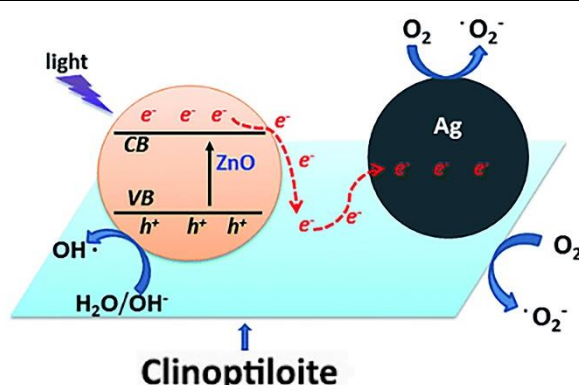


Original paper

## Synthesis and characterization of Ag-ZnO@Clinoptilolite for photocatalytic degradation of Tetracycline

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### GRAPHICAL ABSTRACT



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### ABSTRACT

In this research, degradation of Tetracycline by Ag doped ZnO based on Clinoptilolite (Ag-ZnO@CP) as photocatalyst was investigated under visible light. To synthesize of photocatalyst, the wetness impregnation method was used. The synthesized photocatalyst was characterized using XRD, FT-IR, SEM, BET and DRS analysis. The XRD analysis proved the synthesized crystalline phase about 42 nm. Based on SEM images, the morphology of the synthesized particles was spherical with a mean particle size of 55 nm. The FT-IR characteristic peak proved the formation of Ag-ZnO@CP. The photocatalyst bandgap was calculated by the Kubelka-Munk algorithm about 2.95 eV. The bandgap indicated that the photocatalyst was active in the visible light range. The results of degradation were shown that the nanoparticles of Ag-ZnO@CP had a higher efficiency compared with the non-silver state. The efficiency of the synthesized photocatalyst was evaluated with an initial pH of the solution, initial concentration of the pollutant and the amount of photocatalyst. For 60 min irradiation under visible light, the optimal values of the solution pH, the initial concentration of the pollutant and the photocatalyst were 8, 8 ppm and 1 g/L, respectively with 77.2 % degradation of Tetracycline. Also, the photocatalytic degradation of Tetracycline by the synthesized sample follows the first-order kinetic equation.

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### 1. Introduction

The effluents of the medical industry disposed of a large amount of antibiotics content, which generated drug-resistant and decreased the resistance of human bodies, polluted environment, and even affected on the ecosystem. Also, the presence of patients in different cities and their locations in urban areas has led to significant amounts of medicinal compounds such as antibiotics to enter the urban sewage (Čižman et al. 2015; Rodríguez-Mozaz et al. 2015; Wang et al. 2016). Especially, Tetracycline (TC) residues left in the environment, as one of the most commonly used antibiotics, can lead to antibiotic resistance by entering

the environment (Saadati et al. 2016). Due to the antibacterial nature of TC, it is very difficult to purify its waste by traditional methods such as physical adsorption and biological degradation.

Among the most commonly used processes, advanced oxidation processes (AOPs) with a generation of highly oxidizing hydroxyl radicals have exhibited the ability to degrade the recalcitrant and no biodegradable compounds (Habibi et al. 2017; Shaykhi Mehrabadi 2016). So far, TC destruction has been reported with various advanced oxidation processes, including Fenton reagent oxidation (Bautitz et al. 2007), ozonation (Dodd et al. 2009; Khan et al. 2010) and photocatalytic oxidation (Zhao et al. 2010). And the photocatalytic technique is

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considered suitable for the degradation of it with high efficiency, high mineralization rate, simplicity of operation and low cost. ZnO, with bandgap of 3.37 eV is the most commonly used photocatalyst for a wide range of organic compounds (Ahmadi et al. 2016; Bahrami et al. 2015). Limitations of work with this semiconductor include inactivity in visible light and low surface area. Recently, researches have been done to improve its surface area by loading on a porous support. Among the different types of supports, zeolites can be mentioned (Wang et al. 2010). Particularly, natural zeolites due to their large surface area, large ion exchange capacity, more importantly, their relatively low cost and chemical and thermal stability have a great potential in the wastewater treatment (Xingu-Contreras et al. 2017). On the other hand, the doping of ZnO with Ag into its lattice has been found to enhanced the light absorption ability of ZnO nanomaterial (Nezamzadeh-Ejhi et al. 2014).

