



Photocatalysts Capability of Bentonite-ZnO Nanocomposite Synthesized by Solution Combustion in Ciprofloxacin Degradation

H. Nasiri^{*1}, M. Golmohammadi², H. Sazegaran³

¹Department of Materials Engineering, Birjand University of Technology, Birjand, Iran;

²Department of Chemical Engineering, Birjand University of Technology, Birjand, Iran;

³Department of Industrial Engineering, Quchan University of Technology, Quchan, Iran.

Received: 28 January 2023; Accepted: 30 May 2023

*Corresponding author email: nasiri@birjandut.ac.ir

ABSTRACT

The increasing industries and population growth, make various new needs for water. So, scientists and researchers try to invent new methods for processing and synthesizing new materials to recycle used water sources. In this research, Zn (NO₃)₂·6H₂O (zinc nitrate) and C₂H₅NO₂ (glycine) were used as raw materials in Solution Combustion Synthesis technique (SCS) to synthesize ZnO nanoparticles. Also, the bentonite is added to the reaction container during the synthesis to act as substrate for nanoparticles to produce Bentonite-ZnO nanocomposite in-situ in less than 10 min at the air atmosphere. The successful synthesis was confirmed by X-ray diffraction analysis and the reason of that was explained by DSC-TGA of raw materials. It proved the same thermal behaviors of zinc nitrate as oxidizer and glycine as fuel could carry out the reaction. The SEM and TEM images demonstrated the decoration of ZnO on bentonite. Finally, the photodegradation of an antibiotic (ciprofloxacin) in presence of synthesized nanocomposite was examined under direct sunlight. The results showed about 97% degradation efficiency and 81% for total organic carbon removal after 3h reaction at the rate constants of 1.04 h⁻¹. The blank test from just bentonite shows less than 10% degradation efficiency that proves the presence of ZnO increases this value more than 87%.

Key Words: Photocatalyst, Combustion Synthesis, Decomposition, Nanocomposites, Zinc oxide.

1. Introduction

In new century and by development of industries, the increasing expansion of technology and population growth, make various new needs for the human race. In order to meet these challenges, scientists and researchers try to invent new methods for processing and synthesizing new materials for recycling past sources [1-3]. The increasing need of industries for water in different sectors on the one hand and the limited water resources on the other is caused the necessity of treatment and reuse of industrial effluents [4]. Cosmetics, textiles, food, cosmetic, paper, and pharmaceutical are the main industries that used a large volume of water [5].

Pharmaceutical industry effluents are known as one of the most harmful runoffs because they contain compounds with long half-lives. As a result, they will have high persistence in the aqueous environment even at low concentrations [6]. Antibiotics are one of the most important pharmaceuticals that are widely consumed in the treatment of pathogenic diseases of humans or animals. Ciprofloxacin as a fluoroquinolone antibiotic is a widely consumed antibiotic to treat a variety of bacterial infections [7]. Many of this antibiotic is excreted non-metabolized and eventually enter the environment through wastewater, which contaminates water resources [8]. The release of effluent containing

this substance even in small amounts, without any treatment causes the development of antibiotic resistance, adverse effects on non-target pathogens, alteration of the structure of algae, destructive effect on photosynthesis of plants and as a result the apparent abnormalities of plants [9]. Considering these risks, the development of an efficient method to remove ciprofloxacin from effluents is an undeniable necessity. One of the most effective methods for removing various organic compounds is photocatalytic degradation [10]. On the other hand, producing particles with photocatalytic properties in nanoscale and placing them on a suitable support can improve their performance [11, 12].

So, a new branch of synthesis methods with low cost, fast and the ability to synthesize pure nanoparticles is useful. This method did not require expensive equipment and its raw materials were easily available. Also, the biggest advantage of this method is, there is no need for an external energy source to carry out the synthesis. Because the process is based on oxidation-reduction reactions between raw materials. The researchers named this method self-propagation high temperature synthesis (SHS). In this method, the metal oxide(s) at the top of the Ellingham diagram is mixed with the metal at the bottom of the diagram [13-15].

