# The efficiency of UV/$S_2O_8^{2-}$ and UV/ ZnO photo-oxidation process for the removal of Acetominophen from aqueous solution: A comparative study

## Abstract

These days, water has a special importance in human life, and access to safe drinking water is essential to maintaining human health. The presence of residual pharmaceutical compounds as emerging contaminants (ECs) in wastewater deteriorates aquatic life and water quality due to the lack of effective treatment processes to remove them. This paper deals with the degradation and demineralization of acetaminophen (ACT) from its aqueous solution under UV-Vis irradiation using ZnO (UV/ZnO) and $K_2S_2O_8$ (UV/PS). Detailed batch tests were evaluated to investigate the effect of different variables such as pH, catalyst dose, reaction time, drug concentration and mineralization rate. The results showed the higher performance of the UV/PS process and the UV/ZnO at acidic and natural conditions, respectively. The constant reaction rate for ACT removal in the UV/PS process is almost double that of the UV/ZnO process. The results of the remaining TOC tests show that the processes can convert the ACT in the solution into harmless minerals such as carbon dioxide after degradation. Increasing the dose of catalysts to an optimum amount led to an increase in elimination efficiency. The UV/PS process is able to degrade 20 mg/L of acetaminophen in 50 minutes, while the UV/ZnO process breaks down this amount of acetaminophen in 100 minutes. This work can be developed for the removal of ECs related to the pharmaceutical group from contaminated water.

**Keywords**: Pharmaceutical, Persulfate, Photodegradation, Wastewater

## 1. Introduction

Emerging contaminants in drinking water have raised great concerns because of the long-term deleterious risks and their influence on human health and aquatic ecosystems [1]. In general, the sources of emerging contaminants include industrial sources, pesticides, pharmaceutical sources, and personal care products. Among these, the production and use of pharmaceutical compounds to treat human and animal diseases is one of the most challenging tasks. A large proportion of these compounds are excreted in the urine and feces without any change or metabolism. Thus, pharmaceutical compounds enter the sewage collection system and eventually the wastewater treatment plant. The commercial wastewater treatment systems are usually designed to remove suspended solids, biochemical required oxygen (BOD), and pathogens, so they cannot effectively eliminate drug compounds. Therefore, these compounds enter the environment through effluent without effective removal in the treatment plant. Pharmaceutical compounds can also enter the environment through direct discharge (such as pharmaceutical industry wastewater) and indirect (such as municipal and hospital effluents). Different drug compounds, like antibiotics, should be removed from water due to their wide use throughout the world and their dangerous effects. For example, the development of antibiotic-resistant bacteria poses a serious threat to the entire world and is a matter of great worry. Furthermore, the overuse of drugs, as well as the serious adverse effects associated with drugs in water, are unmistakable indicators that new removal methods for these drugs must be developed immediately. [2, 3]. These compounds have been proposed as one of the emerging pollutants because of their concentration levels higher than their ecotoxicity endpoints [1, 4, 5]. Acetaminophen ($C_8H_9NO_2$), as an antipyretic pharmaceutical, is excreted from the body after digestion of therapeutic dosage and frequently observed in the municipal wastewater systems [6]. It is sold without a prescription and has become one of the drugs that many people are not afraid to use with the slightest feeling of pain [7, 8]. Various treatment methods have been investigated to remove drug compounds from contaminated waters, such as activated sludge systems, membrane filtration, surface coagulation and adsorption, and advanced oxidation processes (AOPs).

