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Photocatalytic removal of cefazolin from aqueous solution by AC prepared from mango seed+ZnO under UV irradiation

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Abstract

Presence of antibiotics in the environment specially in aqueous environments is considered a major warning about health and environment. Thus, this study aims the efficiency of coupled process of Activated Carbon (AC) prepared from mango seed+ZnO under UV irradiation as an advanced oxidation process in removing cefazolin antibiotic from aqueous solutions. This experimental study was carried out in a discontinuous reaction chamber with volume of one liter. In this process, the effect of initial pH parameters of the environment (3– 9), initial concentration of cefazolin (20 – 200 mg/L), concentration of modified, photocatalyzer (20 – 100 mg/L) and reaction time (10 – 60 min) were studied. The pilot used consisted of a low pressure mercury lamp with a 55-watt beam radiation power inside the steel chamber. The kinetic of the process was studied based on pseudo first order kinetics. Results showed that the highest removal efficiency of cefazolin antibiotics in the reaction of UV/AC + ZnO, at optimal conditions of pH= 3, contact time of 60 min, initial concentration of 100 mg/L and modified photocatalyzer of 0.1 g/L was equal to 96%. The kinetic model determined for the process followed kinetic model of pseudo- first order kinetics with high correlation of (R^2 = 0.99). Results of present study revealed that photocatalyzer process of nanoparticles oxidation on synthetic activated carbon can be effectively used as an advanced oxidation reaction to remove cefazolin and similar pollutants.

Keywords: Advanced Oxidation, Cefazolin Antibiotic, Modified Photo-Catalyst, AC prepared from mango seed, ZnO

1. Introduction

Presence of antibiotics in the environment especially in aqueous environments is considered a major warning. These antibiotics are used to improve human and livestock and also to increase growth in fish and livestock farms (Díaz-Cruz *et al.*, 2008). These medicines are normally weakly absorbed in the body and the major part of them are dismissed from body through urine and stool without deformation or with slight deformation and usually enter the sewage system and finally enter wastewater treatment plants (Almasi *et al.*, 2016b). Given that most of the sewage treatment plants are not capable of treating antibiotics and these materials ultimately enter the receiving waters along with wastewater (Sui *et al.*, 2012). Low concentration of these antibiotics leads to antibiotics resistance in bacteria and genes (Rizzo *et al.*, 2013). In addition, livestock medicines and antibiotics at low concentrations lead to disorders in reproduction and endocrine glands (Park *et al.*, 2007). In recent years, these pharmaceutical ingredients have been continuously evacuated into the environment with no limitation; although their entry into the aqueous environments may be low, their continuous entrance can be a potential hazard to aqueous ecosystems microorganisms due to their cumulative effect (Elmolla and Chaudhuri, 2010). Studies conducted in Australia, Brazil, Canada, Germany, Greece, Italy, Spain and America have shown that more than 80 types of pharmaceutical compounds and metabolites resulting from taking different medicines have entered the aqueous environments. In the samples taken from inlet sewage, wastewater and surface waters located downstream of urban wastewater treatment plants, high concentrations at microorganism scale per liter of pharmaceutical compounds have been reported (Lindberg *et al.*, 2004; Shokoohi *et al.*, 2017). Cephaspoorins family antibiotics are highly consumed antibiotics. Results of studies demonstrate that 50 to 70 percent of the antibiotics consumed in most countries belong to this family (Kümmerer, 2009). Cefazolin is a semi-synthesized antibiotic that is used in the treatment of bacterial diseases such as pulmonary, bone, stomach, heart and urinary tract diseases (Xiao *et al.*, 2017). The concentration of this antibiotic in environment depending on the release source can vary from several nanograms to several mg per liter (Gurkan *et al.*, 2012; Jiang *et al.*, 2010).

Numerous methods have been recommended to remove antibiotics from aqueous environments of which the use of ultraviolet ray (Dantas *et al.*, 2010), coagulation, pent-fenton, and other advanced oxidation methods (Yazdanbakhsh *et al.*, 2011), such as nanofiltration (Zazouli *et al.*, 2009), carbon nanotubes (Samadi *et al.*, 2014) methods can be referred to. Each of the above-mentioned methods despite their advantages, have disadvantages that make them difficult to use in most cases. For example, in physical methods like coagulation and centrifuge method, secondary pollutants are usually produced and also in biological methods, much time requirement and low efficiency of the process create problems (Homem and Santos, 2011), in contrast, cases such as simplicity, low cost and high efficiency cause oxidation processes to turn into one of the common technologies for removing most of the pollutants (Khan and Jung, 2008). Advanced oxidation processes (AOPs) are based on production of strong oxidative radicals such as hydroxyl radical, sulfate radical, super-oxide radical, and hydroxyl radical that have high tendency to destroy antibiotics (Xiao *et al.*, 2017). Over the past years, combined processes such as combined use of ozone and hydrogen peroxide, ozone and ultraviolet ray, the process of oxidation combined with the Fenton process and the catalytic ozonation process (De Bel *et al.*, 2009; Shokri *et al.*, 2016). Photocatalysis is an advanced technique by which organic pollutants are completely decomposed and removed. In heterogeneous catalytic processes, reaction materials are not in single phase and are not easily dissolved in reaction environment. In order to prevent the decline in overall efficiency due to the reduction of active surface, a bed was used as catalyst support, that is, a reactive carbon bed with high porosity and high active surface produced from mango seedlings, was used.