In this work, Iranian natural zeolite was used to obtain Ag-ZnO@Natural zeolite by wetness impregnation method as a heterogeneous photocatalyst for degradation of TC pharmaceutical capsule in an aqueous solution under visible light.

## 2. Materials and methods

Zinc Oxide Nanoparticles (ZnO), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and silver nitrate ( $\text{AgNO}_3$ ) were bought from Merck Company. Semnan natural zeolite tuffs were obtained from Semnan Negin Powder Company. Common TC ( $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_8$ ) pharmaceutical 250 mg capsule was purchased from Iran Daru Company. All chemicals in this study used without further purification.

The structure of the samples was examined by using a diffractometer Bruker, D8 (with X-ray tube anode and Cu K $\alpha$  wavelength: 1.5406 Å). The surface morphology of samples was studied using a KYKY-EM-3200 scanning electron microscope (SEM). The BET surface areas of samples were determined from isotherm data of nitrogen adsorption data obtained at 77.35 K using Quanta chrome Autosorb-1 analyzer. UV-Vis spectra were obtained on a Shimadzu UV-1650PC spectrophotometer. Fourier transform-infrared spectroscopy (FTIR) in the range of 400-4000  $\text{cm}^{-1}$  was recorded (Shimadzu FT-IR 8400S).

### 2.1. Preparation of CP

At first for preparation of natural zeolite, 25 gr of natural Clinoptilolite (CP) powders was added in 250 ml deionized water and stirred at 70 °C for 5 hours. The precipitate was then strained with 250 ml sulfuric acid (1M) at 70 °C for 3 hours. The precipitate obtained after separation and washed with deionized water, dried at 110 °C and crushed in ceramic mortar. Finally, it was calcined at 500 °C for 3 hours.

### 2.2. Preparation of ZnO@CP

To prepare the ZnO@Clinoptilolite (ZnO@CP), 4 gr of CP and 0.44 gr ZnO was added to 40 ml distilled water and stirred (15 min, 70 °C). The sample was filtered off, washed and dried at 120 °C and then calcined at 500 °C for 2 h (Mahboobi et al. 2018).

### 2.3. Preparation of Ag-ZnO@CP

To prepare Ag-ZnO@CP, the above procedure was repeated. With the difference, 0.5 gr  $\text{AgNO}_3$  was added from the beginning to the initial solution. Then,  $\text{Na}_2\text{CO}_3$  solution (50 ml, 0.25M) was added drop by drop and stirred (1 hr, 45 °C). The sample was filtered off, washed and dried at 120 °C and then calcined at 500 °C for 2 h.

## 3. Results and discussion

### 3.1. Characterization

The XRD patterns of natural zeolite (CP) after activation, synthesized ZnO@CP and Ag-ZnO@CP are shown in Fig. 1. The characteristic peaks at  $2\theta$  values of 9.85°, 22.5° and 27.7° in the pattern (a) confirms that the used zeolite has a typical zeolite clinoptilolite structure as major phase (JCPDS no. 39-1383) (Korkuna et al. 2006; Bahrami et al. 2015). The presence of the new peaks at  $2\theta$  values of 31.8°, 34.46°, 36.2°, 47.5°, 56.78°, 62.8°, 66.3° and 68.9° in the XRD pattern of ZnO@CP and Ag-ZnO@CP corresponding to a wurtzite hexagonal phase of ZnO (JCPDS 75-0576) (Bahrami et al. 2015; Singh et al. 2008). For the Ag-ZnO@CP sample, the main reflection of the Ag phase located around 38.11° and 44.31° was also detected which are

in good agreement with the face-centered cubic structure of Ag (JCPDS FileNo.04-783) (Bahrami et al. 2015; Motshekga et al. 2015). In addition to the mentioned peaks, there are no other peaks in the patterns. Also, the intense and sharp peaks created by it confirm the synthesis of crystalline and pure crystalline structures. The average crystallite size of the nanoparticles was calculated using the Debye-Scherrer equation (Table 1) (Nezamzadeh-Ejhi et al. 2010).