Physical methods such as surface adsorption are merely an operational unit with phase change that only transmits pollution to another phase (on the adsorbent surface) and is still considered an environmental concern. Although biological processes are a good way to treat biodegradable pollutants, they do not have the ability to completely decompose biodegradable compounds such as pharmaceuticals. AOPs produced reactive oxygen species (ROS) containing oxy radicals to degrade contaminants. The heterogeneous photocatalysts can be considered one of the most promising AOPs to remove many different types of contaminants worldwide [1, 9-12]. In this process, the photogenerated electron–hole pairs in semiconductors (ZnO, $TiO_2$) led to the formation of ROS. However, oxy-radical reacts unselectively with the dissolved organic materials through a multistep mechanism, limiting their efficiency in complex environmental matrices (sustainability). To overcome such limitations, AOP treatment, based on the generation of sulfate radicals, has been developed and widely investigated. Photocatalyst semiconductors can produce photo-induced electrons and holes by absorbing photon energy. The produced active species on the surface of the semiconductor can attack the organic molecules, which results in the decomposition of the pollutant into less dangerous species like $CO_2$ and $H_2O$ [13]. Sulfate radicals act as powerful oxidants with a standard redox potential of 2.6 V and have been developed to control AOPs. They can be generated in situ by activating some precursors, i.e., potassium persulfate (PS) or peroxymonosulfate salt (PMS), by using different methods such as radiation, photolysis, and thermal activation. Zinc oxide is a well-known semiconductor with a band gap energy of 3.2 eV. This oxide ceramic is used extensively as a white pigment and as a filler.

It is a low-cost material with environmental sounds. It has a good photocatalytic activity. However, this semiconductor works under UV light and suffers from fast electron-hole recombination. Therefore, some modifications are necessary to overcome these drawbacks [14].

The present work aims to test the adequacy and efficacy of UV/PS in comparison to UV/ZnO for ACT removal as the ECs water and uncover controlling mechanisms of the treatment. Then, research variables and data analysis were studied by designing purposeful experiments based on scientific methods.

## 2. Materials and methods

In this study, $H_2SO_4$, NaOH, and $Na_2S_4O_8$ were purchased from Merck and used without further purification, while nano ZnO was supplied from Sigma-Aldrich (544906, PubChem Substance ID 24878793). Acetaminophen Tablet was gifted by Aburaihan pharmaceutical company. The concentration of ACT was determined by an Agilent HPLC (Eclipse plus C18 column; 3.5µm, 4.6×100 mm) equipped with a UV detector at wavelength of 242 nm. The mobile phase was a combination of phosphate buffer (pH = 4.8) and acetonitrile with a volume ratio of 85 to 15% at a flow rate of 1 mL per minute. Fig. 1 shows ACT solution at 242 nm using HPLC before and after UV/PS photodegradation when the ACT removal efficiency is 100%.

.

**Fig. 1.**

In this study, a photochemical reactor (200 mL) was used with two low-pressure mercury lamps (LP Hg lamps, Cole-Parmer, 9W) with monochromatic emission at 254 nm, which is commonly used in studies and is also available in the market.

The photoreactor is made in a cylindrical shape (with a diameter of 5 cm and a height of 40 cm) so that the lamps can be placed inside it. In order to prevent the direct contact of the liquid with the lamp, a quaternization sleeve is used. In the present study, this reactor was operated in a continuous manner, and its contents were mixed by a stirrer.

The degradation of ACT was measured according to the following equation:

$$ACT\ removal\ efficency\ (\%) = \frac{ACT_0 -\ ACT_t}{ACT_0} \times 100 \qquad (1)$$

$ACT_0$ and $ACT_t$ related to the concentration of ACT before and after the reaction.

Determination of total organic carbon (TOC) as a non-specific test has special importance in controlling the quality of water and effluent samples. It investigates the total amount of carbon in the sample and cannot be used as a method to detect organic molecules in the sample. Although several methods have been proposed for measuring TOC, all of them use two main steps, which include the oxidation of organic carbon to carbon dioxide and then the measurement of carbon dioxide content.

In this study, the amount of TOC was measured using the TOC analyzer (Shimadzu, TOC analyzer—VCSH Model), and the degree of ACT mineralization was then calculated from equation 2:

$$ACT\ minerallization\ efficency\ (\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \qquad (2)$$

where, $TOC_0$ and $TOC_t$ are the total organic carbon (TOC) concentration in the solution before and after reaction, respectively.