There are some drawbacks of SHS method, such as: it needs high compression to compact the raw materials and relatively has high ignition temperature. It caused to invent, a new method called solution combustion synthesis (SCS). This sub-branch method is the same as SHS. The difference is that, the raw materials are metal nitrates that dissolve in water. In addition, one or more water-soluble organic compounds (urea, glycine and etc.) are used as fuel. The reaction energy in this method is supplied by the redox reactions between metal nitrate(s) and fuel(s) [16-18].

Solubilization allows the reactants to be dispersed at the molecular scale. It causes a uniform distribution and as a result a uniform composition of the synthesized nanoparticles. Also, the ignition temperature in this method is much lower than the SHS and rarely exceeds 350 °C. All of the above has led to a tendency to produce nanoparticle materials, either individually or in complex compounds, in this way [19, 20].

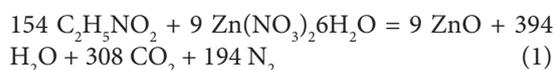
In the current study, for the first time, a fast and efficient route to simultaneously synthesize

and immobilize ZnO nanoparticles on bentonite via SCS was reported. Then, the photocatalytic activity of synthesized nanocomposite is examined in elimination of ciprofloxacin from an aqueous solution.

2. Materials and Method

2.1. Nanocomposite synthesis

In this study, glycine (C₂H₅NO₂) as fuel (Mark, purity >99%), zinc nitrate (Zn(NO₃)₂ .6H₂O) as oxidant (Sigma-Aldrich, purity >99%) and crude powdered bentonite as substrate were used. The reaction equation is shown below (Equation 1). Because bentonite does not participate in the combustion reaction and only acts as a bed for the synthesized zinc oxide nanoparticles, it is not written in the combustion reaction.



All raw materials solve in the distilled water at room temperature. The amount of used water in this method is as minimum as possible, because it only has a role of suitable environment for dissolving and mixing raw materials. Excess water can delay the reaction or even cause it not to happen [21]. For 3g of the raw materials, 3 cc of the distilled water is enough. First, the raw materials were poured into a 100 cc porcelain plant and after complete dissolution in water, they were placed on a hot plate with an initial temperature of 300 °C. About 3 min later and after evaporation of distilled water, the temperature can exceed 100 °C to reach its ignition temperature. It occurred after 4 min and synthesis was performed by intense flame. All the preparation process from the beginning to the end takes less than 10 min. The synthesized powder particles were collected. Due to the insolubility of bentonite in water, the solution of raw materials (nitrate + fuel) and bentonite were mixed by stirring at a speed of 120 rpm until ignition to prevent deposition of bentonite. All other parameters were similar to the first reaction (without bentonite).

2.2. Characterization

The zinc nitrate and glycine were sent for differential scanning calorimetry (DSC-TGA) analysis (SETARAM, SETYS Evolution-1750) to investigate the heating behaviors. In DSC-TGA test, the heating rate was set at 10 °C / min. The synthesized zinc oxide nanoparticles and

synthesized zinc oxide on bentonite were studied by XRD (Philips PW 1800 model, angle of 4° to 70° and Cu (Kα) with a wavelength of 0.15406 nm and a step length of 0.02°). Microscopic evaluations were carried out by both scanning electron microscope (SEM) model VP 1450 and transmission electron microscope (TEM) model Zeiss (EM10C -Germany) operating at 100 kV.

2.3. Photocatalytic degradation of ciprofloxacin

In order to study the catalytic activity of synthesized bentonite-zinc oxide nanocomposite, photocatalytic degradation of ciprofloxacin were performed under direct sun light. In all experiments, 15 mg of the nanocomposite was mixed with 15 ml of 100 ppm aqueous solution of ciprofloxacin in a dark environment for 30 min to accomplish the adsorption-desorption equilibrium. Afterward, the resultant suspension was exposed to direct sunlight (11 am to 2 pm, full sunny day, ambient temperature 35-38 °C). After specified reaction times, i.e. 0.5, 1, 2 and 3h, the nanocomposite was separated by centrifugation (5 min, 10000 rpm) and the concentration of non-degraded ciprofloxacin in solution was monitored by the UV-Vis spectroscopy. The efficiency of degradation can be calculated by degradation efficiency (DE) defined as:

$$DE(\%) = \frac{(C_0 - C_f)}{C_0} \times 100$$

Where C denotes the concentration of ciprofloxacin in the aqueous solution. Moreover, the TOC removal percentages for treated solution was estimated by the equation:

$$TOC\ Removal(\%) = \frac{[TOC]_0 - [TOC]_f}{[TOC]_0} \times 100$$

Where TOC denotes, the total amount of organic

carbon. The subscripts “0” and “f” refer to initial and final condition, respectively.