Gurkan *et al.*, studied the efficiency of different photo-catalytic processes in destroying cefazolin antibiotics in 2012. Results showed that photo-catalytic processes are of high efficiency in removing cefazolin and most of the resulting compounds consist of Beta lactam rings, Tio-diazone, Tetrazole and Dihydro diozone (Gurkan *et al.*, 2012). This study aims to use advanced oxidation technology activated carbon prepared from mango seed+ZnO under UV irradiation in removing cefazolin antibiotics from aqueous solutions in order to be able to use this method for the treatment of pharmaceutical industry and hospital sewage in case of having access to acceptable results.

2. Materials and Methods

This experimental study was at laboratory scale that was carried out in discontinuous photochemical chamber (Batch Reactor). The pilot used (Fig. 1) consists of a cylindrical photochemical reaction chamber made of steel with efficient volume of one liter consisting of a low-pressure mercury lamp with radiation power of 55 watts. The place of reaction was the space between the quarts membrane around the lamp and the steel chamber. Samples studied, were synthetic wastewater prepared in laboratory with different and definite concentrations of cefazolin. The parameters of initial pH of the environment (3- 9), modified photocatalyzer concentration (20 – 100 mg/L), concentration of cefazolin (20 – 200 mg/L) and reaction time (60 min) were studied. The number of samples was calculated using OFAT (one- factor- at – a-time method) and 32 samples were prepared.

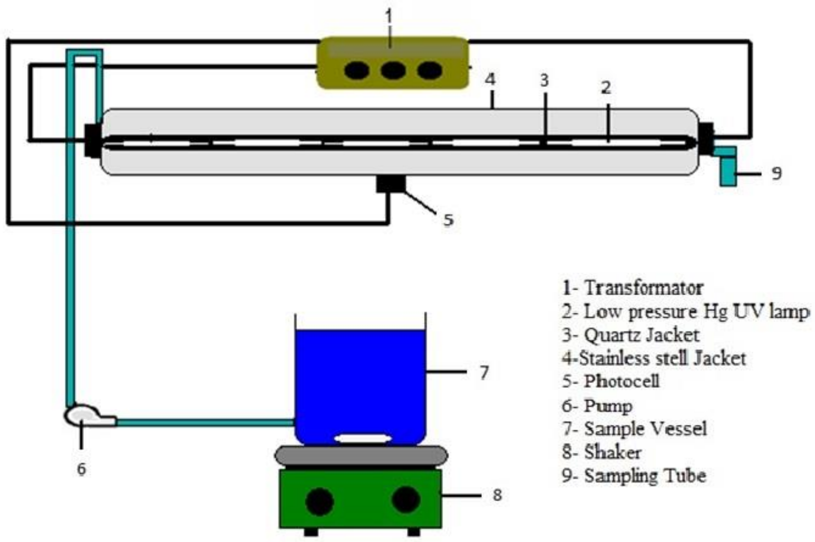


Figure 1. Schematic of studied reactor

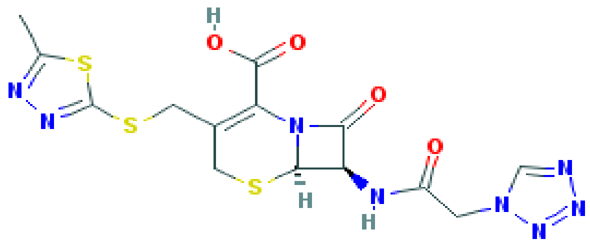
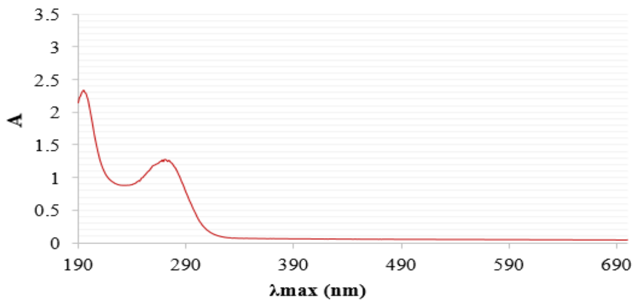
2.1. Cefazolin analysis method

First, the stock solution of cefazoline (1000 mg/L) was provided, then different concentrations of cefazolin from the stock solution were prepared. After adjusting all components of the freshly prepared solution, samples were collected at predetermined time intervals by passing through 0.45µm membrane filter and measured for the final cefazolin content by using a spectrophotometer at a wavelength of 262 nm.