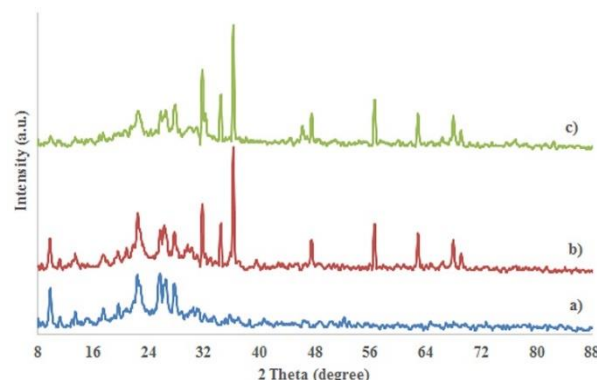


**Fig. 1.** XRD patterns of a) Natural zeolite (CP), b) Synthesized ZnO@CP, and c) Synthesized Ag-ZnO@CP.

**Table 1.** Average crystallite size of samples by XRD patterns.

| Sample               | $2\theta$ , ° | FWHM   | Crystallite size, nm |
|----------------------|---------------|--------|----------------------|
| Natural Zeolite (CP) | 25.67         | 0.4723 | 18.6                 |
| ZnO@CP               | 36.27         | 0.2952 | 33.37                |
| Ag-ZnO@CP            | 36.26         | 0.2362 | 41.7                 |

The FTIR spectra of natural zeolite (CP), synthesized ZnO@CP and Ag-ZnO@CP are shown in Fig. 2. The broad peak around 3427 and 1627  $\text{cm}^{-1}$  can be assigned to the O-H stretching and vibration of adsorbed water, respectively (Mohan Kumar et al. 2010). As shown in the spectrum of zeolite in all samples, the peak at 1060.77  $\text{cm}^{-1}$  corresponds to the Si-O-R (Si or Al) stretching vibration. The stretching modes of Zn-O appeared around 460 and 600  $\text{cm}^{-1}$  (Vieira et al. 2019). The peak at 799  $\text{cm}^{-1}$  is attributed to symmetric stretching vibrations of (Si-O-Si); and the band at 459-463  $\text{cm}^{-1}$  are attributed to the bending vibration of (Si-O-Si) (Sanaeishoar et al. 2015) and the bands 646.1  $\text{cm}^{-1}$  are presents in the spectrum evidence of Ag/ZnO tensional tremble (Jafari et al. 2011).

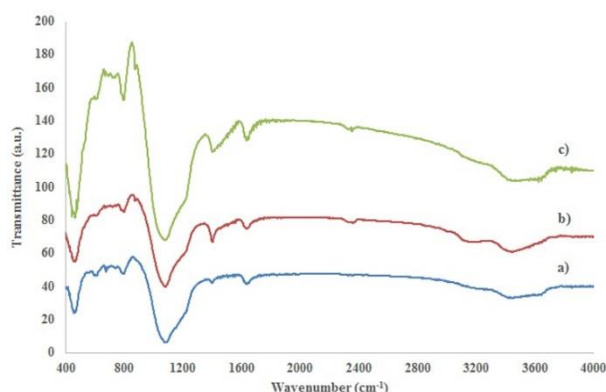


**Fig. 2.** FT-IR patterns of a) Natural zeolite (CP), b) Synthesized ZnO@CP, and c) Synthesized Ag-ZnO@CP.

DRS analysis was used to investigate the optical properties of the samples and the results are shown in Fig. 3. The bands-gap energy ( $E_g$ ) of synthesized ZnO@CP and Ag-ZnO@CP samples were obtained by the Kubelka-Munk algorithm and reduced to 3.1 and 2.95 eV in comparison with pure ZnO, respectively. By reducing the bandgap, the sample will be able to activate in visible light. In pure zinc oxide, only Zn-O bonds can absorb photons, but when zeolite was used as support, Al-O-Zn bonds can also be formed. The short-wave absorption band is inherently present in a variety of zeolites, and they can transfer the charge from oxygen to aluminum in the presence of aluminum in certain locations (Amiri et al. 2015; Bahrami et al. 2015). The decrease in the bandgap of the Ag-ZnO@CP may be due to the

generation of an additional energy level within the ZnO after the penetration of silver in the zinc oxide network, which can absorb light through zinc oxide at lower energy levels (Wang et al. 2010).

