

Elsevier Editorial System(tm) for Applied
Catalysis B: Environmental
Manuscript Draft

Manuscript Number:

Title: Enhanced photocatalytic removal of phenol from aqueous solutions
using ZnO modified with Ag

Article Type: Research Paper

Keywords: Phenol removal; Ag/ZnO; silver loading; UV irradiation

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Dear Editor,

I kindly ask you to consider for possible publication in “**Applied Catalysis B: environmental**”, our research paper entitled:

**Enhanced photocatalytic removal of phenol from aqueous solutions
using ZnO modified with Ag**

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, the manuscript is focused on the photocatalytic activity of Ag/ZnO photocatalysts (synthesized by photodeposition method) in the treatment of aqueous solutions containing phenol under UV light irradiation. It was observed an enhancement of photocatalytic phenol removal under UV light irradiation from aqueous solutions by silver addition in comparison to commercial ZnO.

The results presented in the manuscript are an encouraging step forward in the possible application of heterogeneous photocatalytic technology in the treatment of waters polluted by phenolic compounds.

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,

The corresponding author.

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Enhanced photocatalytic removal of phenol from aqueous solutions using ZnO modified with Ag

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Abstract

Different photocatalysts based on commercial ZnO modified by silver photodeposition were prepared in this work. The samples are characterized by X-ray fluorescence spectrometry (XRF), specific surface area (SSA), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and UV-Vis diffuse reflectance (UV-Vis DRS). XRD and XPS showed that Ag/ZnO samples are composed of metallic Ag (Ag⁰) and ZnO structure was identified. Furthermore, TEM analysis evidenced that the number of silver particles increases with the Ag content. At last, UV-Vis DRS results revealed a new reflectance band for Ag/ZnO samples, ascribed to the surface plasmon resonance (SPR) absorption of metal silver particles. Commercial ZnO and Ag/ZnO samples were evaluated in the phenol removal under UV light irradiation. It was observed an enhancement of photocatalytic phenol removal from aqueous solutions by silver addition in comparison to commercial ZnO. In particular, the phenol removal increased with the silver content from 0.14 to 0.88 wt %, after this content (i.e 1.28wt %) the phenol degradation significantly decreased indicating that the optimal Ag content was equal to 0.88 wt %. The influence of the best photocatalyst dosage and the change of the initial phenol concentration in

1 solution were also investigated in this work and the best photocatalytic performance was obtained
2 by using 50 mg.L⁻¹ of phenol initial concentration and 0.15 g.L⁻¹ of photocatalyst dosage. Finally,
3 the optimized Ag/ZnO photocatalyst was employed for the treatment of a real drinking wastewater
4 containing phenol in which the total phenol removal after 180 minutes of UV irradiation time was
5 achieved.

6 **Keywords:** Phenol removal, Ag/ZnO, silver loading, UV irradiation

7

8 1 Introduction

9 Phenol and phenolic compounds are considered as priority pollutants since they are dangerous for
10 living organisms due to their acute toxicity and bio-recalcitrant nature [1, 2]. These compounds are
11 released into the environment through wastewaters from a large number of industries, such as
12 tanning, refineries, manufacturing paints, pharmaceuticals, petroleum production, paper making,
13 coke and iron-smelting processes [3-7]. Phenol and its derivatives were found in concentrations of
14 more than 1 mg.L⁻¹ in different industrial wastewaters and because of its stability and solubility in
15 water, it is difficult to reduce its concentration up to the security level (0.1-1 mg.L⁻¹) [6, 8]. For this
16 reason, International Organizations for Environmental Protection have established permissible
17 limits, in the order of a few micrograms per liter, for their discharge into the environment [9].
18 However, it is difficult to eliminate the phenol with conventional treatment processes; in particular,
19 the biological process is usually ineffective because of a self-inhibitory effect on the
20 microorganisms in the presence of phenolic compounds [10]. For this reason, photocatalytic
21 treatment represents an advanced oxidation technology able to remove organic pollutants thanks to
22 its extremely efficient degradation rate, high mineralization efficiency, leading to CO₂, H₂O, and
23 other minerals as final products [11-17]. In particular, photocatalysis has been extensively
24 investigated as a technology for the removal of phenol and phenolic compounds from waters [18,
25 19]. Among various semiconductor materials, ZnO have received considerable scientific interest as

1 an alternative to TiO₂ due to its remarkable performance in electronics, optics and photonics, non-
2 toxicity, low cost, high catalytic efficiency, wide band gap energy (3.37 eV at room temperature),
3 large exciton binding energy (60 meV) and high potential to adsorb UV light irradiation. In some
4 cases, it was also reported that ZnO was more efficient than TiO₂ in photocatalytic degradation of
5 some organic compounds in aqueous solution [18, 20, 21]. The use of ZnO was investigated in the
6 photocatalytic degradation of phenolic compounds and their derivatives under UV light irradiation
7 [1, 6, 18, 22, 23]. Because of the rapid recombination of photoexcited electron–hole pairs formed in
8 photocatalytic processes, the photocatalytic efficiency of ZnO is limited. In fact, the recombination
9 has faster kinetics than surface redox reactions and greatly reduces the quantum efficiency of
10 photocatalysis process [20]. To retard the recombination of photoexcited electron–hole pairs and to
11 enhance the photocatalysis efficiency of ZnO, one of the approaches used is to couple ZnO with
12 other materials that act as an electron sink to eliminate or slow down the recombination process of
13 photoinduced electron-hole pairs [20]. Several materials, like carbon nanotube and graphene [20]
14 were used as electron sink to enhance the photocatalytic activity of ZnO. Furthermore, noble metal
15 deposited on ZnO surface, such as Au/ZnO [24] nanocomposites prepared by coprecipitation,
16 Pt/ZnO [25], Pd/ZnO [26] and Ag/ZnO catalysts [20, 27] have already found a wide application in
17 the field of photocatalysts. Unlike Au, Pt, and Pd, Ag is cheaper and so Ag/ZnO catalysts have
18 become priority for further scientific investigations and in particular, many methods have been
19 studied to synthesize them such as chemical bath deposition [20], sol–gel method [20],
20 hydrothermal method [20] and so on. However, most of these methods of preparation are limited for
21 scientific research purpose because of high temperature, high pressure, expensive equipment, toxic
22 reagents or long reaction time. So, it is necessary to develop a simple and low-cost method to
23 fabricate the Ag/ZnO photocatalysts with high crystallinity. Thus, a simple and fast method for the
24 synthesis of Ag/ZnO catalysts could be the photodeposition method [28-34]. For this reason, in this
25 work silver nanoparticles were reduced and deposited on commercial ZnO surface by using a
26 photodeposition method under UV light irradiation. It was investigated the photocatalytic activity of

1 the prepared Ag/ZnO photocatalysts at different Ag content and compared with the photocatalytic
2 properties of commercial ZnO for the treatment of phenol aqueous solutions. It is worthwhile to
3 note that, at our knowledge, the most papers about Ag/ZnO photocatalysts prepared by
4 photodeposition method were devoted to the degradation of organic dyes [28, 29] and only few
5 published studies regard the degradation of phenol [31], showing, in all cases, that the complete
6 removal of phenol was never achieved in less than 3 hours of UV irradiation.

7

8

9 **2 Experimental**

10 **2.1 Synthesis of Ag/ZnO photocatalysts**

11 Ag/ZnO photocatalysts were synthesized through photodeposition method starting from 1 g of
12 commercial ZnO (Aldrich, 99%) suspended into 50 mL of distilled water at room temperature.
13 Different amount of silver nitrate (AgNO₃, Aldrich, 99%) was added into the suspension that was
14 irradiated for 30 minutes by two UV lamps emitting at 365 nm (nominal power of 8 W, Philips). A
15 gaseous nitrogen flow (30 NL·h⁻¹) was bubbled inside the suspension during the UV irradiation.
16 During the irradiation, oxidation and reduction occur simultaneously in Ag ions photoreduction: in
17 the reduction, the conduction band electrons, generated in the ZnO (e⁻(CB)) by UV irradiation, can
18 reduce adsorbed Ag⁺ ions, giving rise to Ag atoms (Ag⁰), the reduced Ag⁰ is then deposited on the
19 ZnO surface [29]. Photochemical reactions are summarized as follows:



23 After the photodeposition, the suspension was centrifuged, washed with distilled water for several
24 times and finally dried at 90°C in an oven. The obtained Ag/ZnO photocatalysts will be denoted as

1 $x\%$ Ag/ZnO, where x indicates the nominal Ag loading expressed as weight percentage (wt %) (Eq.
2 4).

$$3 \quad \%Ag = \frac{gAg}{gZnO + gAg} \cdot 100 \quad \text{Eq. 4}$$

4 Where:

5 gAg is the weight of silver calculated from $AgNO_3$ used in the preparation;

6 $gZnO$ is the weight of commercial ZnO fixed at 1 g and used in the preparation.

7 Ag/ZnO samples with different Ag loadings were synthesized and these samples are enlisted in
8 Table 1.

9

10 **2.2 Characterization of the photocatalysts**

11 Different characterization techniques were used to analyze Ag/ZnO photocatalysts. In particular, the
12 specific surface area (SSA) analysis was performed by BET method using N_2 adsorption with a
13 Costech Sorptometer 1042 after a pretreatment at $150^\circ C$ for 30 minutes in He flow (99.9990 %).
14 Total Ag loading of the photocatalysts was obtained by X-ray fluorescence spectrometry in a
15 Panalytical Axios sequential spectrophotometer equipped with a rhodium tube as the source of
16 radiation. XRF measurements were performed onto pressed pellets (sample included in 10 wt% of
17 wax).

18 Silver particles sizes were evaluated by Transmission Electron Microscopy (TEM) in a Philips
19 CM200 instrument, equipped with X-ray EDX X-Max 80T system, Oxford instruments. For this
20 analysis the samples were dispersed in ethanol using an ultrasonicator and dropped on a carbon
21 grid. Determination of the metal particle average diameter in the different samples was
22 accomplished by counting particles in a high number of TEM images from different places of the
23 samples.

1 X-ray photoelectron spectroscopy (XPS) studies were carried out on a Leybold–Heraeus LHS-10
2 spectrometer, working with constant pass energy of 50 eV. The spectrometer main chamber,
3 working at a pressure $<2 \times 10^{-9}$ Torr, is equipped with an EA-200MCD hemispherical electron
4 analyzer with a dual X-ray source working with Al K α ($h\nu = 1486.6$ eV) at 120 W and 30 mA C 1
5 s signal (284.6 eV) was used as internal energy reference in all the experiments. Samples were
6 outgassed in the prechamber of the instrument at 150°C up to a pressure $<2 \times 10^{-8}$ Torr to remove
7 chemisorbed water.