## 3. Results and discussion

### 3.1. Investigating the effect of pH on the performance of photodegradation of ACT

The obtained results showed the maximum removal efficiency of acetaminophen is achieved at acidic pH=3 and neutral pH for the UV/PS process and UV/ZnO process, respectively. The pH plays an important role in advanced oxidation processes; therefore, different pH was examined to obtain the optimal pH. Acetaminophen (20 mg/L) was added to the photoreactor in the presence of PS (200 mg/L) at selected pH for 30 min. Fig. 2 shows the effect of pH on the UV/PS process. The elimination efficiency of ACT is the highest in acidic pH=3 (Fig. 2a). In addition, the final pH of the solution has also decreased after the degradation of ACT due to the formation of acidic products. The maximum efficiency of ACT removal in the UV/ZnO process at pH = 7 is obtained at about 23%. With increasing pH from 3 to 7, the removal efficiency increases and then decreases sharply in alkaline pH (Fig. 2b). In acidic pH, ACT is often present in molecular form, and the corrosion of ZnO occurs. Under such conditions, the hydrophobicity of ACT is maintained, and the accumulation of acetaminophen molecules occurs more frequently. Therefore, it creates more effective collisions and higher efficiency with hydroxyl radicals in the solution [15]. In other words, at high pH, ACT molecules often become ionic (pKa acetaminophen is 9.38). At pH values above pKa, the ionic state of ACT is predominant, leading to the tendency of catalysts in alkaline conditions to reduce surface reactions with the ionic state of ACT. Thus the rate of its elimination relative to the acidic pH of ACT is reduced. Mena et al. [16] reported that the rate of elimination of sulfamethoxazole at acidic pHs is higher than at alkaline pHs using the photofenton process in the presence of sunlight and visible light.

Regarding the UV/PS process, in which a sharp decline in degradation efficiency is observed with increasing pH, radical sulfate can be considered as a decomposing factor supported with published data [16]. It can be attributed to the production of high-energy sulfate radicals as oxidizing species in this process [17, 18].

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \tag{3}$$

$$HS_2O_8^- \rightarrow SO_4^{-\cdot} + SO_4^{2-} + H^+ \tag{4}$$

$$SO_4^{-\cdot} + OH^- \rightarrow SO_4^{2-} + HO^\cdot \tag{5}$$

$$HO^\cdot + OH^- \rightarrow O^{\cdot -} + H_2O \tag{6}$$

Under alkaline conditions, hydroxyl ions are the predominant species, which react with radical sulfate produced by UV radiation and eventually produce hydroxyl radicals (Equation 5). On the other hand, comparing the potential of oxidation of ($\varepsilon$=2. V) at alkaline conditions with (dominant species at acidic conditions) can be the reason for the decrease in removal efficiency in alkali [19].

In addition, another reaction that occurs under alkaline conditions is the conversion of the hydroxyl radical species to the weaker oxygen radical (Equation 5-4), in which case the oxidation power of the process decreases [20].

The reason for the decrease in efficiency at alkaline pH can also be explained in this way. The surface of catalysts becomes negatively charged at alkaline pHs because the pHzpc for ZnO is 9 [21]. Consequently, the electrostatic repulsion between the catalysts and ACT decreases the effective absorption of contaminants into the catalyst and therefore reduces the removal efficiency. The drop in initial pH of the solution is observed after degradation of ACT due to the conversion of ACT into by-products with acidic properties [17]. In addition, Mouamfon et al. reported photodegradation of antibiotics using UV and UV-Vis with the highest removal efficiency in acidic pH [22]. It must be mentioned that the initial pH of the solution decreases after acetaminophen degradation because the complete degradation of acetaminophen has not occurred, and acetaminophen converts to secondary products with acidic properties [19]. It was reported that because the hydrogen ion is one of the byproducts produced during the oxidation of acetaminophen, the common ion effect causes the high quantity of hydrogen ion to impede acetaminophen oxidation at acidic conditions [23].