2.2. Chemicals and instruments

Chemical materials required such as cefazolin (with degree of purity, 99.9 percent), sodium hydroxide and sulfuric acid were purchased from Merk and Aldrich companies. In this study, a pH-meter model Denial (HACH), centrifuge machine (Sigma) and Spectrometer machine model (HACH) DR5000 were used. Experiments were conducted with changing pH factors, radiation time, initial concentration of cefazolin solution, concentration of modified and unmodified activated carbon with zinc oxide and concentration of only zinc oxide nanoparticles. Then the concentration of remained cefazolin in solutions was measured using spectrophotometer machine at wavelength of 262 nm after the process. After experiments, the optimal amount of each of the parameters under study was selected and the efficiency of each one of the processes were compared using Excel software. Specialized experiments including SEM and XRD on activated carbon produced in modified mode with zinc oxide nanoparticles were carried out to determine physical and chemical characteristics. The characteristics of cefazolin antibiotics have been presented in Table 1.

Table 1. Properties and chemical structure of the cefazolin antibiotic

Chemical structure	
Chemical formula	$C_{14}H_{14}N_8O_4S_3$
Molar weight	454.498 g/mol
Fixed acid separation of cefazolin	pKa= 3.6 (Carboxylic acid)
UV-Vis Spectroscopy (Cefazolin concentration, 100 mg/L)	

2.3. Preparation of activated carbon from seeding of mango

50 gr of dried seedling of mango with definite volume of phosphoric acid with concentration, 95%, was mixed with mass ratio of 1 to 10. Resulting mixture was transferred to a metal reactor, 50 mm in diameter, a 250 mm long, then it was transferred into an electric furnace in such a way that it's temperature reached 900 °C within 3 hours. At 900 °C, the reactor was adjusted at this temperature for an hour and then, it was turned off until it reached the ambient temperature. The carbon produced during above stages, was washed using distilled water until it's pH exceeded 6.5. The carbon produced, was placed inside oven at 120 °C so as to be re-dried. After being dried, the carbon was crushed, then, it was passed from sieves with 20, 30, 40 and 50 meshes. The remainder sieved carbons were mixed on 30, 40 and 50 sieves and in order to prevent from moisture absorption, it was kept inside a sealed glass water.

2.4. Modification of activated carbon produced using ZnO particle

Preparation of modified activated carbon was conducted using hybrid mechanical method, in this way that activated carbon and ZnO nanoparticles were weighed in required amounts using a digital scale and mixed (the ratio of ZnO nanoparticles mass to activated carbon was in the range of 0.1, 0.2, 0.3, 0.4 mmol/g), then it was poured into twice distilled water and magnet was used for completely mixing, and the process should be continued for 24 hours. Then, after filtering the mixture, the remainder on the filter was placed in the mine at 95 °C for 24 hours in order to be dried completely. In the end, modified activated carbon was obtained according to above stages.

2.5. Effect of pH changes

The operation was conducted at laboratory scale using modified activated carbon catalyst with zinc oxide at different pH ranges (pH: 3- 9). To determine the effect of pH changes on the process, concentration of initial cefazolin was considered 100 mg/L, modified activated carbon, 80 mg/L, and contact time of the reaction, 60 min. To adjust the desired pH, NaOH and 0.1 normal H_2SO_4 were used.

2.6. Effect of changes in the amount of modified activated carbon

To determine the amount of modified activated carbon, experiments were carried out under similar conditions to previous stage at optimized pH. Concentration of modified activated carbon was studied at 20 – 100 mg/L range. At selected pH from previous stage, different amounts of modified activated carbon were added, and its optimal amount was achieved.

2.7. Effect of changes in cefazolin concentration

Following the experiments and optimal values achieved from previous parameters, the optimal amount of cefazolin was obtained. To determine the optimal value, concentration of cefazolin was studied at the range of 20 to 200 mg/L.