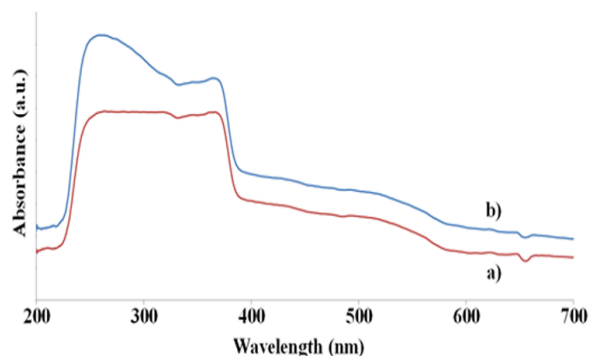


**Fig. 3.** UV-vis diffuse reflectance spectra of a) Synthesized ZnO@CP, and b) Synthesized Ag-ZnO@CP.

The corresponding images of synthesized ZnO@CP and Ag-ZnO@CP samples by SEM are shown in Fig. 4a and b, respectively. It can be seen from Fig. 4a that the morphology of the synthesized ZnO@CP is quasi-spherical nanoparticles (50 nm). According to the images, the addition of silver to the ZnO@CP sample has not caused a significant change in particle size, and its particle size is about 55 nm. This result was also observed with another researcher (Hosseini et al. 2015).

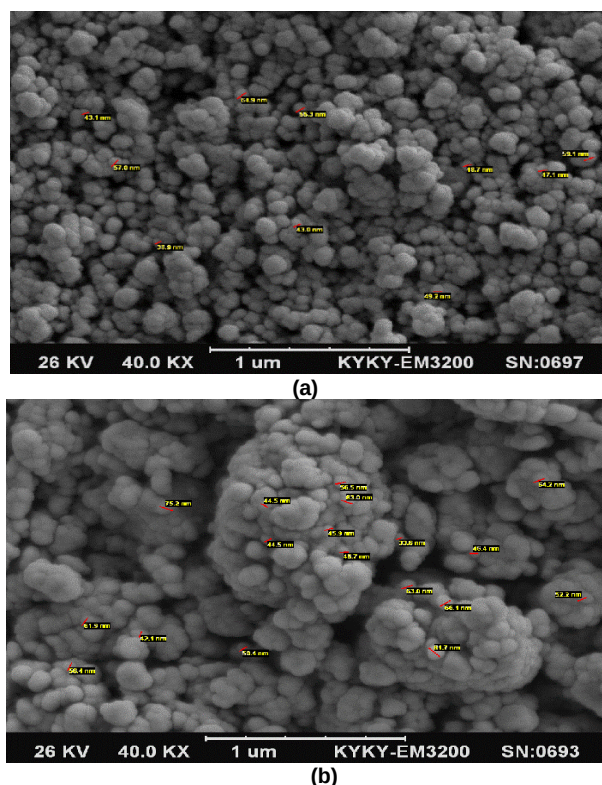


**Fig. 4.** SEM images of a) synthesized ZnO@CP, and b) Ag-ZnO@CP.

The measured BET surface areas of the samples were decreased from 235.93 m<sup>2</sup>/gr for CP to 212.83 for ZnO@CP and 169.21 for Ag-ZnO@CP. In the adsorption-desorption isotherm (Fig. 5), the created hysteresis loop indicates the presence of a mesoporous material. When the P/P<sub>0</sub> ratio is too large, the material has very narrow pores in the form of capillaries, in which case the number of adsorption sites increase significantly and the absorbing material is dense on the surface. This type of isotherm is often observed for industrial catalysts, and besides, the corresponding curve for determining pore size distribution (BJH) is also used. To determine of cavity size distribution, the BJH chart (Fig. 5) is used. According to this diagram, the most common cavity size is 6.6 nm. The point of zero charge (pzc) of Ag-ZnO@CP was found to be 8.5 and is shown in Fig. 6. This value corresponded to the pH at which