3. Results and Discussion

3.1. Characterization of bentonite-zinc oxide nanocomposite

In solution combustion synthesis (SCS) the oxidation- reduction reactions between metal nitrate and fuel cause the release of high energy at few seconds (less than 2 sec). Such exothermic reaction causes, the high temperature that named combustion temperature. It can produce crystal synthesis productions [22, 23]. The main factor to have acceptable synthesis is the same behavior of metal nitrate and fuel. If these two do not decompose at the same range of temperatures, there will be no synthesis. As mentioned, the main source of energy in this method is redox reactions. So if the metal nitrate and fuel have different range of decomposition, they cannot release the reaction agents (NO_x groups from the metal nitrate and NH_x groups from the fuel) at the same time and it causes waste of them without any reaction. As a result, the DSC-TGA of zinc nitrate as oxidant and glycine as fuel are shown in Fig.1a and 1b at the rate of 10 °C/min, respectively. The zinc nitrate diagram shows a weight lost from 150 to 350 °C that indicates the dehydration and decomposition range. According to previous studies on different metal nitrates, the first weight loss of nitrates backs to dehydration. The molecular water can be evaporated till 200 °C or even higher. The next step is emission of NO₂ and O₂ that causes zinc nitrate decomposes to ZnO [24-26].

For glycine thermal decomposition (Fig.1b), the first endothermic peak occurs at 240 °C that causes 40 wt. % weight loss. This peak can be attributed to releasing of amino group. It can be named the beginning of polymerization reaction [27]. As it

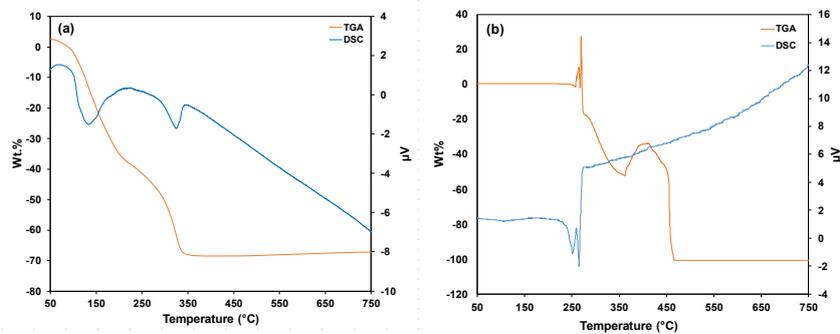


Fig. 1- The DSC-TGA graphs for a: Zn (NO₃)₂.6H₂O and b: Glycine.

can be seen, zinc nitrate and glycine have the same range of decompositions and also both of these ranges are less than preheated temperature (300 °C) by the hotplate. As a result, it can guarantee that synthesis occurs correctly.

In the Fig.2 is illustrated (2a to 2c) the XRD patterns of synthesized ZnO, bentonite and ZnO synthesized in the presence of bentonite. The ZnO peaks indicate themselves in Fig.1a. The crystal size of ZnO was calculated using Scherrer formula (Eq. 1) [11].

$$D = 0.9\lambda / \beta \cos\theta \quad (1)$$

In equation 1, D and β are the crystallite size in nm and broadening of diffraction line at full width at half maxima (FWHM), respectively. Also, θ is obtained from the main peak position and λ comes from the wavelength of $Cu_{K\alpha}$ ($\lambda = 0.15406$ nm). The calculation proves the synthesized ZnO is in nano-scale (21 nm according to Scherer's equation).