**Fig. 2.**

### 3.2. Effect of ACT concentration and contact time on process performance

Another factor that affects the performance of advanced oxidation processes is the initial concentration of the pollutant in question [24]. The obtained results showed the removal efficiency decreases with increasing pollutant concentration (Fig. 3). Increasing the concentration of ACT from 5 mg/L to 80 mg/L has led to a decrease in elimination efficiency in both processes supported with published data [19, 25, 26]. During advanced oxidation processes, the amount of oxidizing species produced in these processes is constant due to the constant concentration of the catalyst added to the solution. On the other hand, increasing the concentration of ACT in the desired solution leads to a decrease in the ratio of pollutants to oxidizing agents and a reduction of elimination efficiency.

In advanced photocatalytic oxidation processes, the formation of electron-hole at the surface of the catalyst leads to the production of radicals and destruction of organic matter. These reactions occur in a series of continuous photocatalytic processes so that increasing the duration of the reaction leads to more radical production and the amount of reactions between these radicals and pollutants increases. This causes the increased reaction time in advanced oxidation processes to lead to further removal of contaminants [19, 25]. This can be explained by either deactivation of the catalyst's active sites or saturation of the few available active sites on the photocatalyst surface. High concentrations of the drug cause intermediate components to develop, which have the potential to adsorb onto the catalyst surface and deactivate the active sites. Additionally, as the drug concentration increased, fewer photons reached the catalyst's surface, which resulted in a decrease in photodegradation activity [27].

**Fig. 3.**

### 3.3. Investigation of the effect catalyst dosage on ACT removal

The results of the study show that increasing the dose of catalysts leads to an increase in elimination efficiency, but increasing their amount is somewhat effective, and after a point, there is no significant effect on elimination efficiency and even in some cases leads to the reduction of efficiency (Fig. 4). Increasing the dose of ZnO catalyst in the solution leads to an increase in the level of available active sites for UV radiation, which leads to producing higher amounts of radicals and increasing the rate of ACT degradation [28, 29]. After optimum dosage, the removal efficiency decreases due to the fact that the surface space required by the catalyst to receive radiation has increased sufficiently. Thus, the accumulation of catalyst particles occurs, and less effective radiation is available for the active site of the catalyst [30].

If the catalyst concentration exceeds one limit, then the radical production concentration also increases. However, the produced hydroxyl radicals can react with each other before their reaction with the pollutant [31]. The same is true for radical sulfate species.

$$\dot{\mathrm{O}}\mathrm{H} + \dot{\mathrm{O}}\mathrm{H} \rightarrow \mathrm{H_2O} \qquad (7)$$

$$SO_4^{-\cdot} + SO_4^{-\cdot} \rightarrow S_2O_8^{2-} \qquad (8)$$

Therefore, high catalyst concentrations lead to constant and even loss of efficiency. In addition, it was reported that a rise in amount caused a reduction in the degradation of the drug due to the electron scavenger effect of [32]. The results of this part of the study are in line with other studies of photocatalytic degradation and advanced oxidation of pollutants in which the efficiency of removal has decreased with increasing the optimal catalyst dose [33-35]. ACT removal by UV radiation could be expected because of the presence of π-bonds in its molecule. ACT is not eliminated in the presence of UV radiation alone (when the concentration of used catalysts is zero). Under these conditions, due to the radiation exposure of the acetaminophen solution for 30 minutes, there is no change in the initial concentration of acetaminophen, which indicates that acetaminophen is slowly degradable.