the straight line (pH<sub>initial</sub> = pH<sub>final</sub>) crossed the sigmoid curve passing through the experimental points (Keramati et al. 2014). The electric charge properties of both the photocatalyst and pollutant play an important role in the adsorption process. The surface of the catalyst was positively charged at a pH < pH<sub>pzc</sub>, negatively charged at a pH > pH<sub>pzc</sub>, and remained neutral at a pH = pH<sub>pzc</sub>. Such behavior significantly affected not only the adsorption-desorption properties of the catalyst surface, but also the changes of the pollutant structure at various pH values (Keramati et al. 2015).

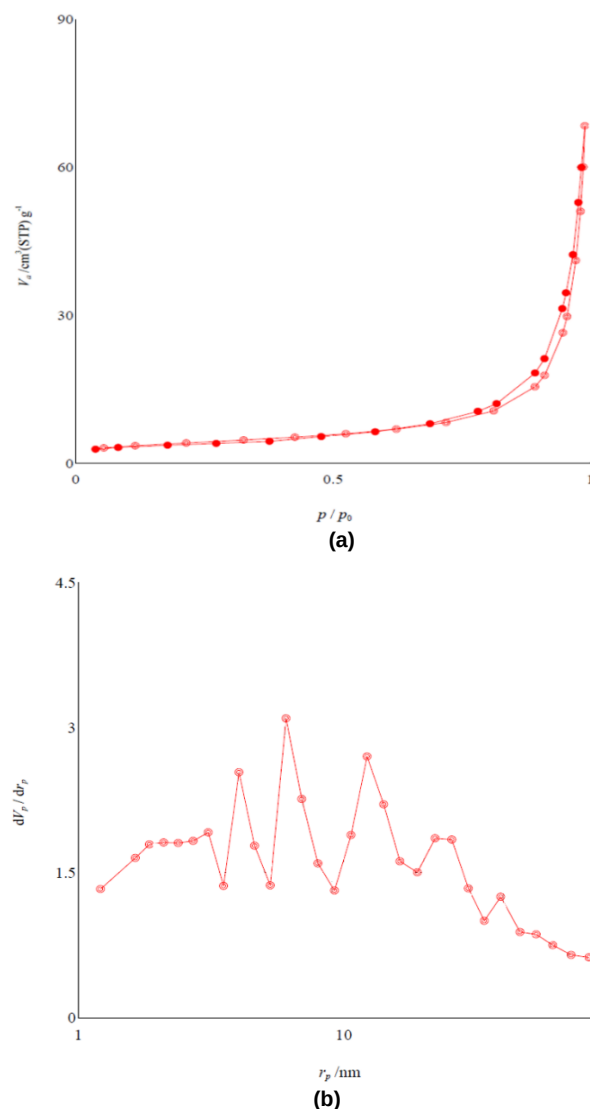


**Fig. 5.** a) Adsorption-desorption isotherms and b) BJH plot of synthesized Ag-ZnO@CP.

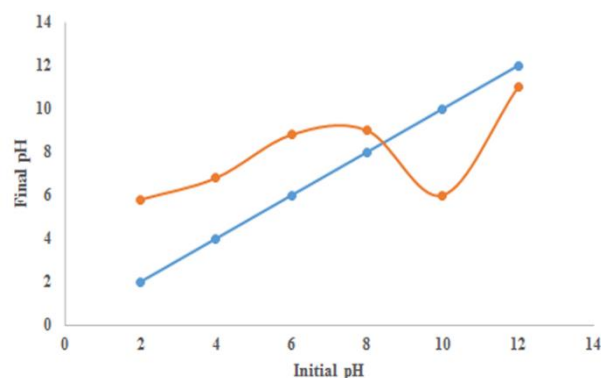


**Fig. 6.** pH<sub>pzc</sub> of synthesized Ag-ZnO@CP sample.

### 3.2. Photocatalytic degradation of tetracycline

The effect of the initial concentration of pollutant on the rate of degradation was determined by changing the initial concentration of TC from 6 to 10 ppm by loading constant catalyst at pH=8. Fig. 7 shows that with increasing concentrations of pollutants, degradation efficiency was decreased due to the reduction of active sites on photocatalyst for the oxidation of the pollutant molecule. A similar result was reported by satdeve (2019) for the degradation of Methylene Blue by Ag/ZnO. With increasing in the initial concentration of TC, more reactants and reaction intermediates were absorbed at the photocatalyst level, so the available hydroxyl radical was not sufficient to degrade TC at higher concentrations. Thus, its degradation rate was decreased with increasing its concentrations. To evaluate the optimal amount of photocatalyst loaded, experiments with different amounts of Ag-ZnO@CP photocatalyst were performed. Fig. 8 shows the degradation of TC contamination