In Fig.2b is given the XRD pattern of used pure bentonite powder without any extra treatment. At last in Fig.2c, the SCS result of zinc nitrate and glycine in presence of bentonite in the reaction chamber is proved the synthesized zinc oxide can put correctly on bentonite. The synthesis process from begging to the end takes less than 10 min. The both main peaks of ZnO and bentonite showed in that pattern. Because bentonite does not participate in the combustion reaction and remains without changes before and after reaction, it can be considered as substrate and zinc oxide after synthesis can put on it.

In Fig.3 is given (3a. to 3c) SEM images of synthesized ZnO by SCS, bentonite and synthesized zinc oxide in the presence of bentonite, respectively.

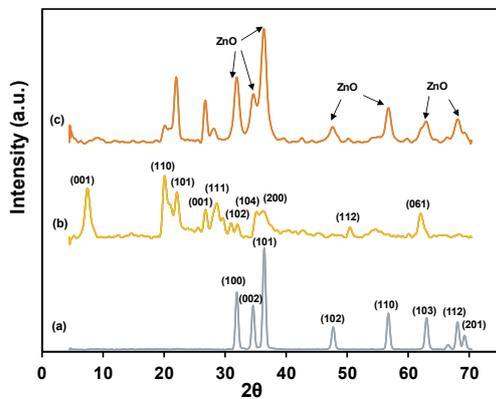


Fig. 2- The XRD patterns for a: synthesized ZnO, b: bentonite and c: Bentonite-ZnO nanocomposite.

The porous synthesized zinc oxide in Fig.3a shows not only the crystal size is in nano-scale but also the particle size is in nano range too. The observed porosity backs to many produced gases during combustion reaction (refer to Eq.1). Emission of many moles gases such as: N_2 and CO_2 in few seconds of reaction make those porosity.

The SEM image of used bentonite in Fig.3b shows, the material is almost dense whit micro size particles and without any porosity. The final result of synthesis ZnO in the presence of bentonite (Fig.3c) proves the ZnO particles put on bentonite substrate. Also the gases of reaction could produce some porosity even in the bentonite. Higher surface area helps better yield in applications like wastewater recycling. In Fig.4 is illustrated the EDX analysis of bentonite-ZnO nanocomposite.

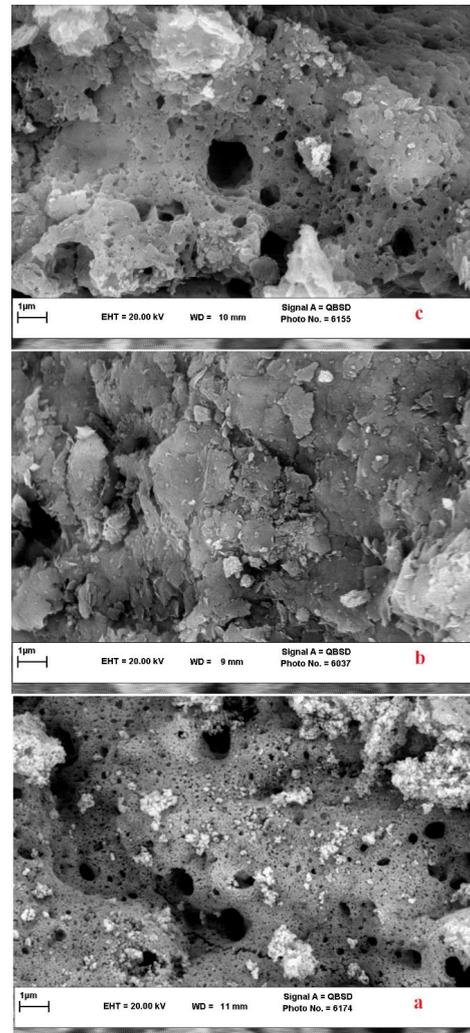


Fig. 3- The SEM images of a: synthesized ZnO, b: Bentonite and c: Bentonite-ZnO nanocomposite.

As it can be seen, the taken spectrum from an area of synthesized nanocomposite proves the successful of reaction. The Au peak in the EDX backs to coating applied on the powder before taking images by operator. In Fig.5 TEM images of final nanocomposite are illustrated in two magnifications. It can be seen in Fig 5a. the final nanocomposite has particle size less than 600 nm and in Fig.5b this size is different from less than 100 nm to more than 800 nm (dark particles in the image). It proves the substrate of bentonite has the main effect on the final size of synthesized composite. The agglomeration of bentonite determines the final particle size, because the ZnO nanoparticles just are decorated on the bentonite (refer to Fig.3).