**Fig. 4.**

### 3.4. Investigating the amount of mineralization

Mineralization of organic compounds indicates the end of the oxidation path of an organic compound. Therefore, the remaining TOC in the samples was measured at different times in order to determine the mineralization rate. In order to evaluate the final product of ACT degradation, the total organic carbon at different times was investigated (Fig. 5). The results of the remaining TOC tests show that the processes are able to convert the ACT in the solution into harmless minerals such as carbon dioxide after degradation. However, the rate of mineralization in the UV/PS process occurs at a higher rate compared to the UV/ZnO process, and better mineralization occurs in less time. This could be due to the production of radical sulfate (UV/PS process) with higher oxidation power than that of hydroxyl (UV/ZnO) species for mineralization and decontamination ACT.

Since ACT dissolved in distilled water, the resulting TOC is only related to the drug composition. This is also confirmed by measuring the initial TOC of the samples and comparing it with the theoretical TOC. For example, in the case of acetaminophen, which used a concentration of 20 mg/L, the calculation of theoretical TOC shows that the concentration of this drug has a TOC equal to 12.7 mg/L. TOC measurement using TOC Analyzer also confirms this position to some extent, and the initial measured TOC is 13.9 mg/L. It must be mentioned that a small difference in the numerical amount of TOC measured with theoretical (calculated) TOC was observed. It can be attributed to the used ACT tablets instead of their active ingredient. Since this difference is negligible, it will not have much effect on the performance of the processes. Its complete mineralization is achieved within 200 minutes in the UV/ZnO process, although ACT is completely removed within 100 min.

**Fig. 5.**

### 3.5. Kinetic comparison of UV/PS and UV/ZnO processes in ACT degradation

Chemical kinetics was used to study the influence of various laboratory conditions on the chemical reaction. Different laboratory conditions can affect the reaction mechanism and its transition state. Chemical kinetics used mathematical models to explain the properties of a chemical reaction in the removal of pollutants during the process. A lot of reactions may occur in advanced oxidation reactions, but the removal of the wanted contaminant is only observed and measured. In this study, the removal of ACT in various processes was used based on the pseudo-first-order kinetic model (Eq. 9).

$$ln\left(\frac{C_t}{C_0}\right) = -k_{app}t \qquad (9)$$

where $C_0$ is the initial concentration of the pollutant at the beginning of the reaction and $C_t$ is the concentration of the pollutant at time t of the reaction. Kapp is also a constant rate of ACT removal obtained from the slope [28].

#### 3.5.1. Kinetic comparison of the studied processes

Kinetic models are used to calculate the constant speed of chemical reactions and the possibility of direct comparison of results with other studies. During the present study, the pseudo-first-order kinetic model was used for this purpose, and high correlation coefficients indicate the adherence of contaminant removal reactions from this model. Due to the fact that many chemical reactions occur in the elimination of pharmaceutical compounds, especially in advanced oxidation processes. It is not possible to directly calculate the individual rate of these reactions; the pseudo-first-order kinetics is used, which is based on the initial concentration. And the final pollutant is the target, and finally, the apparent (observed) velocity constant in the pollutant removal is reported [28].

In the present study, the kinetics of degradation in both processes and at different concentrations of pollutants were investigated (Fig. 6). The results show that the constant reaction rate at the same concentrations in the UV/PS process is almost double that of the UV/ZnO process. It indicates the high performance of this process in acetaminophen degradation (Table 1). Another point in this part of the study is the constant decrease in reaction rate with increasing pollutant concentration, which is also due to the decrease in the ratio of oxidant to pollutant, which reduces the rate of acetaminophen degradation, followed by a steady decrease in reaction rate.