in different amounts of photocatalyst at pH=8 and contaminant concentration of 8 ppm. By increasing the catalyst concentration to 1 g/L, degradation efficiency was increased but then decreased with increasing catalyst concentration. Reducing the degradation efficiency at concentrations higher than 1 g/L due to the reflection of light by catalyst particles. In other research, this phenomenon suggests that due to the excessive increase in the catalyst, aggregation was occurred (Satdeve et al. 2019).

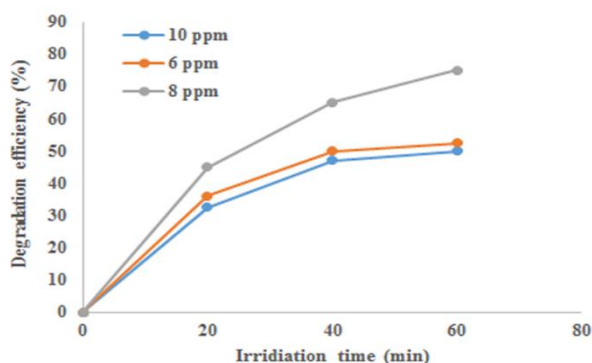


Fig. 7. Effect of initial concentration of TC on degradation efficiency.

The pH of the solution plays a significant role in the process of photocatalytic degradation of various pollutants. The effect of pH on the photocatalytic degradation of TC was studied in the range of 6-10. As shown in Fig. 9, the highest degradation efficiency was obtained at pH=8, which was selected as the optimum value. By reducing pH under pH<sub>PZC</sub>, and eliminating alkalinity, the efficiency of the system was increased and reached a maximum at pH=8. But again, with decreasing pH, the efficiency of the system was reduced, which was due to the dominance of the electron/hole mechanism instead of the mechanism of free radicals of hydroxyl (Mokhtarani et al. 2014). To investigate the type and nature of photocatalyst used in the photocatalytic degradation process, three samples of CP, ZnO@CP, and Ag-ZnO@CP were compared in a similar situation. As shown in Fig. 10, for all three samples, degradation efficiency was increased over time, which was higher for Ag-ZnO@CP than the others. In another study, the key role of silver has been investigated for enhancing the photocatalytic activity of zinc oxide and a similar result has been reported (Zhu et al. 2018).

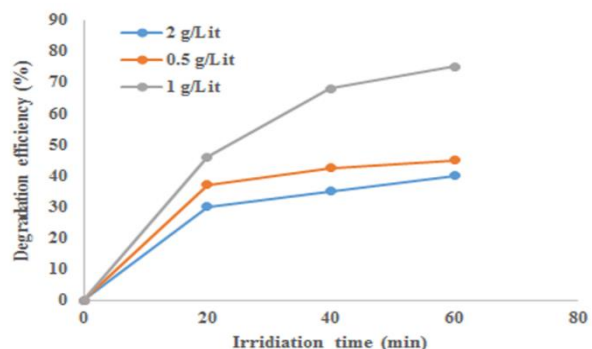


Fig. 8. Effect of photocatalyst dosage on degradation efficiency.