8 The detailed information about the crystalline structure of the photocatalysts was measured by X-
9 ray diffraction analysis (XRD) using Brucker D8 diffractometer and the crystallite sizes were
10 calculated through the Scherrer equation.

11 The ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) of the samples were recorded
12 using a Perkin Elmer spectrometer Lambda 35 spectrophotometer using a RSA-PE-20 reflectance
13 spectroscopy accessory (Labsphere Inc., North Sutton, NH). The band gap values of photocatalysts
14 were determined through the corresponding Kubelka–Munk function (KM) (which is proportional
15 to the absorption of radiation) and by plotting $(KM \times h\nu)^2$ against $h\nu$.

16

17 **2.3 Photocatalytic tests**

18 The photocatalytic activity of commercial ZnO and Ag/ZnO samples was tested under UV
19 irradiation. The photocatalytic tests were conducted in a cylindrical photoreactor ($ID = 2.6$ cm, L_{TOT}
20 $= 41$ cm and $V_{TOT} = 200$ mL) equipped with: (i) An air distributor device (flow rate of 142
21 $Ncc \cdot min^{-1}$); (ii) four UV lamps (Philips, nominal power: 8W each and main emission peak at 365
22 nm) around the external surface of the photoreactor at an equal distance from it (about 30 mm) in
23 order to irradiate the volume of the solution uniformly; (iii) a peristaltic pump (Watson Marlow) in
24 order to maintain continuously recirculated the suspension.

1 In a typical photocatalytic test, the treated solution volume was 100 mL at the spontaneous pH of
2 the solution (pH = 6.5) with an initial concentration of phenol at $50 \text{ mg}\cdot\text{L}^{-1}$ while the photocatalyst
3 dosage was $1.5 \text{ g}\cdot\text{L}^{-1}$.

4 Prior to the irradiation, the suspension was left in dark for 120 minutes to provide an
5 adsorption/desorption equilibrium on the photocatalyst surface and after, the photocatalytic test was
6 began under UV light irradiation up to 240 minutes. At different times, about 4 mL of the solution
7 was withdrawn and filtered to remove solid particles powders.

8 The photodegradation of phenol was monitored by measuring its absorption at 270 nm using a UV
9 Vis spectrophotometer (Evolution 201) [19] while the total organic carbon (TOC) was measured by
10 the high temperature combustion method on a catalyst ($\text{Pt-Al}_2\text{O}_3$) in a tubular flow microreactor
11 operated at 680°C , with a stream of hydrocarbon free air to oxidize the organic carbon [35].

12 In this study, photocatalytic activities of the commercial ZnO and prepared Ag/ZnO catalysts was
13 estimated by evaluating the influence of Ag loading on ZnO catalyst, the influence of catalyst
14 dosage, the influence of initial phenol concentration and finally, a photocatalytic test using the best
15 Ag/ZnO photocatalyst was carried out to treat a drinking water containing phenol.

16

17 **3 Results and discussion**

18 **3.1 Characterization of the photocatalysts**

19 Commercial ZnO and Ag/ZnO photocatalysts were characterized by different techniques such as X-
20 ray fluorescence spectroscopy (XRF), specific surface area (SSA), transmission electron
21 microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and UV-Vis
22 spectroscopy.

23

24

3.1.1 XRF results

The total loading of Ag on the photocatalysts prepared was analyzed by XRF measurements (Table 1). As it can be seen, for all the samples, the real Ag content is lower than the nominal Ag loading, thus indicating an incomplete reduction of the metal precursor, however, the Ag content effectively deposited on ZnO increased by increasing the nominal Ag content from 0.14 to 1.28 wt%.

3.1.2 SSA results

SSA results are shown in Table 1. In particular, for Ag/ZnO samples with Ag content in the range of 0.14-0.88 wt%, the SSA values are not changed compared to commercial ZnO ($5 \text{ m}^2 \cdot \text{g}^{-1}$). With the increase of Ag content up to 1.28 wt%, the SSA decreased to $3.5 \text{ m}^2 \cdot \text{g}^{-1}$ indicating a possible agglomeration of the Ag nanoparticles on ZnO surface, previously observed in literature [36].

3.1.3 TEM analysis

Figure 1 shows selected images of commercial ZnO. The particle sizes were clearly of the order of nanometers (ca.90 nm); this sample exhibit homogeneity on shapes and sizes, there are particles that show the hexagonal face, along with another type of square or rod-like structures. As it can be seen in Figure 2, these shapes are maintained after Ag deposition. Silver nanoparticles can be identified as black dots located on ZnO surface, these particles are heterogeneously distributed over the ZnO surface with places with a high concentration of deposits and others relatively empty (Figure 2). It was found that the number of particles on surface increases with the nominal Ag content, the particle size also increases, thus, for example, for the catalyst prepared with 1.28 wt % of Ag, the average particle size corresponds to 3.2 nm. TEM pictures of samples with other metal loadings are not shown for the sake of brevity but they all present similar morphology and heterogeneous distribution than pictures shown in Figure 2.

1 In order to achieve an accurate identification of the silver particles in the samples, EDX analyzes
2 were also performed and as it can be observed in Figure 3, Ag particles are present in the Ag/ZnO
3 samples.

4

5 *3.1.4 X-ray photoelectron spectroscopy (XPS)*

6 The surface structure of bare and Ag modified ZnO was analyzed by using XPS. Selected spectra of
7 the O1s, Zn 2p and Ag 3d regions corresponding to the 2%Ag/ZnO sample are shown in Figure 4.
8 In the obtained spectra, Zn was identified in all the samples by two peaks located at binding
9 energies of 1043 and 1020 eV; in the O 1s region, a peak located at a binding energy of 529.5 ± 0.2
10 eV was registered in all the samples, this peak is assigned to lattice oxygen in ZnO. No changes in
11 the position of these peaks were observed after Ag addition. In Figure 4, peaks located at 373 and
12 367 eV are assigned to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively, these peaks corresponds to metallic
13 silver (Ag⁰).

14

15 *3.1.5 X-ray diffraction (XRD)*

16 The XRD analysis was employed to identify the phase structure and the purity of the photocatalysts.
17 The XRD patterns of commercial ZnO and prepared Ag/ZnO photocatalysts were recorded. The
18 results, showed in Figure 5, evidenced strong diffraction peaks indicating that the synthesized
19 products have high crystallinity. All the prepared samples have the typical hexagonal Wurtzite
20 structure of ZnO [37, 38], with 2θ diffraction peaks at 31.7° , 34.5° , 36.2° , 47.7° , 56.84° , 63° , 68.1°
21 (Figure 5) corresponding to (100), (002), (101), (102), (110), (103) and (112) planes, respectively.
22 The maximum diffraction intensity is observed at 36.2° . Ag/ZnO samples revealed three small
23 additional diffraction peaks at 38.2° , 44.2° , and 64.5° that correspond to (111), (200), and (220)
24 crystal planes due to the presence of Ag. These peaks are associated with the face-centered-cubic

1 phase of metallic Ag⁰ [29, 39, 40]. No characteristic peaks of impurity phases, such as silver oxide
2 phases, were observed from the patterns and in addition, there is no remarkable shift of all
3 diffraction peaks indicating that silver atoms are positioned onto the ZnO surface excluding the
4 possibility of their incorporation into the ZnO structure substituting Zn sites [20, 36]. Furthermore,
5 the ZnO crystallite size of the samples was calculated using the Debye-Sherrer's formula [30, 41]
6 based on the XRD patterns [30] and considering the diffraction peak at 2θ~36.2° (111). According
7 to the calculations, the average crystallite size of commercial ZnO and Ag/ZnO samples was
8 approximately constant and about 24 nm.

9
10 *3.1.6 UV-Vis diffuse reflectance spectra (UV-Vis DRS)*

11 The UV-Vis DRS spectra of commercial ZnO and the synthesized 2%Ag/ZnO photocatalyst are
12 shown in Figure 6. Compared to commercial ZnO, 2%Ag/ZnO samples reveal a new reflectance
13 band in the range 2.5-3.1 eV corresponding at 400-496 nm. This band is ascribed to the surface
14 plasmon resonance (SPR) absorption of metal silver particles [29, 42]. Similar results were obtained
15 for all the Ag/ZnO samples.

16 The band gap energy of commercial ZnO and Ag/ZnO photocatalysts (Table1) was found to be
17 approximately the same and about 3.1 eV, in agreement with literature data [43].

18
19

20 **3.2 Photocatalytic activity results**

21 *3.2.1 Influence of Ag content photodeposited on ZnO surface*

22 The photocatalytic degradation of phenol under UV light irradiation using commercial ZnO and
23 Ag/ZnO photocatalysts was investigated. The photocatalytic degradation was carried out in a 100
24 mL of phenol solution with an initial concentration of 50 mg.L⁻¹ and a catalyst loading of 1.5 g.L⁻¹.