2.8. Determining the Kinetics of the reaction

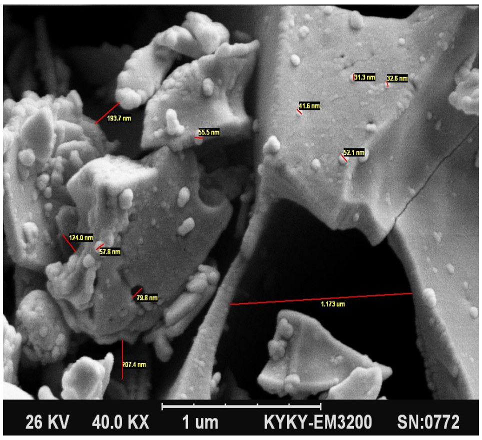
In each study, including chemistry studies determining the reaction speed is an important and effective thing. Thus, to find out the method of pollutants removal reaction, modeling and better performance of the process at applied scale, kinetic studies of the reaction were carried out under laboratory conditions of pH= 3, modified absorbent concentration, 100 mg/L, cefazoline concentration, 100 mg/L and contact time of 60 minutes. In this part, the Kinetic models of pseudo first and – second order Kinetic studies were used.

3. Results and Discussion

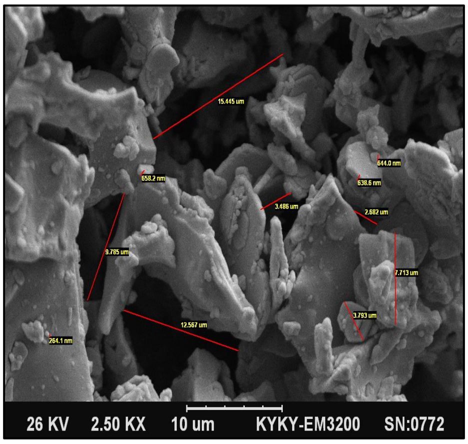
3.1. SEM and XRD analyses

SEM studies provide useful information regarding the surface morphology of the materials. The SEM micrographs of the activated carbon and AC–ZnO mixture is shown in Fig. 2. SEM micrographs photographs of AC–ZnO mixture clearly reveal the surface texture and porosity nature. The immobilization of ZnO in the carbon matrix partially blocked the porosity of the carbon surface, although the composite still displays a porous character with a relatively large pore volume and surface area.

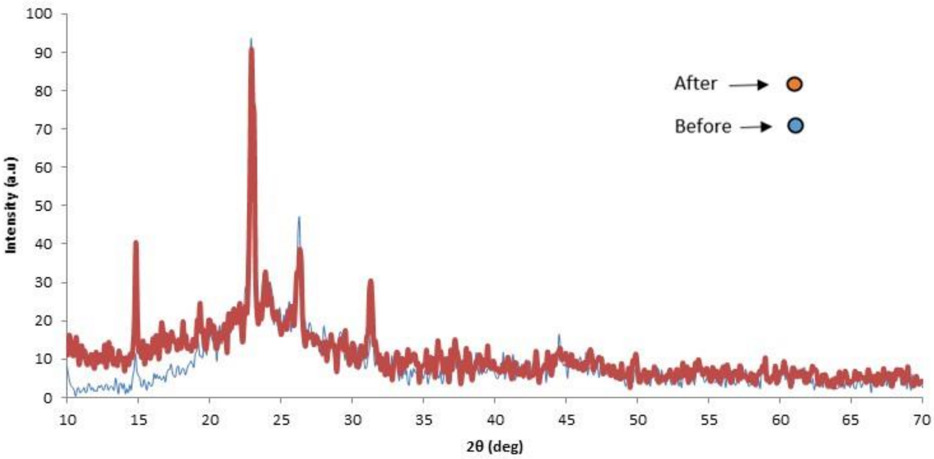
To confirm the formation of AC–ZnO composite, XRD pattern has been observed (Fig. 2). XRD pattern has been observed for activated carbon alone and activated carbon supported with ZnO nanoparticles. The clear and well-defined peaks at 31.6^0, 34.2^0, 36.2^0, 47.4^0 and 56.6^0 (JCPDS 36-1451). The peaks show that there have been correct loading ZnO nanoparticles on the activated carbon.



(a)



(b)



(c)

Figure 2. SEM micrographs AC, a) unmodified, b) modified and c) XRD spectrum AC for before and after modified by ZnO

3.2. Effect of pH and reaction time

In advanced oxidation processes, pH can affect the rate of desired pollutant decomposition. The effect of pH and reaction time on the efficiency of cefazolin removal has been demonstrated in Fig. 3. To study the effect of pH on above process, the values of pH were studied in the range of, 3- 9, contact time, 3- 60 min, concentration of modified activated carbon by zinc oxide (ratio of 0.4 mmol zinc oxide for each gram of activated carbon) with 100 mg/L, and the initial concentration of cefazolin was evaluated 100 mg/L. Results showed that with reducing pH and increasing reaction time, the efficiency of the system rises in a way that the highest efficiency of the process (95%)was achieved at pH= 3, contact time, 60 min, and the lowest efficiency (19%) was achieved at pH= 9, contact time, 3 min.