For investigation on optical properties of nanocomposite is used UV-Vis spectroscopy. The result is shown in Fig.6a. The band gap energy was estimated out by Tauc Mosdel (Eq. 2) [28].

$$\alpha(h\nu) = D[(h\nu) - E_g]^{0.5} \quad (2)$$

where α , $h\nu$, E_g , and D are the absorption coefficient, photon energy, band gap energy, and a constant parameter, respectively. By extrapolating the linear part of $(\alpha h\nu)^2$ to the abscissa axis (Fig. 6b) the band gap energy was obtained. The estimated band gap energy for Bentonite -ZnO nanocomposite was ca. 3.23 eV, which is in agreement with previous studies [29, 30].

3.2. The degradation of ciprofloxacin using bentonite-ZnO nanocomposite

In the next step, the synthesized nanocomposite photocatalytic performance was investigated on the removal of ciprofloxacin from an aqueous solution. The results confirm the excellent activity of nanocomposites to degrade this compound under solar irradiation. The degradation efficiency (DE) and TOC removal percentage versus reaction time for each dyes were displayed in Fig 7. These results indicate, the appropriate photocatalytic catalytic activity of the ZnO-bentonite nanocomposite, so that DE and TOC removal percentage of

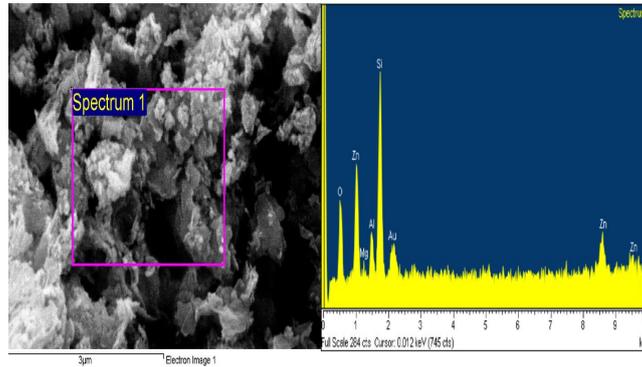


Fig. 4- SEM image and EDX analysis of Bentonite-ZnO nanocomposite.

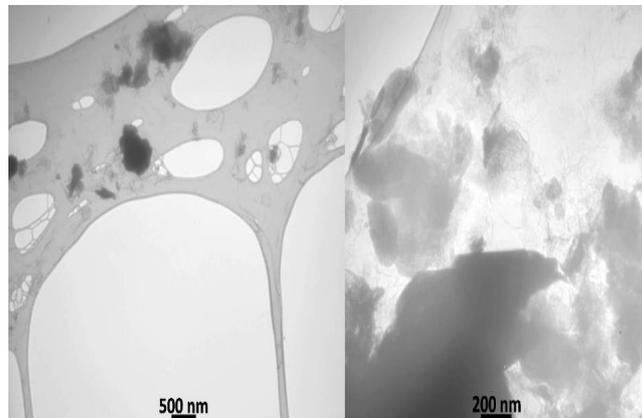


Fig. 5- TEM images of Bentonite-ZnO nanocomposite.

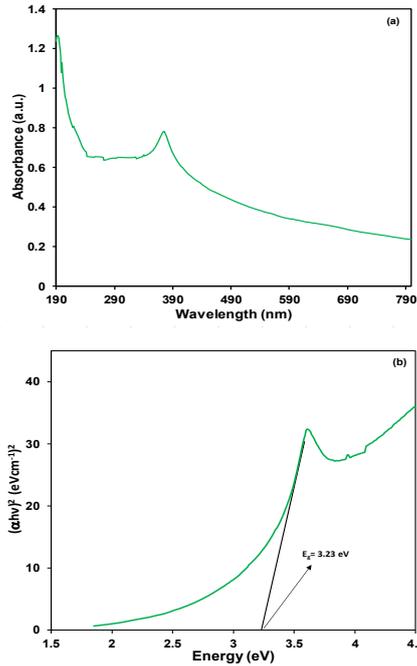


Fig. 6- a: The absorbance spectrum of Bentonite-ZnO nanocomposite, b: Tauc's plots of the same sample.