1 The experiment results, as a function of irradiation time in terms of phenol degradation and
2 mineralization (Figure 7 and Figure 8), showed that, in the absence of the photocatalyst
3 (photolysis), the phenol concentration did not change under UV irradiation for 240 minutes,
4 indicating that the photolysis of phenol can be neglected compared to photocatalysis. Figure 7 and
5 Figure 8 show also the effect of the noble metal Ag photodeposited on the photocatalytic activity of
6 the synthesized catalysts. As it can be seen, the photocatalytic results in terms of phenol degradation
7 (Figure 7) evidenced a rapidly decrease of phenol concentration in the presence of Ag/ZnO
8 photocatalysts that exhibited enhanced photocatalytic activity compared with the commercial ZnO.
9 In particular, the almost complete phenol degradation was reached after 60 minutes of irradiation
10 time using 1%Ag/ZnO photocatalyst (Figure 7). It is worthwhile to note that, at the same irradiation
11 time (60 minutes), the phenol degradation increased with the increase of Ag content until 0.88wt %
12 of Ag content, while for the highest metal loading (1.28wt %) the photocatalytic activity of the
13 samples decreased, thus indicating that the optimal Ag content was equal to 0.88wt %. In the same
14 manner, in terms of TOC removal (Figure 8), the optimal silver loading was found to be 0.88wt %.
15 In fact, 1%Ag/ZnO photocatalyst was able to achieve the total TOC removal after 120 minutes of
16 UV light irradiation. The existence of an optimal silver content indicates that an appreciable amount
17 of Ag is necessary to reach the maximum improvement of the photocatalytic activity [29, 31]. The
18 improvement of commercial ZnO by modifying its surface with Ag, can be explained taking into
19 account the characterization results previously described. Thus, the addition of Ag to ZnO, leads to
20 modify the color of this material, leading to improve the absorption of the metalized samples in the
21 visible region as it can be observed by UV-Vis DRS analyzes, where the SPR of silver was detected
22 (Figure 6). By TEM analyzes it was also observed that the increase of the metal content leads to
23 increase the number of Ag nanoparticles deposited in ZnO surface. However, the biggest silver
24 nanoparticles present in the catalyst prepared with 1.28wt% Ag, can act as a recombination centers,
25 thus leading to decrease the photocatalytic activity of this material, as it can be observed in the
26 present study. On the other hand, taking into account that the Ag reduction on ZnO surfaces is

1 incomplete in all the prepared photocatalysts, as it was observed by XRF analyzes (Table 1), it is
2 expected a certain contribution of Ag oxidized species in the samples prepared with the lowest
3 silver content (i.e 0.14 to 0.88 wt %). However, it was not possible to calculate the percentage of
4 Ag^0 or $\text{Ag}^{\delta+}$ species for these samples, as the ratio signal to noise was too low to allow an accurate
5 enough estimation by XPS. In the case of the samples prepared with 1.28 wt % of Ag, only signals
6 corresponding to metallic species (Ag^0) was identified in the Ag 3d region (Figure 4). In previous
7 studies it has been reported that the oxidized species of metals such as platinum ($\text{Pt}^{\delta+}$) can act as
8 additional adsorption centers for phenol (as a bidentate phenolate) on the semiconductor surface
9 [44], thus leading to improve the substrate adsorption and therefore to increase the effectiveness of
10 the phenol photodegradation over photocatalyst metallized by photodeposition method. A similar
11 behavior can occurs in the case of the silver ZnO modified photocatalysts studied in the present
12 work. Thus, the increase of the Ag content to 1.28wt % leads also to increase the Ag^0 species
13 effectively deposited on ZnO surface, as it can be observed by XPS (Figure 4) and therefore to
14 decrease the available adsorption centers for phenol ($\text{Ag}^{\delta+}$). This reason can contribute to explain
15 why the phenol photodegradation decreased over the 2% Ag/ZnO sample (Figure 7).

16 In order to understand the influence of silver content on photocatalytic activity, the kinetic constant
17 of phenol degradation was evaluated. For this purpose it was considered that the phenol
18 photodegradation reaction follows the pseudo-first-order kinetic [45]. The photodegradation rate (r)
19 depends on the phenol concentration (C) in accordance with the following equation Eq.5:

$$20 \quad r = k \cdot C \quad \text{Eq.5}$$

21 Where C is the concentration of phenol in $\text{mg} \cdot \text{L}^{-1}$ and k is the kinetic constant in min^{-1} .

22 Considering the mass balance on phenol (Eq.6) and integrating it between initial time (t=0) and a
23 generic irradiation time t, it was obtained the equation Eq.7.

$$24 \quad \frac{dC}{dt} = -k \cdot C \quad \text{Eq.6}$$

$$1 \quad -\ln\left(\frac{C}{C_0}\right) = k \cdot t \quad \text{Eq.7}$$

2 The value of the kinetic constant k can be calculated by the slope of the straight line obtained by
3 plotting $-\ln\left(\frac{C}{C_0}\right)$ versus irradiation time (t). The obtained values of k for all the investigated
4 photocatalysts are reported in Figure 9. As it can be seen in this figure, the k values of all Ag/ZnO
5 samples is higher than the calculated for commercial ZnO. The reason of this result could be
6 attributed to the presence of Ag on ZnO surface that effectively inhibit the recombination of
7 photoinduced electron and hole pairs, as reported in literature [31]. This observation is confirmed
8 by UV-Vis DRS spectra (Figure 6) in which it was evidenced the presence of SPR absorption.
9 Possibly, due to SPR and synergetic effect of the Ag particles, a large number of photoexcited
10 electrons are generated from the Ag particles surfaces to the conduction band of ZnO and diffuse
11 into the surrounding medium, consequently increasing the photocatalytic activity [43]. With regard
12 to the influence of metal loading, it is possible to observe that, with the increase of Ag content, the
13 kinetic constant value increases progressively up to Ag content equal to 0.88wt %, while with
14 higher content of Ag, the k values began to decrease. It is clear that the best photocatalyst was
15 1%Ag/ZnO because it exhibited the highest value of k and so the phenol photodegradation takes
16 place more rapidly than the other photocatalysts with a different content of silver. It can be seen
17 that, once again, there is an optimized amount of Ag photodeposited on ZnO. In fact, for Ag content
18 higher than 0.88wt%, Ag particles may become the center for recombining photoinduced electron
19 and hole pairs and so the photoactivity of photocatalysts begin to decrease [29, 31]. Moreover, it is
20 worthwhile to note that the obtained kinetic constant value for 1% Ag/ZnO photocatalyst is
21 significantly higher than the values reported in the scientific literature regarding phenol
22 photodegradation using ZnO modified with Ag through a photodeposition method [31].

1 From these results, it is evident that the optimized photocatalyst is 1%Ag/ZnO. This sample was
2 chosen to investigate the influence of photocatalyst dosage and the change of the initial phenol
3 concentration in solution.

4

5 3.2.2 *Influence of 1%Ag/ZnO dosage*

6 In order to avoid an ineffective excess of catalyst and to ensure a total absorption of efficient
7 photons, the optimum dosage of 1%Ag/ZnO photocatalyst was investigated. The experiments were
8 carried out using different catalyst amounts (in the range 0.075–0.3g) in 100 mL aqueous solution,
9 while the initial phenol concentration was kept constant at 50 mg.L⁻¹. The results, as a function of
10 irradiation time, in terms of phenol degradation and TOC removal were reported in Figure 10 and
11 Figure 11, respectively. It can be noted that the photocatalytic activity of 1%Ag/ZnO gradually
12 improved with the increase of its dosage from 0.075 to 0.15g while with higher dosage (0.3g), the
13 photocatalytic performances did not change reaching the complete phenol degradation after 120
14 minutes of UV light irradiation. In the same manner, Figure 11 shows the results in terms of
15 mineralization of organic compound after 45 minutes of UV light irradiation. In particular, the value
16 of TOC removal increased with the increase of 1%Ag/ZnO amount from 0.075 to 0.15g and then it
17 stayed constant (68%) for 1%Ag/ZnO dosage equal to 0.3g. Both photocatalytic phenol degradation
18 and mineralization did not change significantly when the photocatalyst dosage was increased up to
19 0.3 g, and so it is economically cheap to use the smaller amount of the photocatalyst (0.15g).

20

21 3.2.3 *Influence of phenol initial concentration*

22 The effect of phenol initial concentration in the range 12.5-50 mg.L⁻¹, has been investigated by
23 using 0.15g of 1%Ag/ZnO. In particular, Figure 12 and Figure 13 show the results in terms of
24 phenol degradation and TOC removal as a function of irradiation time, respectively. As regards
25 photocatalytic phenol degradation (Figure 12), the activity of the 1%Ag/ZnO photocatalyst

1 remained unchanged also in presence of high initial phenol concentration, reaching the complete
2 degradation after 120 minutes of UV light irradiation for all photocatalytic tests. From the
3 comparison of the results in terms of TOC removal (Figure 13) after 45 minutes of UV light
4 irradiation, it can be seen that increasing the initial phenol concentration, the TOC removal values
5 did not change significantly. Moreover, the k values for the photocatalytic tests by varying the
6 initial phenol concentrations were obtained and the results (Figure 14) showed that with the increase
7 of the initial phenol concentration, there is no influence on the kinetic constant value and then, on
8 the photocatalytic reaction. These results are in contrast with the most papers dealing with the
9 photocatalytic degradation of phenol [6] in which it was shown that the degradation efficiency of
10 phenol decreased when the initial pollutant concentration increased, possibly due to the formation
11 of intermediates strongly adsorbed on photocatalyst surface. Therefore, our 1%Ag/ZnO
12 photocatalyst could be able to degrade phenol and intermediates in an effective way, as evinced
13 from TOC data (Figure 13) allowing treating aqueous solutions in the presence of also high phenol
14 initial concentration and without changing significantly the kinetic of photocatalytic reaction.

15

16 3.2.4 *Photocatalytic test on a drinking water matrix containing phenol*

17 Photocatalytic test was performed by using 0.15g of the optimal catalyst (1%Ag/ZnO) to treat a
18 drinking water containing phenol with an initial concentration at $50 \text{ mg}\cdot\text{L}^{-1}$ in 100 mL aqueous
19 solution. The physic-chemical characteristics of the treated drinking water are reported in Table 2.

20 Figure 15 shows the comparison between photocatalytic tests in presence of distilled water and a
21 drinking water in terms of phenol degradation and mineralization of the organic substance, in the
22 same experimental conditions. It can be observed that the phenol removal rate was lower
23 considering a real matrix because of the presence of ions scavengers in solution such as carbonates,
24 chlorides and nitrates (Table 2) which are capable to sequestrate a part of the radical species formed
25 during UV light irradiation. However, the total phenol degradation (Figure 15) with the almost

1 complete mineralization for the drinking water was reached after 180 minutes of UV irradiation
2 time. These results confirm the application of the photocatalytic system developed for the treatment
3 of waters containing phenol in order to reuse them since the limit values (lower than 0.5 mg L^{-1})
4 imposed by the Italian Legislation (D.Lgs. 152/06) allowed in the final effluent, are respected.