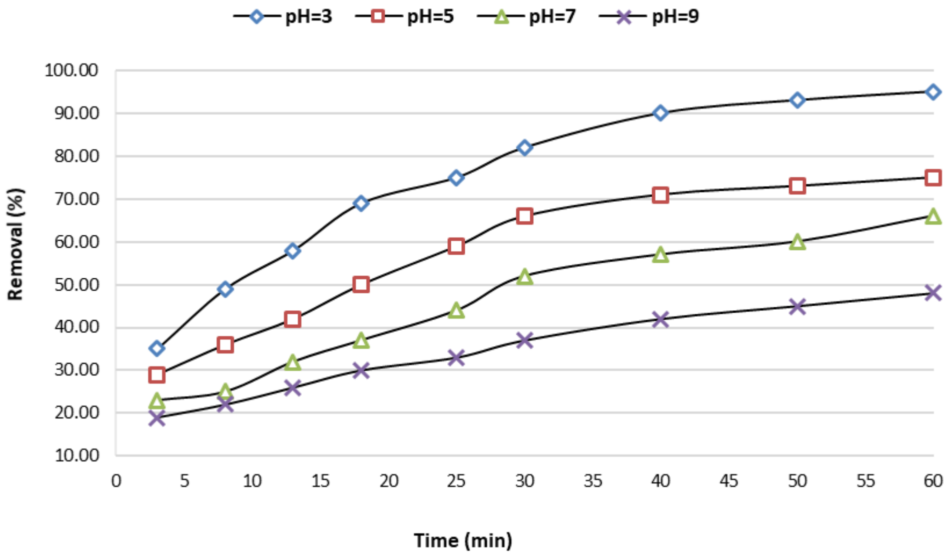


Figure 3. Effect of pH changes on the efficiency of UV/AC+ZnO process in removal of cefazolin (concentration of modified AC,100 mg L^{-1}, Cefazolin initial concentration, 100 mg L^{-1})

pH is one of the most important parameters in catalytic reaction since pH affects the characteristics of surface charge (Almasi *et al.*, 2016a). Results showed that the efficiency of cefazolin removal rose with reducing dissolved pH and increasing reaction time, in a way that the highest efficiency of process under study was obtained at pH= 3, conforming to the study conducted by Shokri *et al.*, 2015. In the study by Shokri *et al.*, the highest removal of cefazolin was achieved at acid pH (pH :5) (Shokri *et al.*, 2016). Also, another study was carried out by Gurkan *et al.* (2012), entitled photocatalytic decomposition of cefazolin antibiotics using N- TiO_2 doped. Results demonstrated that the highest removal efficiency of cefazolin was obtained at acid pH (Gurkan *et al.*, 2012). The reason for increase in removal efficiency at acid pHs is that in acid conditions, the surface of zinc oxide nanoparticles finds positive load and leads to higher absorption of cefazolin that as a result of higher absorption, cefazolin produces hydroxyl radical and the amount of decomposition in acid medium rises. Efficiency reduction in alkaline medium is distributed to the fact that the nanoparticles' surface finds negative charge and causes decline in cefazolin removal, leading to reduction in the production of hydroxyl radical and also decline in the amount of decomposition in alkaline medium and as a result, declining removal efficiency (Muruganandham and Swaminathan, 2004). Another reason for reduction in the efficiency of the process under alkaline conditions (pHs > 3) is the chemical properties of cefazolin. cefazolin is a strong acid (pKa= 3.03) whose chemical structure consists of aromatic rings rich in electrons and is absorbed completely to the surface of zinc oxide photocatalyzer with positive charge, resulting in increase in the progress efficiency (Shokri *et al.*, 2016).

One of the important properties of each absorbent entitled point of zero charge (PZC) that in this study it was measured both for synthesized carbon and zinc oxide nanoparticles and its value for produced activated carbon was determined 6 and for zinc oxide nanoparticles, 6.25. At pHs lower than point of zero charge due to the presence of H^+ ions, the surface of molecule will have positive charge, resulting in higher absorption of cefazolin(Shokri *et al.*, 2016).