**Fig. 6.**

**Table 1**

## 4. Conclusion

The present study examines the performance of advanced UV/PS and UV/ZnO oxidation processes for ACT degradation. During this study, the pH effect, the dose of catalysts, the duration of the reaction, the kinetics of degradation, and the amount of mineralization were examined. In this study, optimal response conditions such as pH and catalyst dose were obtained for each process. The results show that UV/PS performance is better for ACT degradation under acidic conditions and the UV/ZnO process at neutral pH. Examination of acetaminophen mineralization also shows that both processes are able to completely convert acetaminophen to minerals, which is done more rapidly in the UV/PS process. Finally, a comparison of the performance of UV/PS and UV/ZnO processes in acetaminophen degradation shows that both are able to decompose this drug compound, and the UV/PS process can be used as an efficient and effective process for the degradation of pharmaceutical compounds in wastewater.

## Conflict of interest

There is no conflict of interest to declare in this study.

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**Table 1** The summary of kinetic information of ACT degradation

| Photodegradation | ACT concentration | $K_{obs}$ | $R^2$ |
|---|---|---|---|
| UV/PS | 5 | 0/060 | 0/98 |
| | 10 | 0/050 | 0/95 |
| | 20 | 0/049 | 0/95 |
| | 40 | 0/037 | 0/96 |
| | 80 | 0/029 | 0/96 |
| UV/ZnO | 5 | 0/037 | 0/98 |
| | 10 | 0/029 | 0/98 |
| | 20 | 0/026 | 0/98 |
| | 40 | 0/020 | 0/96 |
| | 80 | 0/016 | 0/94 |