5

6 **Conclusions**

7 In this work the photocatalytic activity of Ag/ZnO photocatalysts was investigated for the treatment
8 of aqueous solutions containing phenol under UV light irradiation. Ag/ZnO samples were
9 synthesized by photodeposition method and they were characterized by different techniques. The
10 obtained results evidenced that ZnO is present as hexagonal wurtzite phase and Ag, present as
11 metallic silver (Ag^0), was successfully deposited on ZnO surface. It was found that Ag content
12 effectively deposited on ZnO increases by increasing the nominal Ag content from 0.14 to 1.28
13 wt%. Moreover UV-Vis DRS spectra showed that Ag/ZnO samples reveal a new reflectance band
14 ascribed to the surface plasmon resonance (SPR) absorption of metal silver particles. The silver
15 loading used in the preparation of Ag/ZnO photocatalysts is an important factor influencing the
16 physicochemical properties of the obtained photocatalyst. It was observed an enhancement of
17 photocatalytic phenol removal under UV light irradiation from aqueous solutions by silver addition
18 in comparison to commercial ZnO. In fact, the highest photocatalytic phenol removal from aqueous
19 solution was obtained by using 1%Ag/ZnO as photocatalyst, confirmed also by the evaluation of the
20 kinetic constant for phenol degradation. In particular, 1%Ag/ZnO was able to achieve both the total
21 phenol degradation that the total TOC removal in 120 minutes of UV light irradiation. This
22 enhancement can be explained by the presence of the SPR of silver observed by UV-Vis spectra
23 indicating that a large number of photoexcited electrons are generated from the Ag particles
24 surfaces to the conduction band of ZnO, consequently increasing the photocatalytic activity. With a
25 content of Ag higher than 0.88 wt%, the biggest number of Ag particles can obstruct the active sites

1 on ZnO surface with the consequence of a decrease in the photocatalytic phenol degradation. As it
2 can be observed by XPS, the increase of the Ag content to 1.28wt % leads also to increase the Ag⁰
3 species effectively deposited on ZnO surface, and therefore to decrease the available adsorption
4 centers for phenol (Ag^{δ+}). The optimized phototocatalyst was also able to treat a real drinking
5 wastewater containing phenol; in fact, both the total phenol degradation and the almost complete
6 mineralization was reached using 1%Ag/ZnO photocatalyst after 120 minutes of UV irradiation. At
7 last, 1%Ag/ZnO photocatalyst was tested in the treatment of a real drinking wastewater containing
8 phenol in which the total phenol removal after 120 minutes of UV irradiation time was achieved
9 confirming the possibility to employ the in the treatment of real wastewater.

10

11 **Acknowledgements**

12 This work was financed by Fondo Nacional de Financiamiento para la Ciencia, la Tecnología y la
13 Innovación “Fransisco José de Caldas – Colciencias”, Project 279-2016, Universidad Pedagógica y
14 Tecnológica de Colombia and by research fund from Project Ref. CTQ2015-64664-C2-2-P
15 (MINECO/FEDER, UE).

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17

18

Table 1

List of synthesized photocatalysts and their characteristics

	Commercial ZnO	0.25%Ag/ZnO	0.5%Ag/ZnO	0.75%Ag/ZnO	1%Ag/ZnO	2%Ag/ZnO
Nominal Ag loading [wt%]	-	0.25	0.5	0.75	1	2
Measured Ag loading [wt%]	-	0.14	0.38	0.57	0.88	1.28
Crystallite size [nm]	24	24	24	24	24	24
Band gap [eV]	3.1	3.1	3.1	3.1	3.1	3.1
SSA (m²/g)	5	5.2	5.4	5.5	5.3	3.5

Table 2

Chemical-physical characteristics of the drinking water matrix

	mg·L ⁻¹
HCO₃⁻	249
Ca²⁺	59.80
Mg²⁺	12.90
Cl⁻	6
NO₃⁻	7.10
SO₄²⁻	3.40
Na⁺	3.16
K⁺	1.08
F⁻	0.076

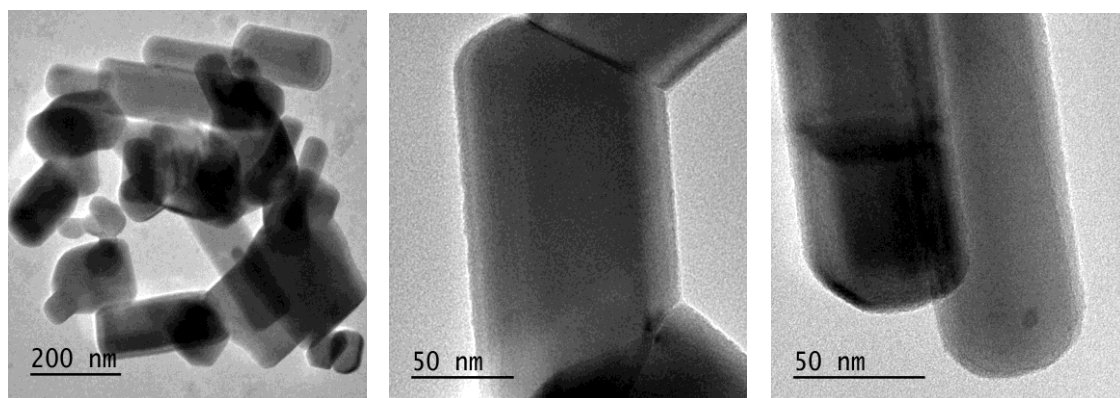


Figure 1. TEM images of commercial ZnO sample.

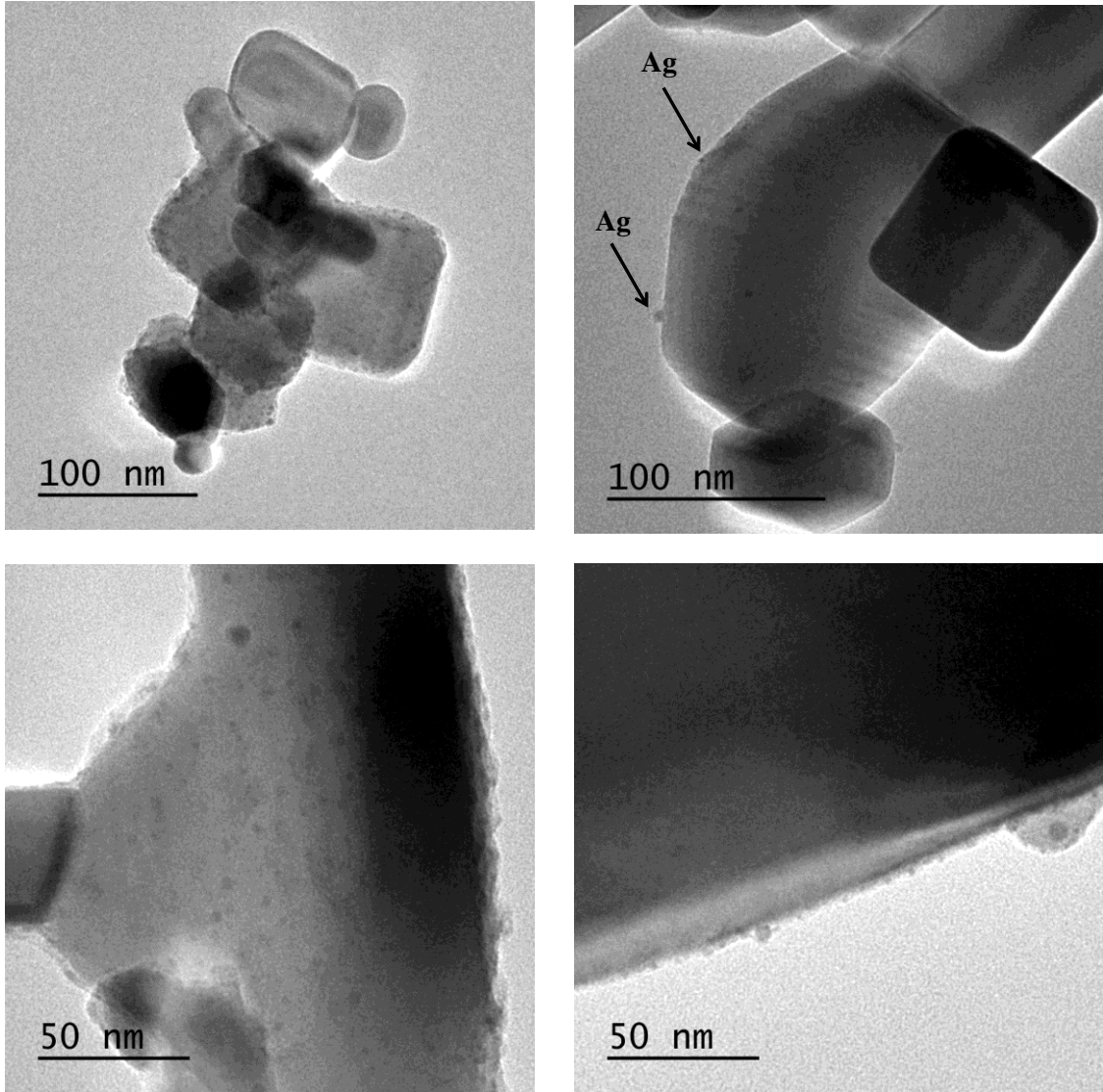


Figure 2. TEM images of 2wt% Ag/ZnO sample.

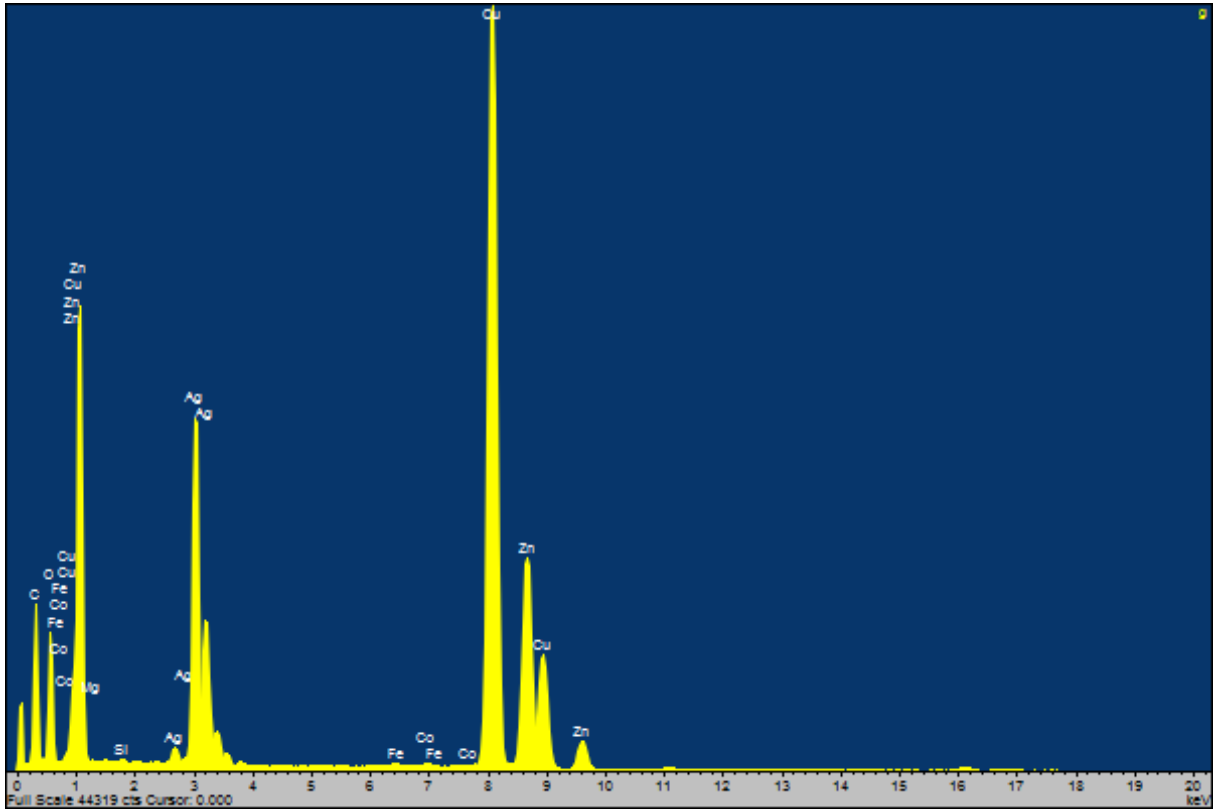


Figure 3. EDX identification of 2wt% Ag/ZnO sample.