3.3. Concentration effect of modified activated carbon

Dependence of cefazolin removal on the concentration of modified photocatalyzer at concentrations of 20, 40, 60, 80 and 100 mg/L was studied and the results are demonstrated in Figure 4. Like previous stage, one parameter was considered as variable and other parameters as constant (time, pH and optimal cefazolin concentration). Results revealed that with increasing the concentration of modified activated carbon, the efficiency of system under study has rose in removing cefazolin in such a way that the maximum and minimum amounts of cefazolin removal by modified absorbent were achieved respectively at concentrations of 100 and 20 mg/L with removal efficiencies of 95 and 56 percent.

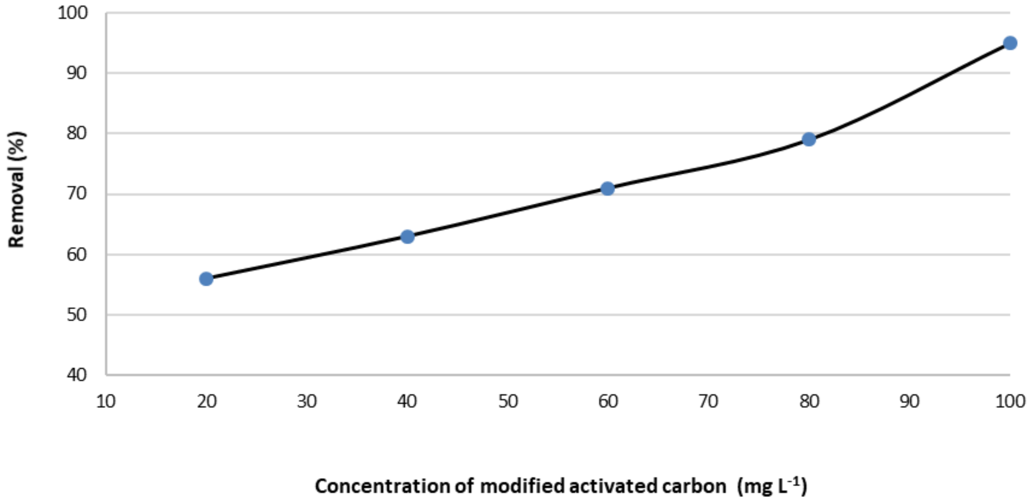


Figure 4. Effect of changes in modified AC on the efficiency of UV / AC + ZnO process in removal of cefazolin (pH= 3, Cefazolin initial concentration, 100 mg L^{-1}, time, 60 min)

Results demonstrated that with increasing the concentration of modified activated carbon, the amount of cefazolin antibiotics removal efficiency rose in a way that the highest amount of removal was achieved at concentration, 100 mg/L, that conforms to the study by Muthirulan *et al.*, (2012) (Muthirulan *et al.*, 2013). In their study in which they used activated carbon stabilized zinc oxide photocatayst to remove alizarin cyanine green dye, results demonstrated that with raising the concentration of modified activated carbon, the amount of dye removal rose. The reason for increase in efficiency with increasing the initial concentration of corrective photocatalyzer, could be attributed to increase in active sites on the surface of the carbon because increasing the initial concentration and also the number of active sites leads to higher absorption of cefazolin antibiotics and as a result raising efficiency.

3.4. Effect of changes in the initial concentration of zinc oxide alone and stabilized zinc oxide on activated carbon

Given the dependence of process efficiency on two parameters of activated carbon and zinc oxide nanoparticles, in this stage, these two parameters were studied separately, and the results have been presented in Figure 5. As it is observed in the data obtained, the efficiency of zinc oxide by itself in all concentrations used, was lower compared to that of settlement on activated carbon, in such a way that the highest and lowest rate of cefazolin removal by UV/AC+ZnO process were respectively 95 and 65% and for UV/ZnO, respectively 55 and 30%. The maximum and minimum rate of cefazoline antibiotics removal were achieved at concentrations of 0.4 and 0.1 mmol/g for both the UV/AC-ZnO and UV/ZnO.