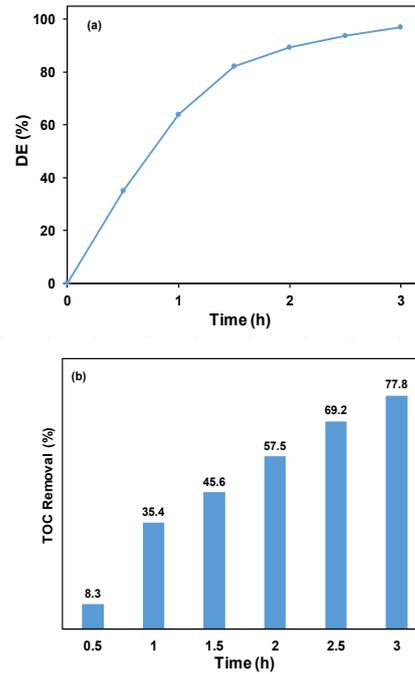


Fig. 7- (a) Degradation efficiency and (b) TOC removal percentage of ciprofloxacin versus reaction time.

ciprofloxacin approach 97% and 78 % after 3 hours reaction, respectively. This performance can be attributed to the specificity of the combustion method in the rapid synthesis of nanoparticles that cause the zinc oxide nanoparticles homogeneously disperse over bentonite flakes without considerable agglomeration. Also, the release of many different gaseous moles in few seconds during the reaction makes many small pores all over of synthesized nanocomposite in both ZnO and bentonite. It means, more active sites are available for the reaction. It causes, the bentonite owns a high adsorption capacity due to its porous structure. This property can accelerate the first stage of the reaction, namely adsorption of reactant molecules on the surface of the catalyst and in this way improve the performance of the catalyst [31]. It is worth mentioning that a blank experiment was conducted in presence of bentonite without synthesized ZnO. The results showed, the DE was less than 10 %, which can be attributed to the adsorption of ciprofloxacin by surface of bentonite. Therefore, it can be concluded that the main role of photocatalytic property plays by zinc oxide nanoparticles.

3.3. Kinetics study

The ciprofloxacin degradation kinetics can be

presented by the following reaction rate equation (Eq. 3):

$$-\frac{dC_{CIP}}{dt} = kC_{CIP}^n \quad (3)$$

Where, C denotes the ciprofloxacin concentration in ppm, t is time in min, k is the rate constant of reaction, and n is the order of reaction. A relationship between the concentration and time can be obtained through integration of the Eqs. 4 to 6 for various reaction orders:

$$\text{Zero-order: } C = C_0 - k_{0\text{-order}}t \quad (4)$$

$$\text{First-order: } C = C_0 e^{-k_{1\text{-order}}t} \quad (5)$$

$$\text{Second-order: } C = \frac{C_0}{1 + k_{2\text{-order}}tC_0} \quad (6)$$

Where, C_0 is the initial concentration of ciprofloxacin. Applying a nonlinear regression and fitting the models to experimental data, the order of reaction as well as the rate constants could be estimated. Fig. 8 compares the fitting of different reaction kinetics model to experimental data.

For better comparison, the kinetic parameters of various models are presented in Table 1. It is obvious that the photocatalytic degradation of ciprofloxacin over the Bentonite-ZnO nanocomposite obey first

Table 1- Kinetic parameters of ciprofloxacin degradation in presence of the bentonite-ZnO nanocomposite

Kinetic model	Regression coefficient (R ²)	Rate constant (k)
Zero order	0.8035	39.93 (mgL ⁻¹ h ⁻¹)
First order	0.9955	1.04 (h ⁻¹)
Second order	0.9439	2.12×10 ⁻² (Lmg ⁻¹ h ⁻¹)