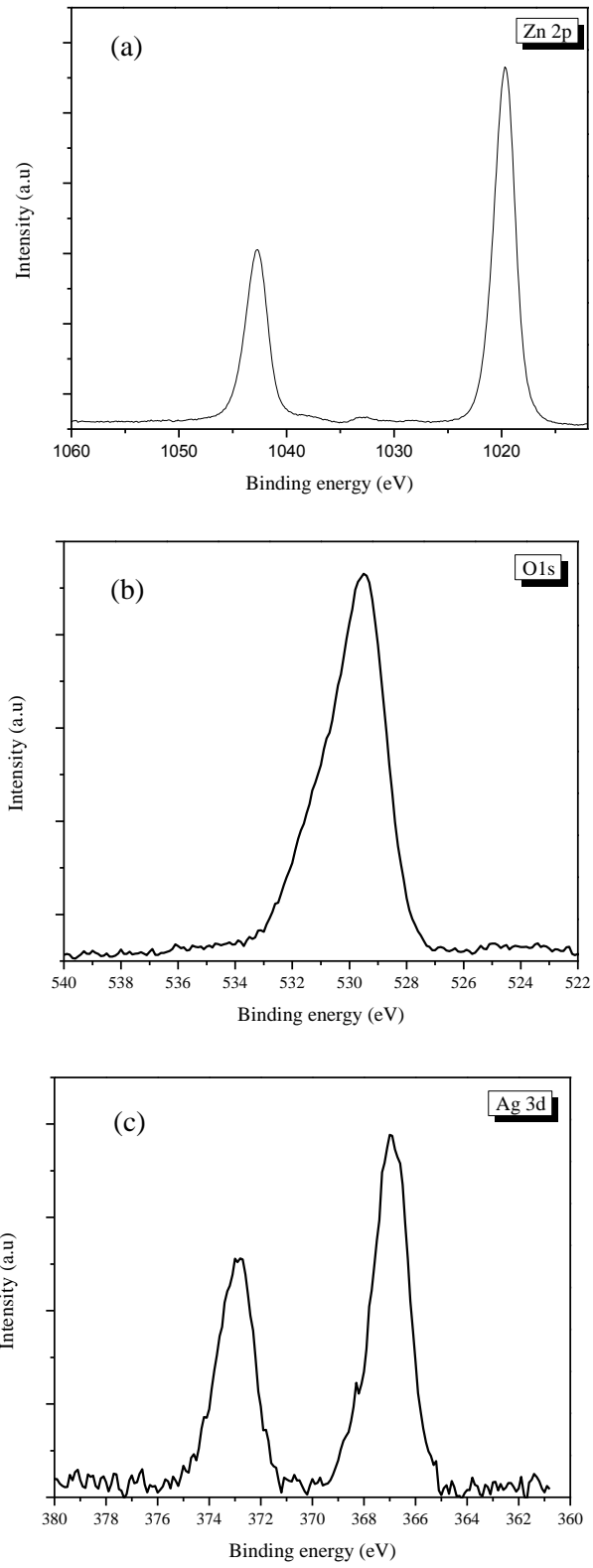


Figure 4. XPS core level spectra of Zn 2p (a), O 1s (b) and Ag 3d (c) regions for 2wt% Ag/ZnO sample.

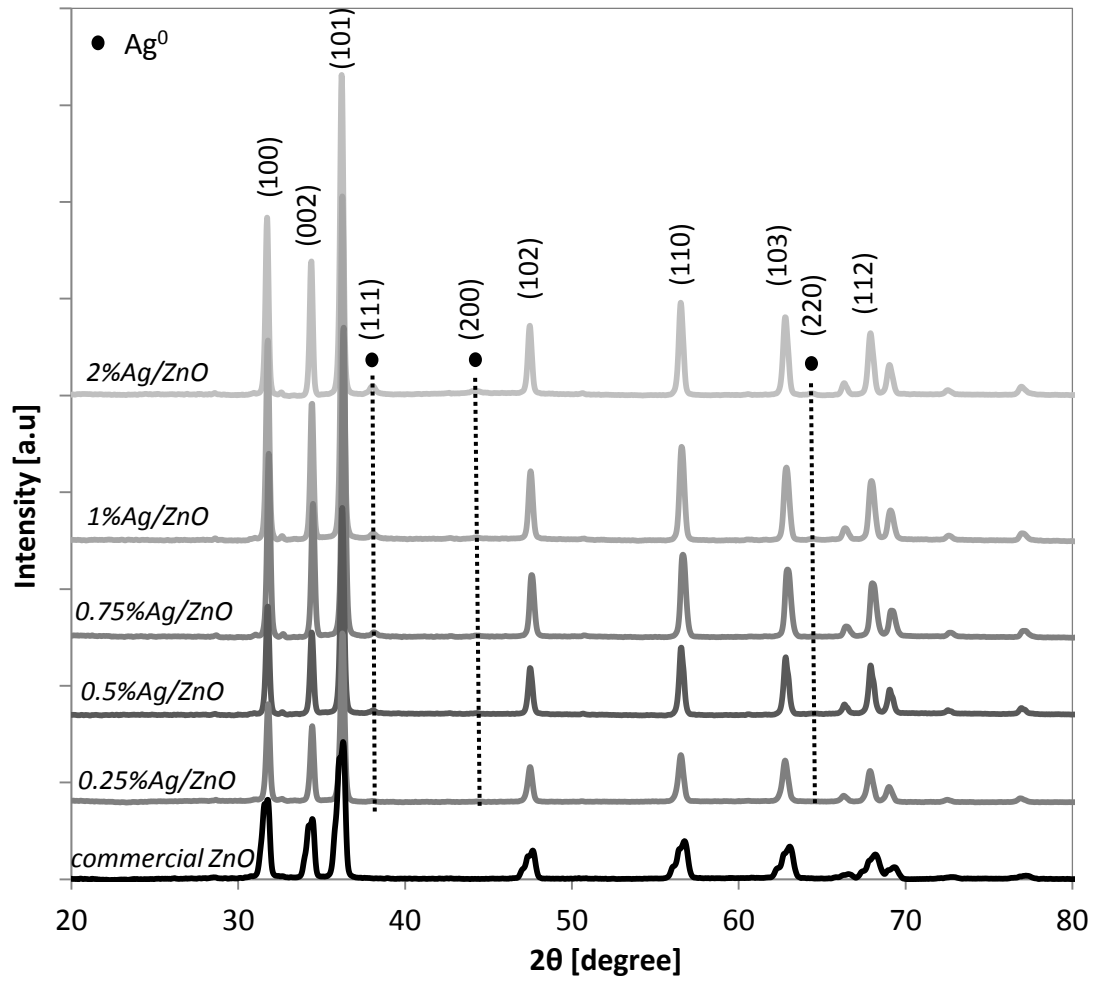


Figure 5. XRD patterns of commercial ZnO and Ag/ZnO photocatalysts in the range 20-80°

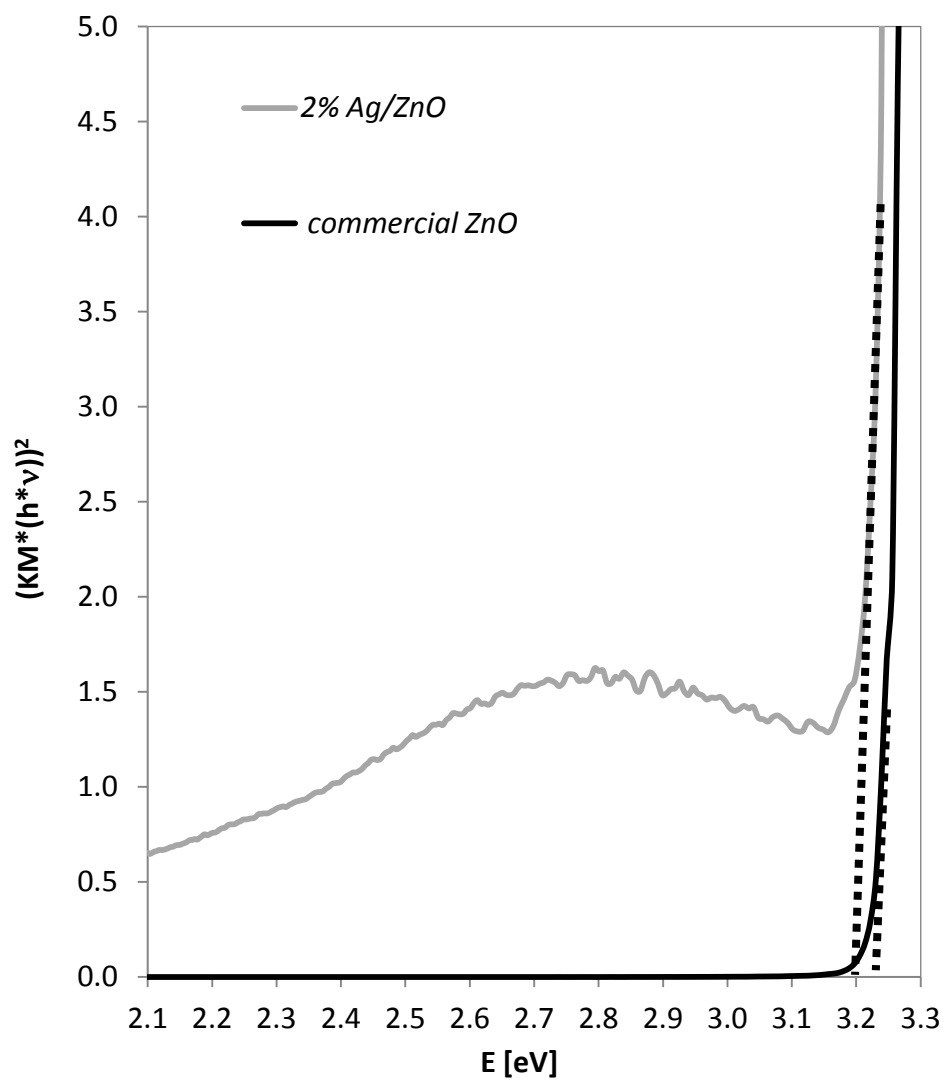


Figure 6. UV-Vis Diffuse Reflectance Spectra of commercial ZnO and 2% Ag/ZnO photocatalyst.