In this study, the radiation time of 20, 40 and 60 min were considered for the destruction of TC by the photocatalytic process of Ag-ZnO@CP nanoparticles under visible light. The results were

indicated that with increasing radiation time (20, 40, 60 min), the efficiency of pollutant degradation was increased (about 48, 69, 77 %). However, the degradation efficiency was the highest during the first 20 min of the reaction, and as time goes on, its increasing trend decreased. This could be attributed to the rapid decomposition of TC contamination in the 20 min before the reaction of free radicals generated by the electron excitement used. With increasing radiation time, although the process of arousal of photocatalyst nanoparticles and the production of free radicals of hydroxyl was not reduced, but due to the formation of intermediate organic compounds due to the decomposition of TC, some of the free radicals produced were exclusively for the decomposition of these compounds, and as a result reduces the amount of pollutant removal.

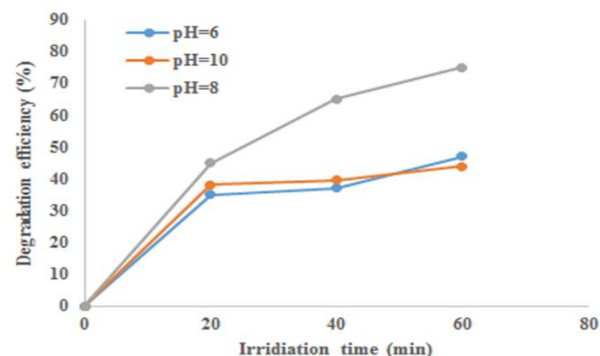


Fig. 9. Effect of initial pH of solution on the degradation efficiency.

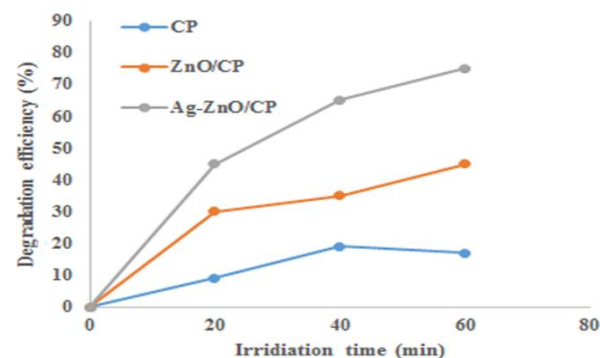


Fig. 10. The effect of photocatalyst on the degradation efficiency.

According to a great number of investigations, the dependence of the photocatalytic degradation rate on the concentration of organic pollutants has been described well by the Langmuir-Hinshelwood (L-H) in simplified form (Keramati et al. 2014; Pascariu et al. 2019).

$$\ln(C_0/C) = Kt \quad (1)$$

where,  $C_0$  is the initial concentration of pollutant and  $C$  is the pollutant concentration at time  $t$ . As shown in Fig. 11, the variation of  $\ln(C_0/C)$  is linear in time and the slope of this line is the constant of the reaction speed ( $K$ ). Hence, the photocatalytic degradation of TC follows the first-order kinetic equation.

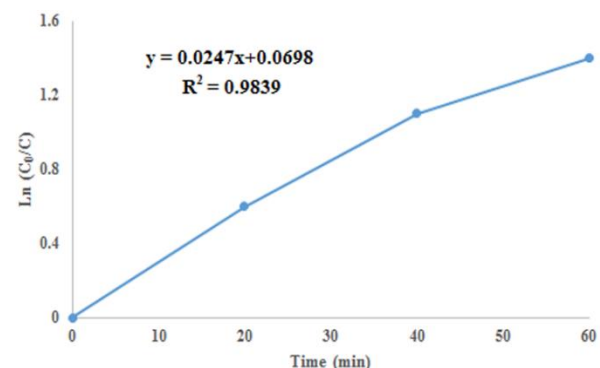


Fig. 11.  $\ln(C_0/C)$  vs. time.

## 4. Conclusions

In this study, Ag–ZnO@CP photocatalysts were prepared by the co-precipitation method and its photocatalytic effect on the degradation of TC under visible light was investigated. It was shown that natural zeolite played a significant role in the increasing of photocatalytic properties at the Ag-ZnO nanoparticles, which gave a higher surface area to the synthesized product. The determination of the bandgap energy showed a shift to the visible region in doped samples (2.95 eV). Approximately 77 % of TC has been eliminated after 60 min in the presence of Ag-ZnO@CP under visible light.

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