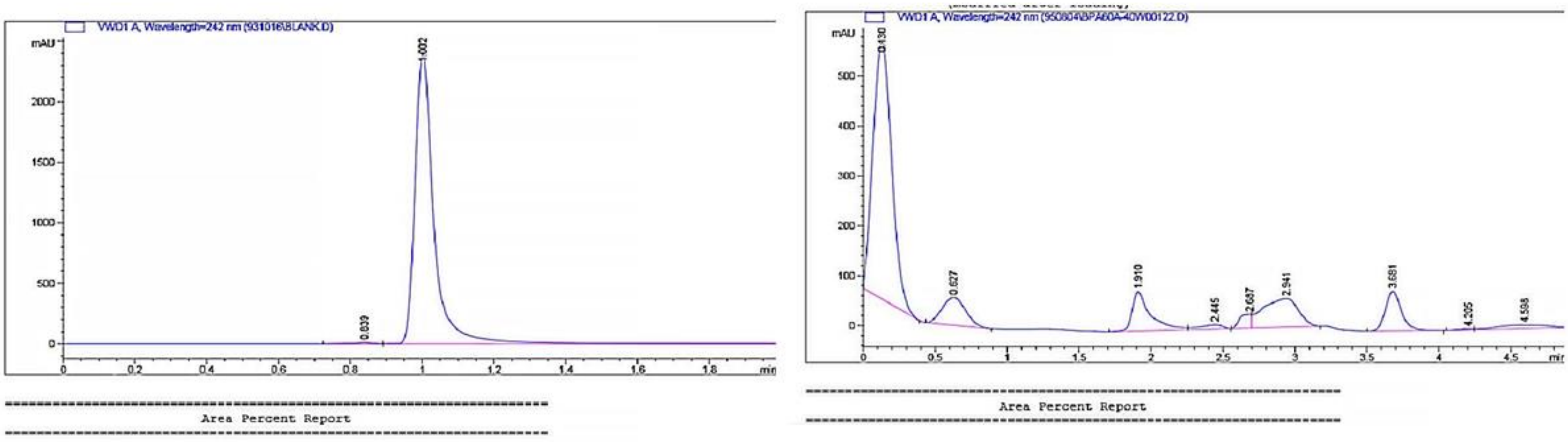

**Fig. 1.** High-performance liquid chromatograms of ACT solution a. before and b. after photodegradation

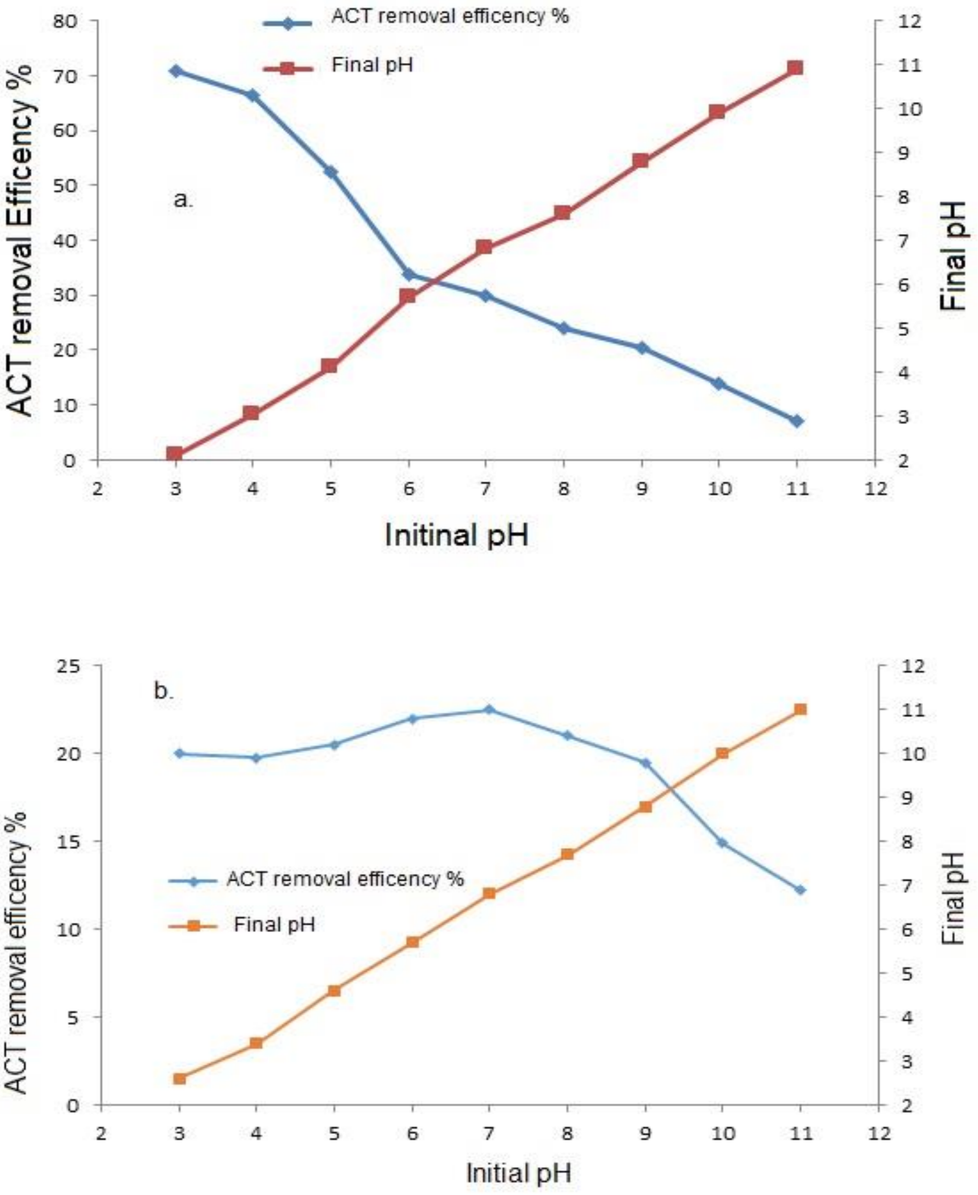

**Fig. 2.** The effect of pH on the removal of ACT a. PS and b. ZnO (ACT = 20mg/L, t= 30 min, PS = 200 mg/L,ZnO= 800mg/L)