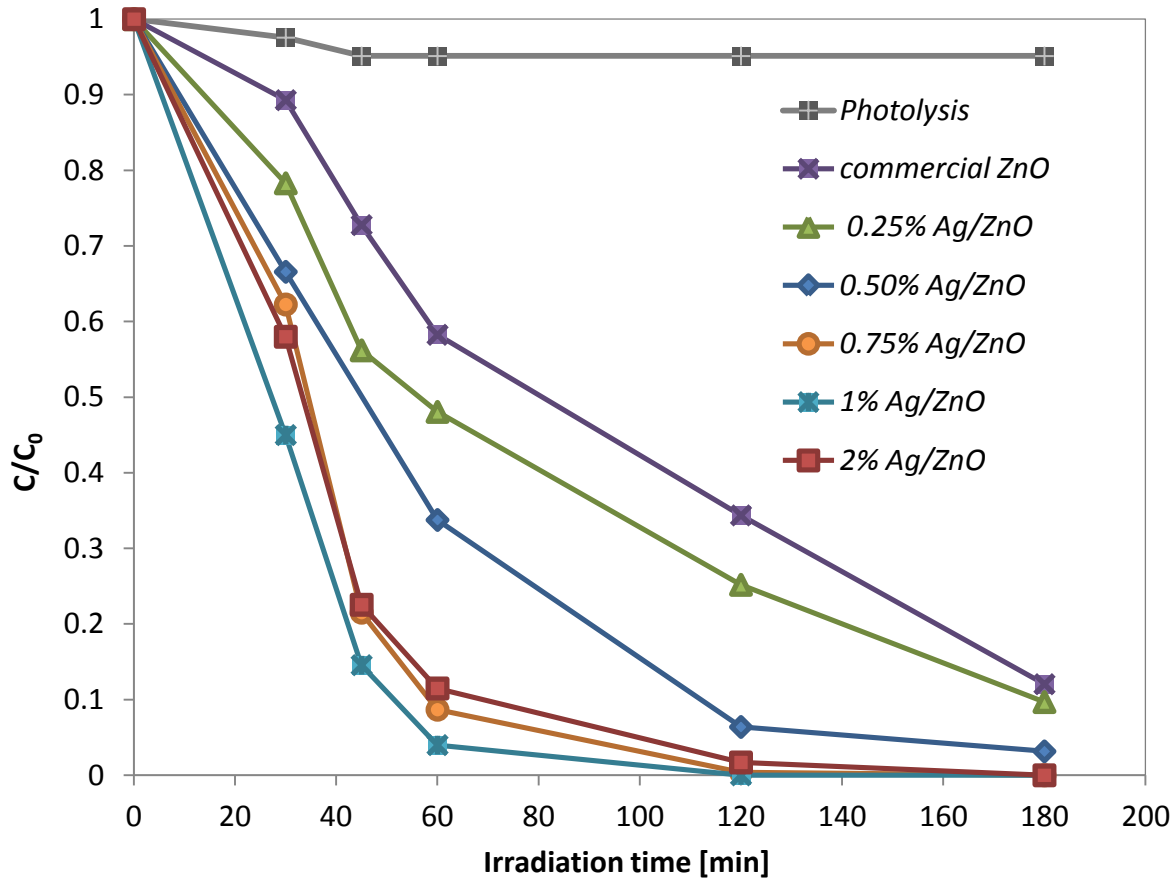


Figure 7. Photocatalytic phenol degradation under UV light using commercial ZnO and Ag/ZnO photocatalysts; phenol initial concentration: $50 \text{ mg}\cdot\text{L}^{-1}$; photocatalyst dosage: $1.5\text{g}\cdot\text{L}^{-1}$

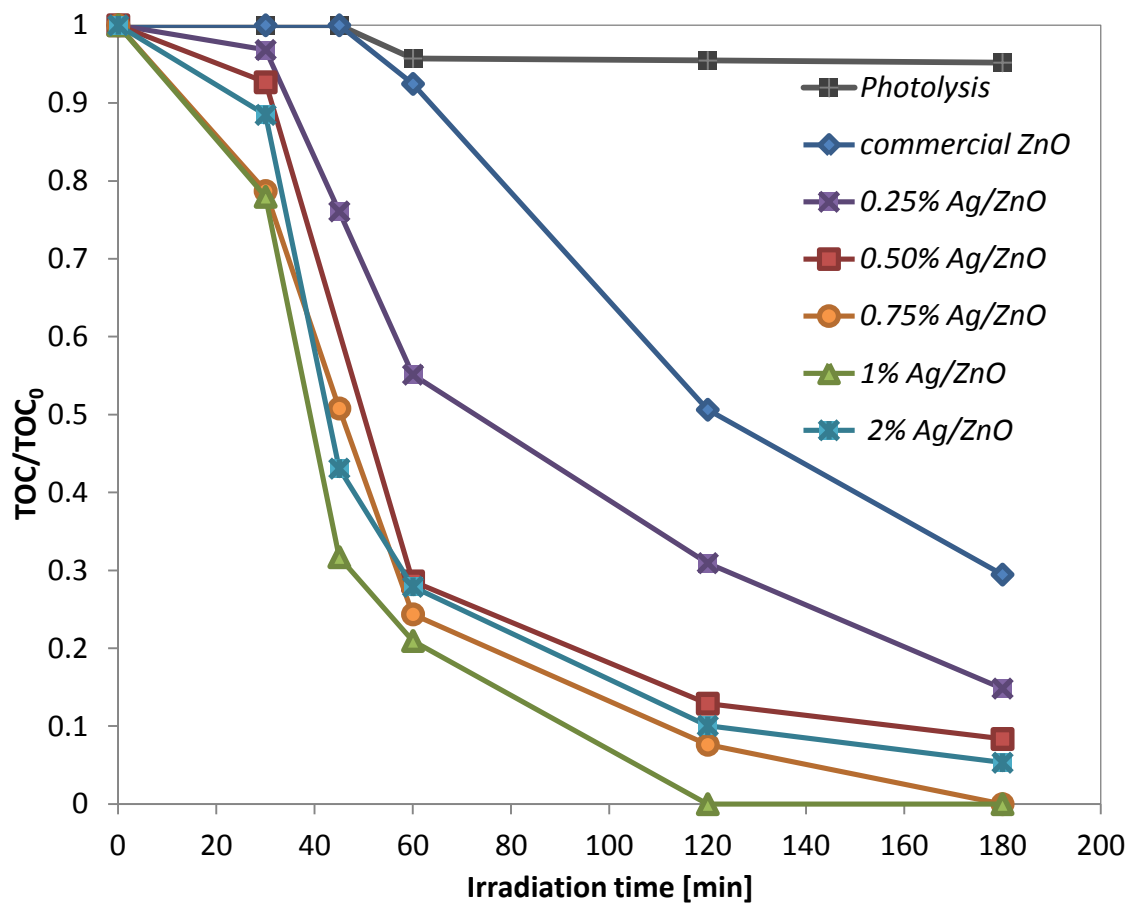


Figure 8. Total Organic Carbon (TOC) behavior under UV light using commercial ZnO and Ag/ZnO photocatalysts; phenol initial concentration: $50 \text{ mg}\cdot\text{L}^{-1}$; photocatalyst dosage: $1.5\text{g}\cdot\text{L}^{-1}$

