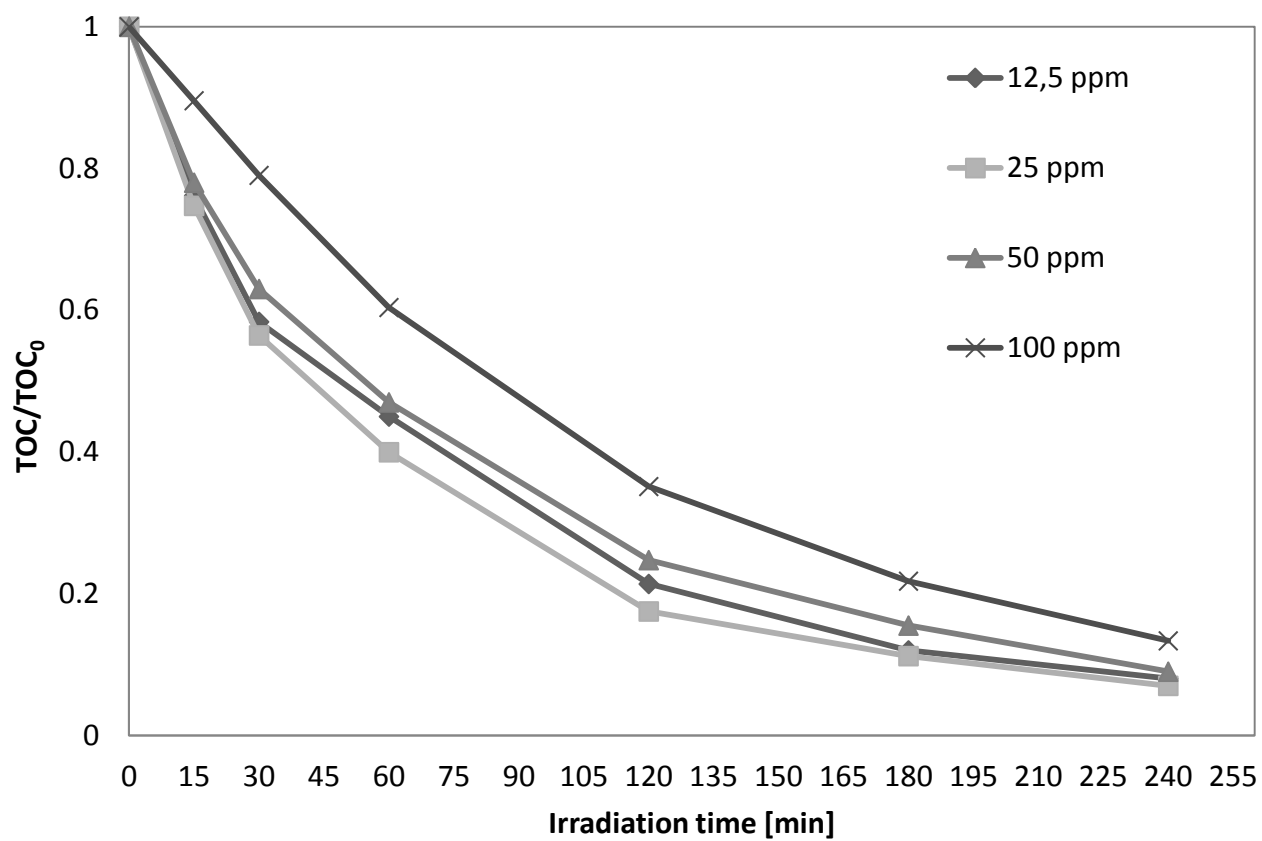
Figure 11. *Influence of the initial dye concentration on the Acid blue 7 mineralization during the irradiation time; liquid flow rate: 130 ml/min.*
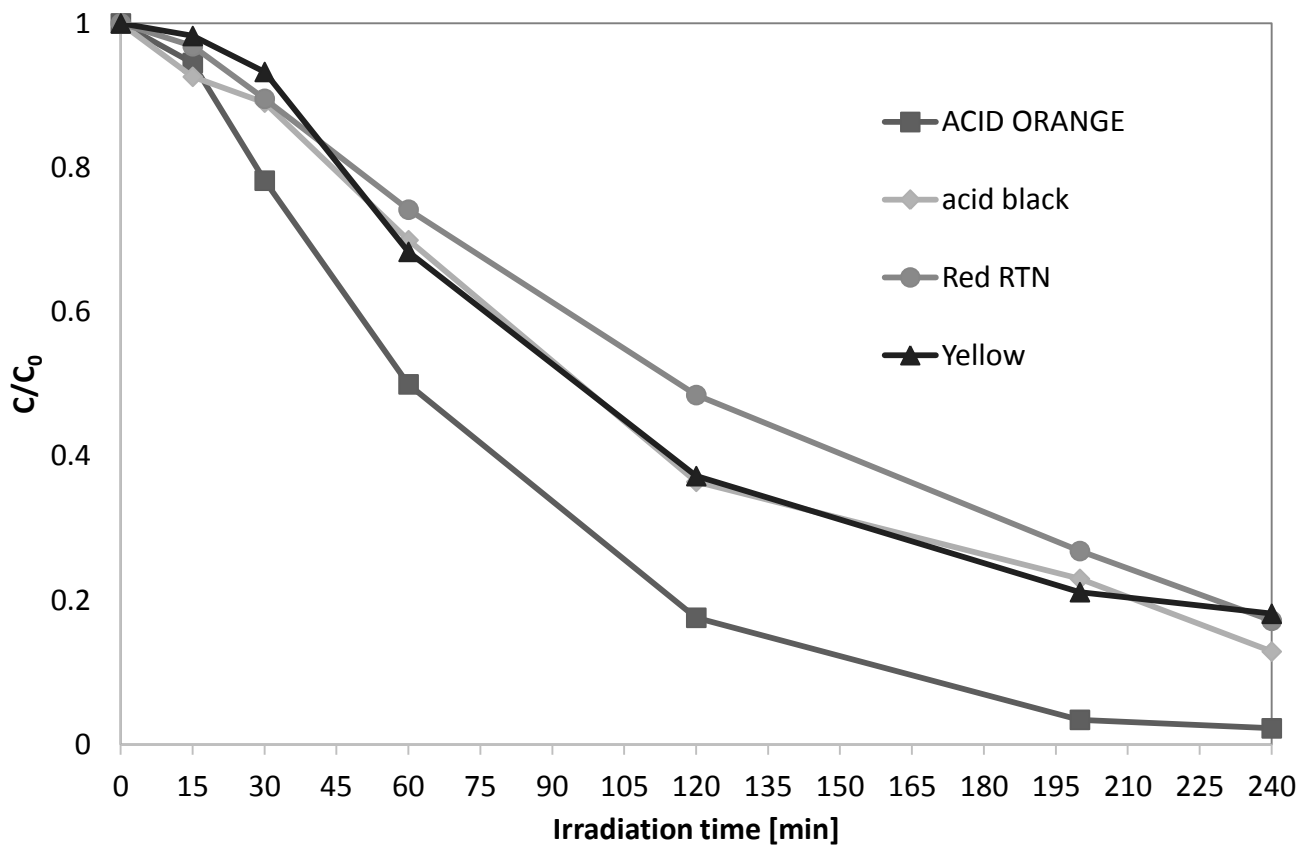
Figure 12. *Efficiency of the ZnO_ac1 photocatalyst in the discoloration of different tannery dyes during the irradiation time; initial dye concentration: 50 mg/L; liquid flow rate: 130 ml/min.*