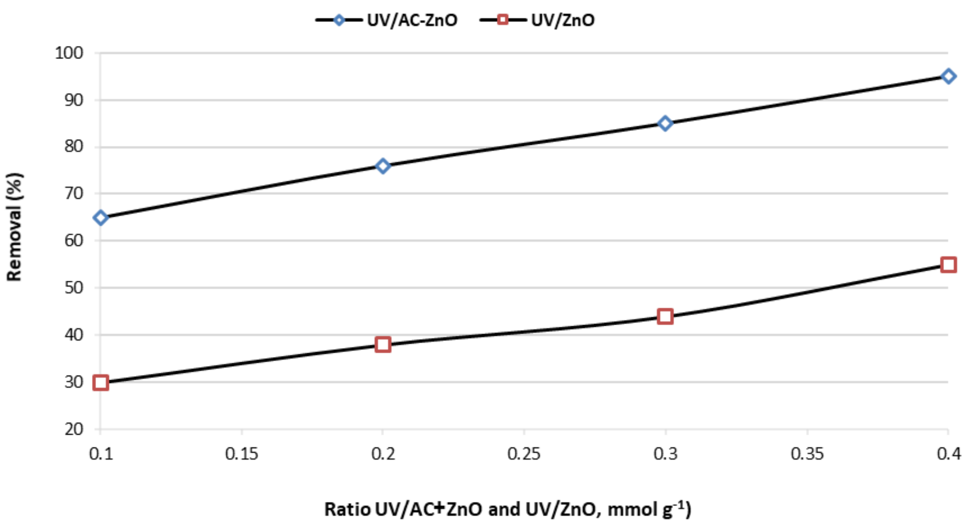


Figure 5. Effect of changes in UV/ZnO and UV/AC+ZnO for removal of cefazolin (pH= 3, cefazolin initial concentration, 100 mg L^{-1} and time, 60 min)

Results demonstrated that zinc oxide by itself has significantly lower efficiency compared to the mode covered activated carbon and the efficiency of the system rose with increasing the concentration of zinc oxide nanoparticles placed on activated carbon that could be due to increase in the active sites produced by zinc oxide that is consistent with the study of Muthirulan *et al.*, (2012) (Muthirulan *et al.*, 2013). What is clear in this stage, is the role of activated carbon as an important and helpful factor in above process for increasing the removal efficiency of cefazolin antibiotics. Activated carbon as a secondary factor alongside zinc oxide has resulted in increase in absorption of pollutant in the process. In these processes, nanoparticles as catalyst, absorb the high energy photons of ultraviolet spectrum and as a result, active chemicals such as hydroxyl radicals are formed (Kumar and Rani, 2013). When photocatalyzers are exposed to ultraviolet rays, this leads to excitement, stimulation and activation of capacity bonding electrons and movement of electron from capacity bonding to conduction band. Activated electrons that have moved to conduction band, enter into reaction with organic materials by forming different radicals such as super oxide or hydroxyl (Daneshvar *et al.*, 2007).

3.6. Effect of the initial concentration of cefazolin

Results obtained from the effect of different concentrations of cefazolin on the efficiency of UV/AC + ZnO process in removing pollutant under study have been demonstrated in Figure 6. Like previous stages, in this stage, all optimal parameters obtained from previous stages were considered constant and only one parameter was considered variable. Results showed that the efficiency of combined process declined with raising the initial concentration of cefazolin antibiotics, in such a way that the highest amount of removal was observed at concentration of 20 mg/L, (100%), and the lowest amount of removal was observed at concentration of 200 mg/L (77%).