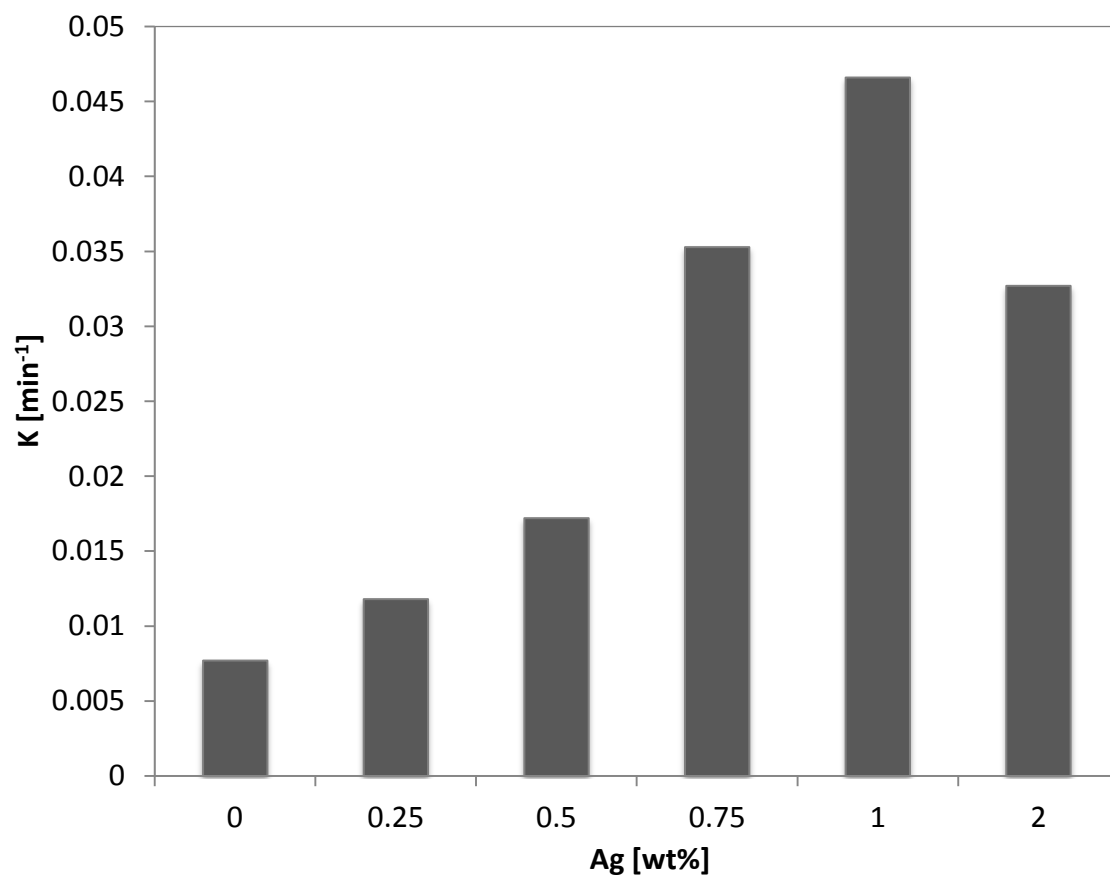


Figure 9. Kinetic constants for phenol degradation using commercial ZnO and Ag/ZnO photocatalysts under UV light; phenol initial concentration: $50 \text{ mg}\cdot\text{L}^{-1}$; photocatalyst dosage: $1.5\text{g}\cdot\text{L}^{-1}$

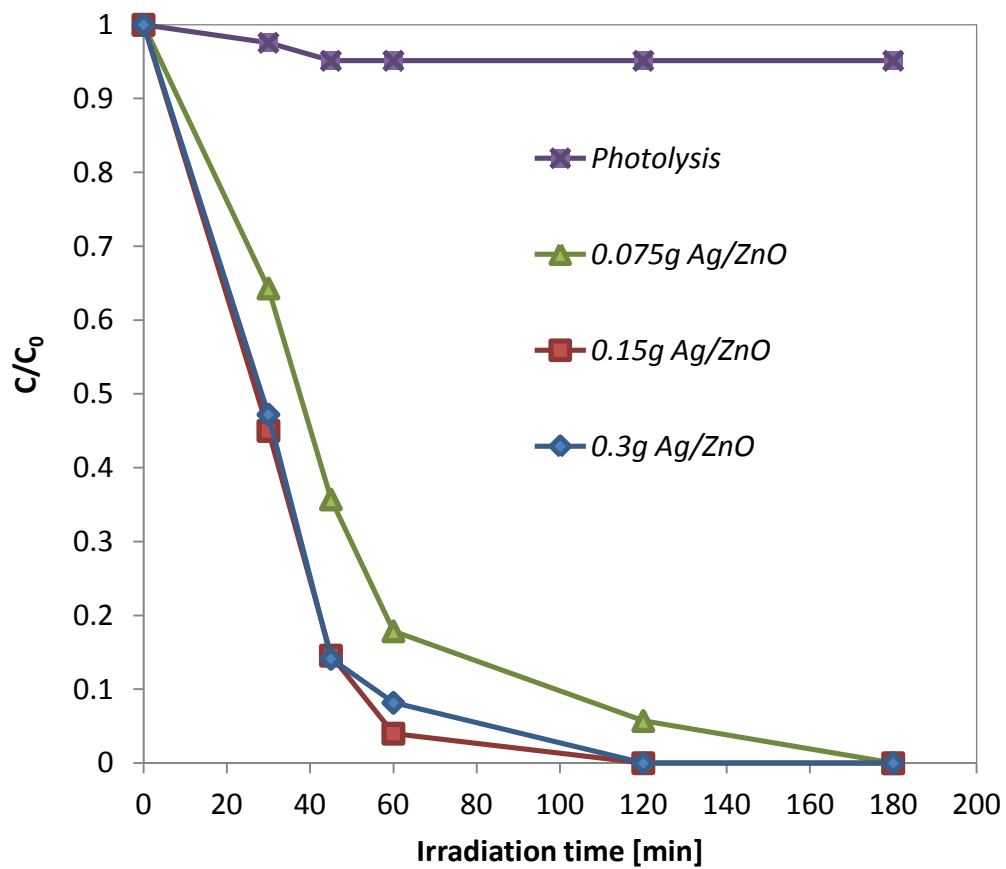


Figure 10. Photocatalytic phenol degradation under UV light using different 1% Ag/ZnO photocatalyst dosage; phenol initial concentration: $50 \text{ mg}\cdot\text{L}^{-1}$; solution volume: 100 mL

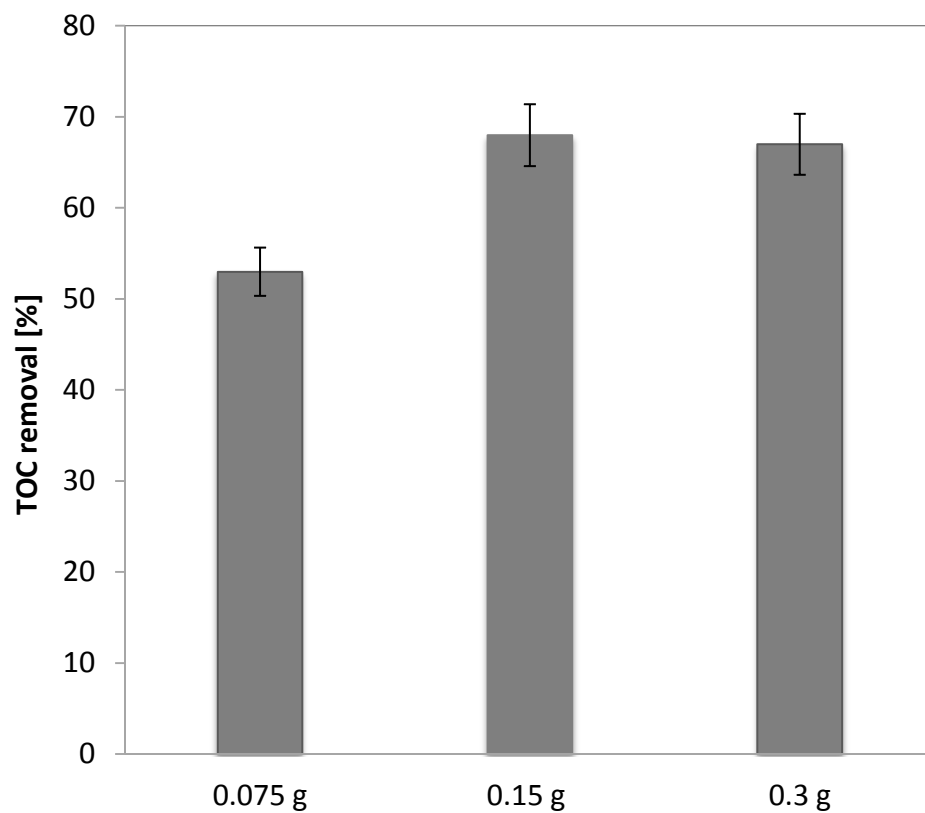


Figure 11. TOC removal after 45 minutes of UV irradiation using different 1%Ag/ZnO dosage; phenol initial concentration: 50 mg·L⁻¹; solution volume: 100 mL

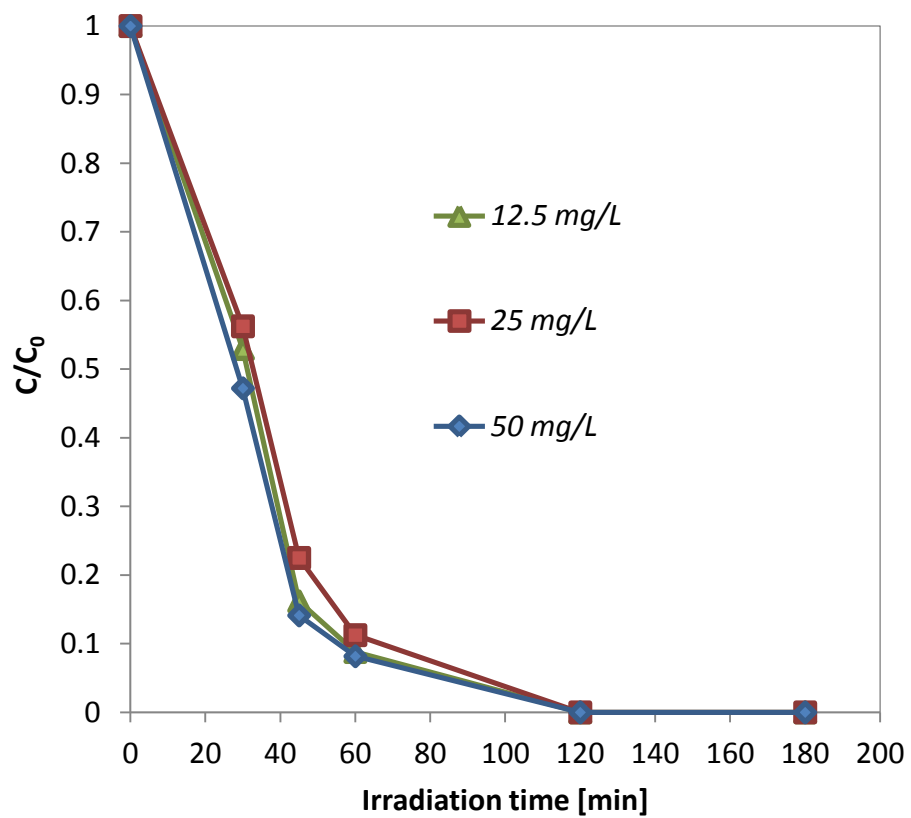


Figure 12. Photocatalytic phenol degradation under UV light at different initial phenol concentration using 1% Ag/ZnO photocatalyst; photocatalyst dosage: $1.5\text{g}\cdot\text{L}^{-1}$