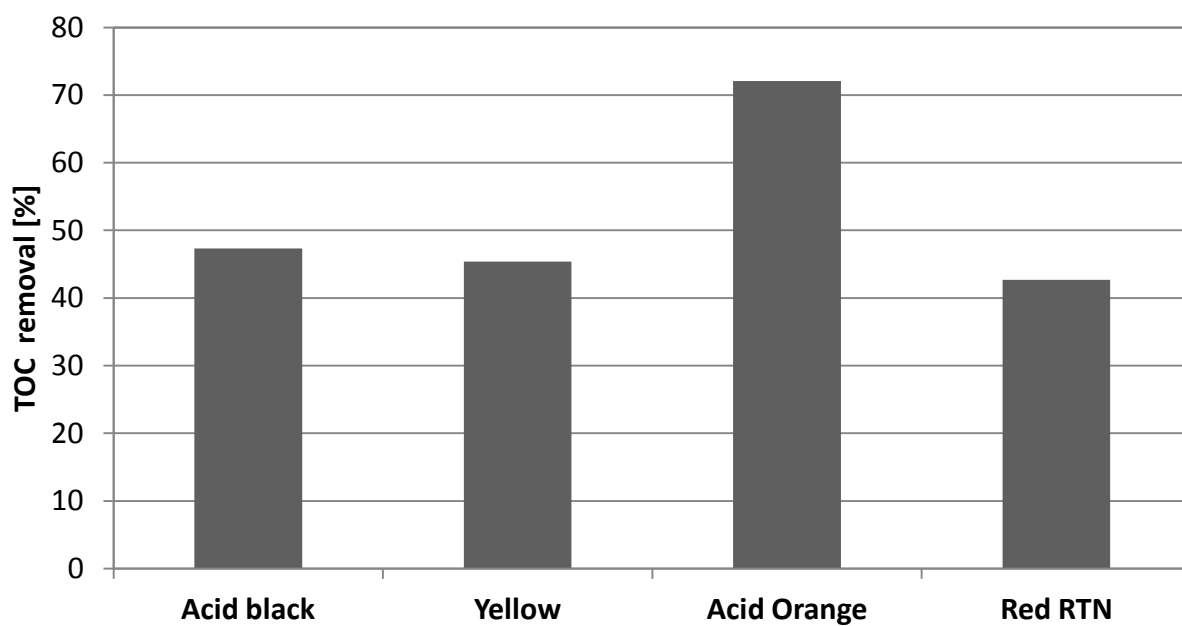

Figure 13. *Efficiency of the ZnO_ac1 photocatalyst in the mineralization of different tannery dyes after 240 min of irradiation time; initial dye concentration: 50 mg/L; liquid flow rate: 130 ml/min.*
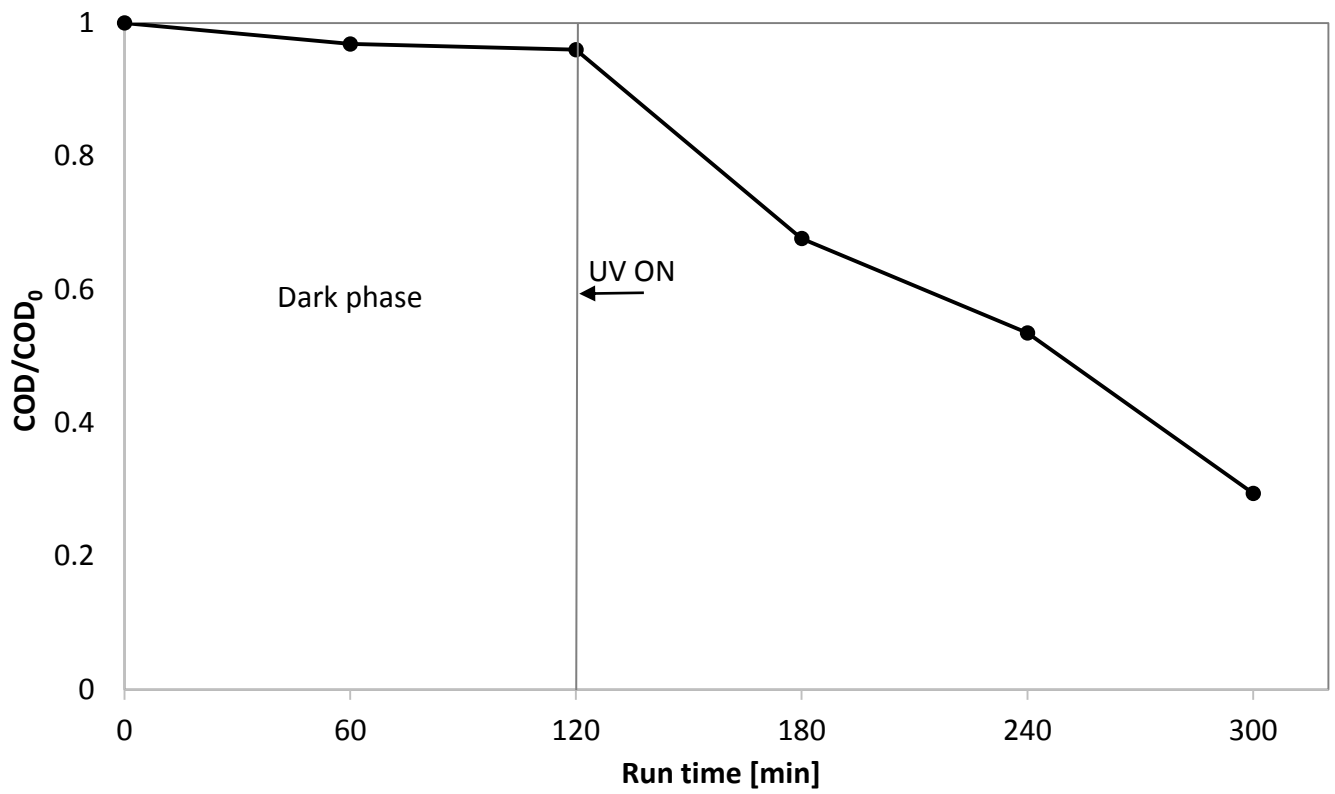
Figure 14. *COD behavior as a function of run time during the treatment of tannery real wastewater using ZnO_ac1 photocatalyst; liquid flow rate: 130 ml/min.*

Table 1: Number of dip-coating steps; ZnO amount immobilized on glass spheres and ZnO crystallites size

Sample	Number of dip-coating steps	ZnO amount [wt%]	ZnO average crystallite size [nm]
Support	0	-	-
ZnO_ac1	1	0.196	19
ZnO_ac2	2	0.256	19
ZnO_ac3	3	0.351	19