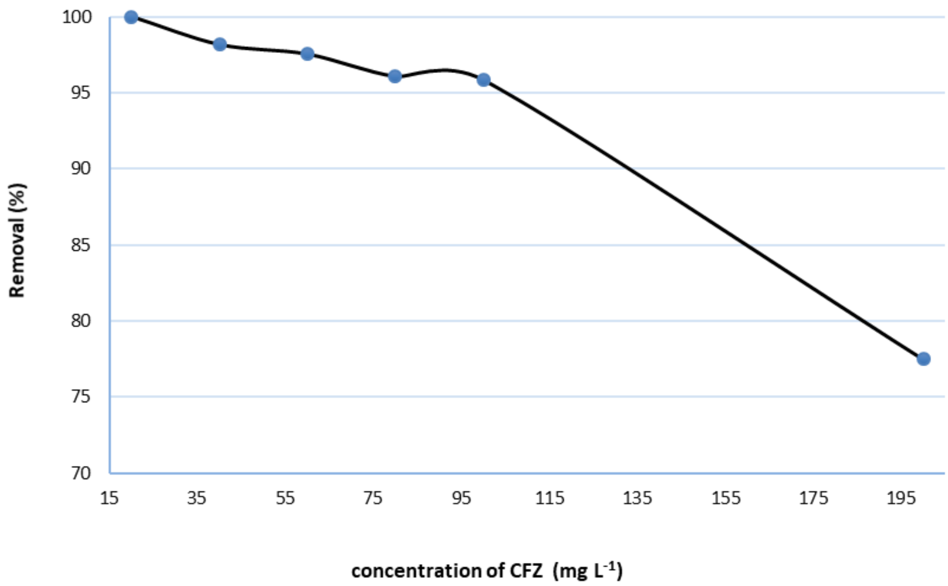


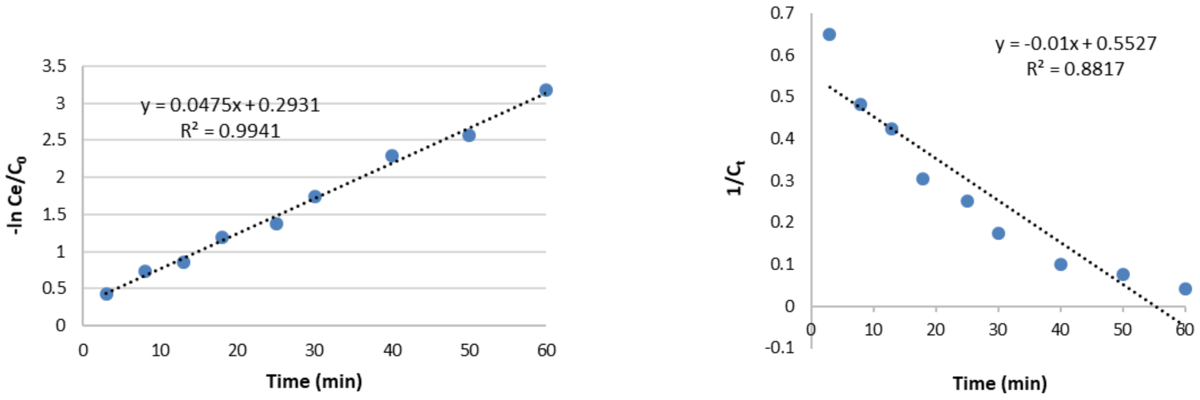
Figure 6. Effect of changes in the cefazolin initial concentration on the cefazolin removal (pH= 3, concentration of modified AC,100 g L^{-1}, time, 60 min)

Efficiency of cefazolin removal declined with increasing the initial concentration of this pollutant. The reason for this reduction is that with increasing the initial concentration, more cefazolin molecules are absorbed on the surface of photocatalyzer and prevents from the reaction between cefazolin molecules and photonic cavities produced an hydroxyl radical due to lack of direct contact between them (Muthirulan *et al.*, 2013). In addition, high concentration of cefazolin in the environment leads to higher consumption of oxidants and growth in the time of treatment that conforms to the results of study conducted by Muthirulan *et al.*, (2013) and Samarghandi *et al.*, (2015). In the study of Samarghandi *et al.*, (2015) that used catalyzer ozonation process with Fe/MgO nanoparticles to remove cefazolin from aqueous environments, results demonstrated that the amount of removal rose with reducing antibiotics concentration.

3.7. Determining the Kinetics of the reaction

In this section**,** the Kinetic of the study obtained in optimal conditions from the process was focused on. Results have been presented in Table 2 and Figure 7. Results revealed that given the correlation coefficient parameter of (R^2), the reaction in desired process conformed to second – order kinetic.

Chemical kinetic studies the speed of chemical reactions. The speed of a reaction can be stated based on reduction in the concentration of a reactive material in time unit or increase in the concentration of a product in time unit. Results demonstrated that the speed of cefazolin removal in the process under study followed pseudo- first -order reaction that is consistent with the study conducted by Muthirulan *et al.* (2013).



(a) (b)

Figure 7. Kinetic of oxidation a) pseudo- first order reaction and b) pseudo- second order reaction UV/AC+ZnO (pH= 3, concentration of modified AC, 100 mg L^{-1}, Cefazolin initial concentration, 100 mg L^{-1})

Table 2. Kinetic coefficients related to UV/AC+ZnO process in removal of CFZ (pH = 3, concentration of modified AC, 100 mg L^{-1}, Cefazolin initial concentration, 100 mg L^{-1})

NO	C_0 (mg L^{-1})	Time (min)	C (mg L^{-1})	C/C_0	$-Ln(C/C_0)$
1	100	3	65	0.64	0.43
2	100	8	48	0.48	0.72
3	100	13	42	0.42	0.85
4	100	18	30	0.3	1.18
5	100	25	25	0.25	1.37
6	100	30	17	0.17	1.74
7	100	40	10	0.1	2.29

Table 3. Ultraviolet reactor characteristics.

Parameter	Property
Light color	White
Lamp power (W)	55
Copacity (GPM)	12
Connectors size (Inch)	3/4
Dimensions of UV chamber (mm)	910 × 310 × 310
Company	OSRAM
Manufacturer country	Germany

4. Conclusions

The photo-catalytic process of zinc oxide nanoparticles placed on the synthetic activated carbon has appropriate efficiency in removing cefazolin and this process can be used to decrease the pollution load of hospital wastewater and manufacturing industries before entering the conventional treatment units and before final discharge of wastewater containing cefazolin as well. Since this process does not produce disposal materials such as sludge, it is considered an important bio-compatible process in line with treating resistant organic pollutants.

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