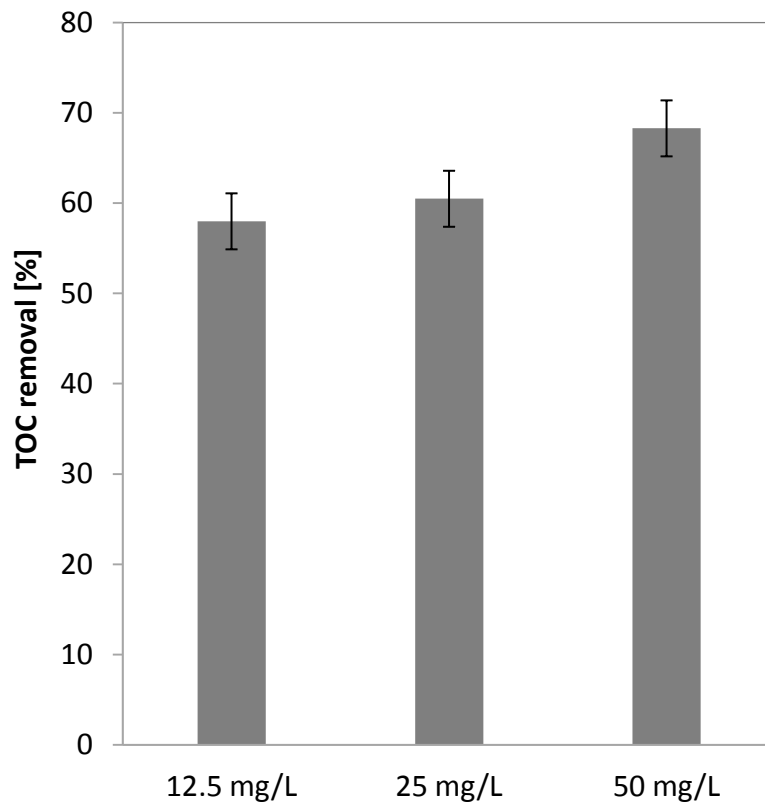


Figure 13. TOC removal after 45 minutes of UV irradiation at different initial phenol concentration using 1% Ag/ZnO photocatalyst; photocatalyst dosage: $1.5\text{g}\cdot\text{L}^{-1}$

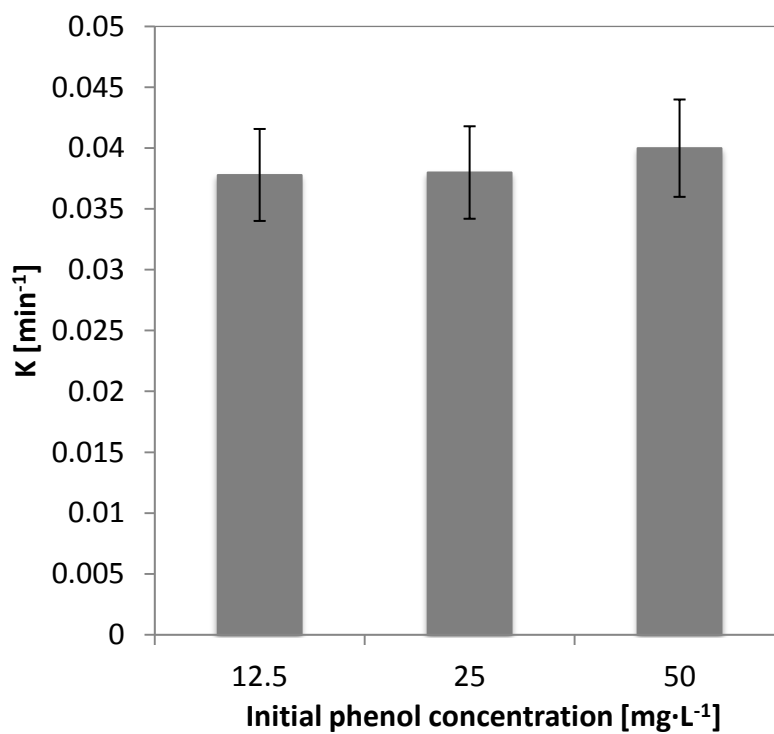


Figure 14. Kinetic constants after 45 minutes of UV irradiation at different initial phenol concentration using 1% Ag/ZnO photocatalyst; photocatalyst dosage: $1.5\text{g}\cdot\text{L}^{-1}$

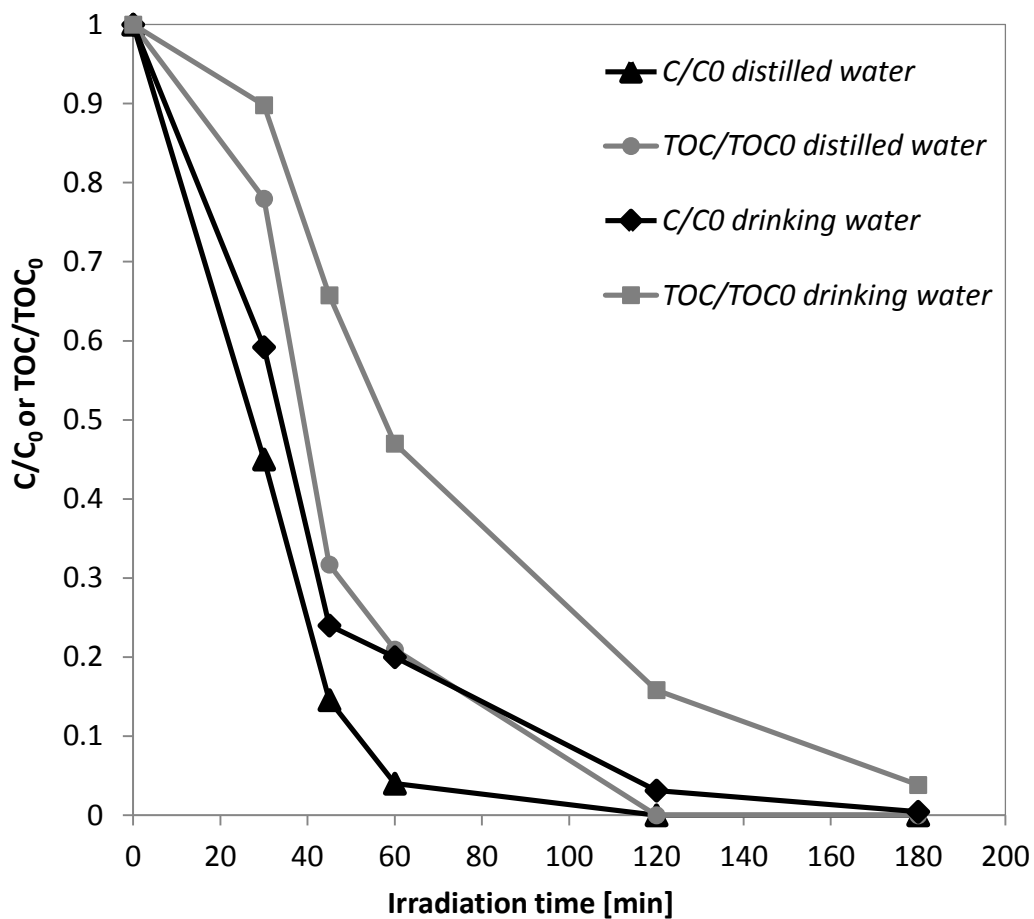
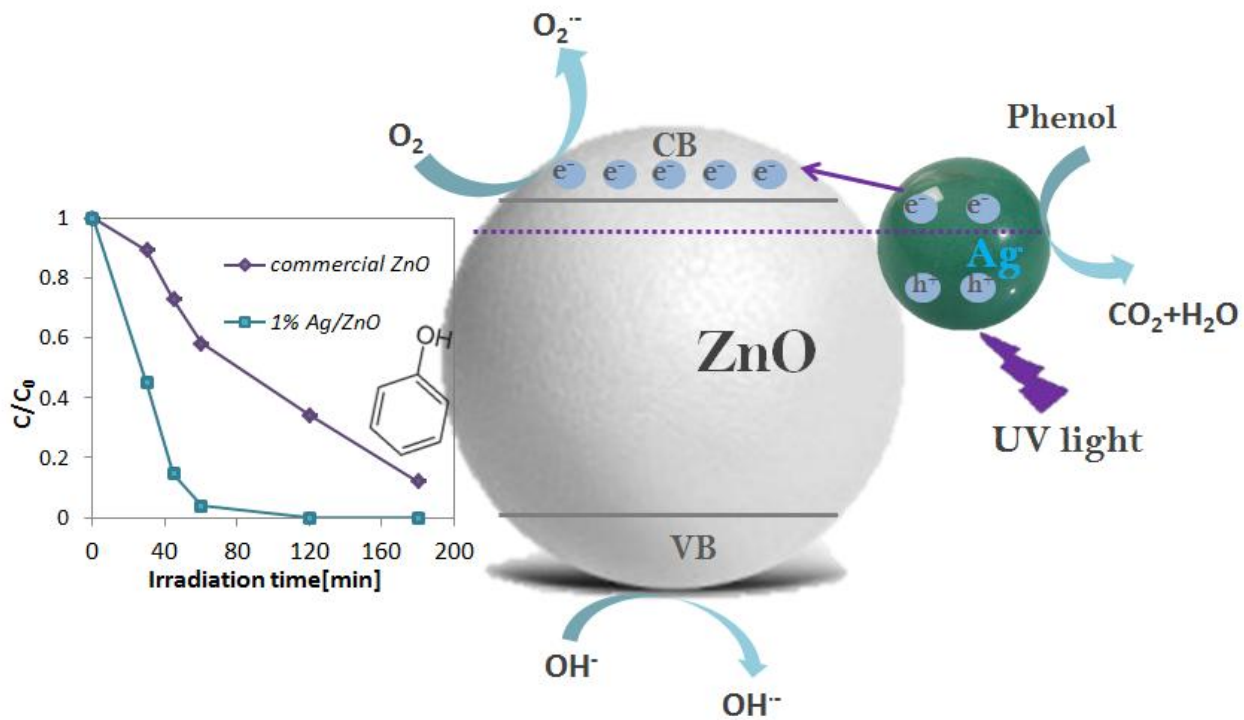


Figure 15. Photocatalytic phenol degradation and mineralization of a drinking water and distilled water under UV light with 1% Ag/ZnO photocatalyst; phenol initial concentration: $50 \text{ mg}\cdot\text{L}^{-1}$; photocatalyst dosage: $1.5\text{g}\cdot\text{L}^{-1}$



- Ag/ZnO photocatalysts were synthesized through photodeposition method
- Photocatalytic treatment of phenol aqueous solutions using Ag/ZnO
- The optimal Ag content was 0.88 wt%
- Complete phenol degradation and mineralization under UV light
- Ag nanoparticles improve the separation of photogenerated electrons and holes