Table 2- Comparison of this study with previous works

Catalyst	Reaction time (min)	Removal efficiency (%)	Catalyst dosage (g/L)	Synthesis time (h)	Reference
Ag ₂ O/Ag ₂ CO ₃ /MWNTs	60	76	0.5	16.5	(32)
Zn-doped Cu ₂ O	240	94.6	1.5	27	(33)
ZnFe ₂ O ₄ @RGO	60	73.4	1	15	(34)
Z-scheme CeO ₂ -Ag/AgB	120	93.05	5	13.5	(35)
Zinc Ferrite/Graphitic	120	92	1.5	Not given	(36)
FeWO ₄ /NC	100	92.23	Not given	24	(37)
Bentonite-ZnO	180	97	1	0.16	This work

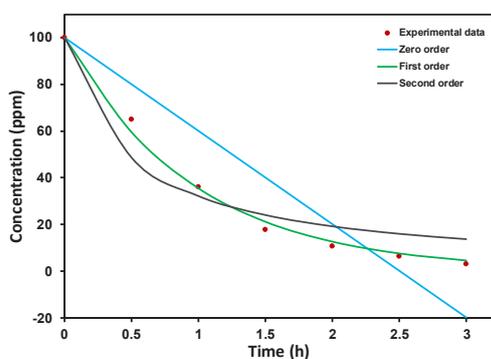


Fig. 8- Comparison of different kinetic models for photodegradation of ciprofloxacin.

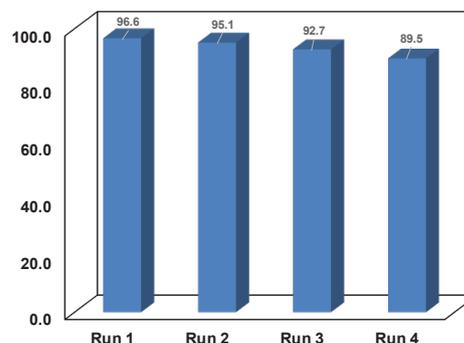


Fig. 9- Degradation efficiency of ciprofloxacin in successive cycles.

order reaction kinetics with reaction rate constant of 1.04 h⁻¹.

In order to evaluate the stability of the produced nanocomposite. It was used in several successive cycles. In each step, the nanocomposite was recycled from the solution after reaction and washed with double distilled water three times. Then, it was used again in the degradation test of ciprofloxacin. The results in Fig.9 showed that the catalytic activity of the nanocomposite has not changed much after four cycles and just decreased from 96.6% to 89.5%.

Considering the excellent performance of nanocomposite and its acceptable stability in the photocatalytic degradation reaction of ciprofloxacin, it can be concluded that the combustion method is a very suitable method for the production of bentonite-based nanocomposites that can be used in a wide range of catalytic reactions.

To compare our results with previous studies

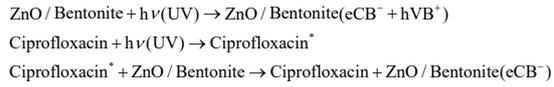
in ciprofloxacin removal, Table 2 was added. As it can be seen from this table, the Bentonite-ZnO nanocomposite is active in the EBT degradation.

According to the Table 2, it can be seen, all times for preparation of final photocatalysts is much more than used time in this work. As mentioned above, this method needs less than 10 min to synthesis the final photocatalysts. The other point is the efficiency of other catalysts that is less than the best result (97%) of this research. All of these advantages back to many gases that produce in few seconds during the synthesis and increase the amounts of porosity in the catalyst.

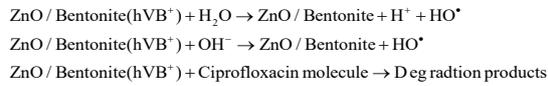
3.4. Degradation mechanism

The uniform distribution of photocatalytic ZnO nanoparticle in pores and surface of bentonite thanks to the SCS method, provides many active sites for the photocatalytic reactions. By absorbing energy equal to or greater than the gap energy of

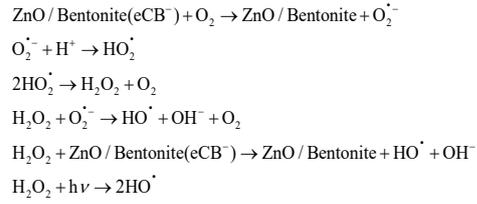
the immobilized nanocatalyst, an electron is excited from the capacitance band to the conduction band and creates a positive hole in the capacitance band. Moreover, ciprofloxacin molecules may be directly excited by solar radiation and transfer an active electron to the conduction band of the photocatalyst [11]:



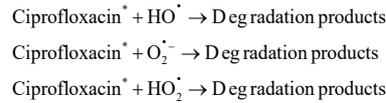
The electron-hole can react with H_2O or OH^- to form hydroxyl radicals (HO^\bullet) or even can directly oxidizes ciprofloxacin molecules [38]:



Furthermore, if there is enough oxygen in the solution, the electron in the conduction band may react with electron acceptors, including O_2 molecules attached to the surface of ZnO nanoparticles to produce OH^\bullet as follow [39]:



Eventually, the ciprofloxacin molecules adsorbed on the surface of nanocomposite are decomposed by different oxidants such as hydroxyl and peroxide radicals.



The schematic of the photocatalytic reaction of ciprofloxacin in the presence of Bentonite-ZnO nanocomposite is shown in Fig. 10.

4. Conclusion

In this investigation, solution combustion synthesis was used for the synthesis of Bentonite-Zinc Oxide nanocomposite. The research has some

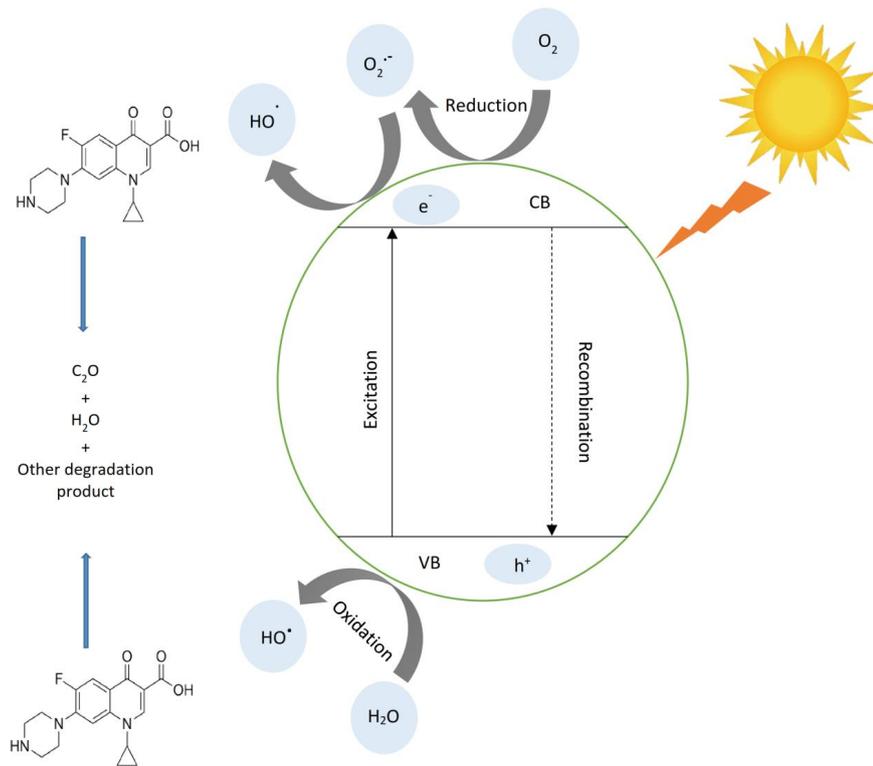


Fig. 10- Schematic illustration of photocatalytic degradation of ciprofloxacin.

results such as:

Solution combustion method, synthesized Bentonite-Zinc Oxide nanocomposite just in one-step in less than 10 min at air atmosphere.

The estimated band gap energy for Bentonite-ZnO nanocomposite was ca. 3.23 eV.

The blank test from bentonite just showed less than 10% degradation efficiency.

The synthesized ZnO increased degradation efficiency more than 87%.

The Bentonite-Zinc Oxide nanocomposite exhibited fantastic performance in degradation of ciprofloxacin, so that the degradation efficiency approaches 100% and TOC removal percentage reaches 78% after 3h reaction at the rate constants of 1.04 h^{-1} .

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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