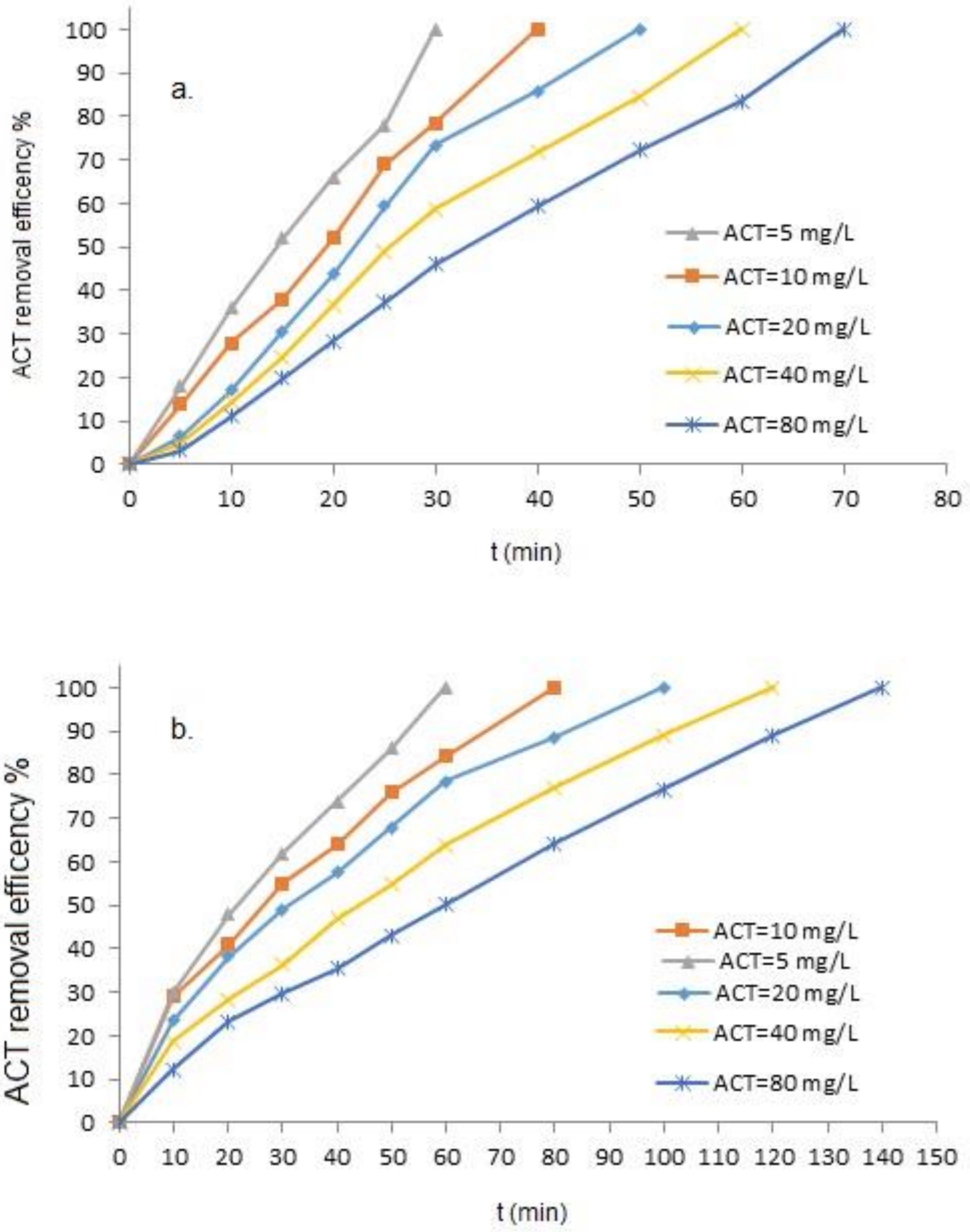

**Fig. 3.** The effect of t and ACT concentration of the ACT removal efficiency % (pH=3, PS=200 mg, ZnO=800 mg/L)

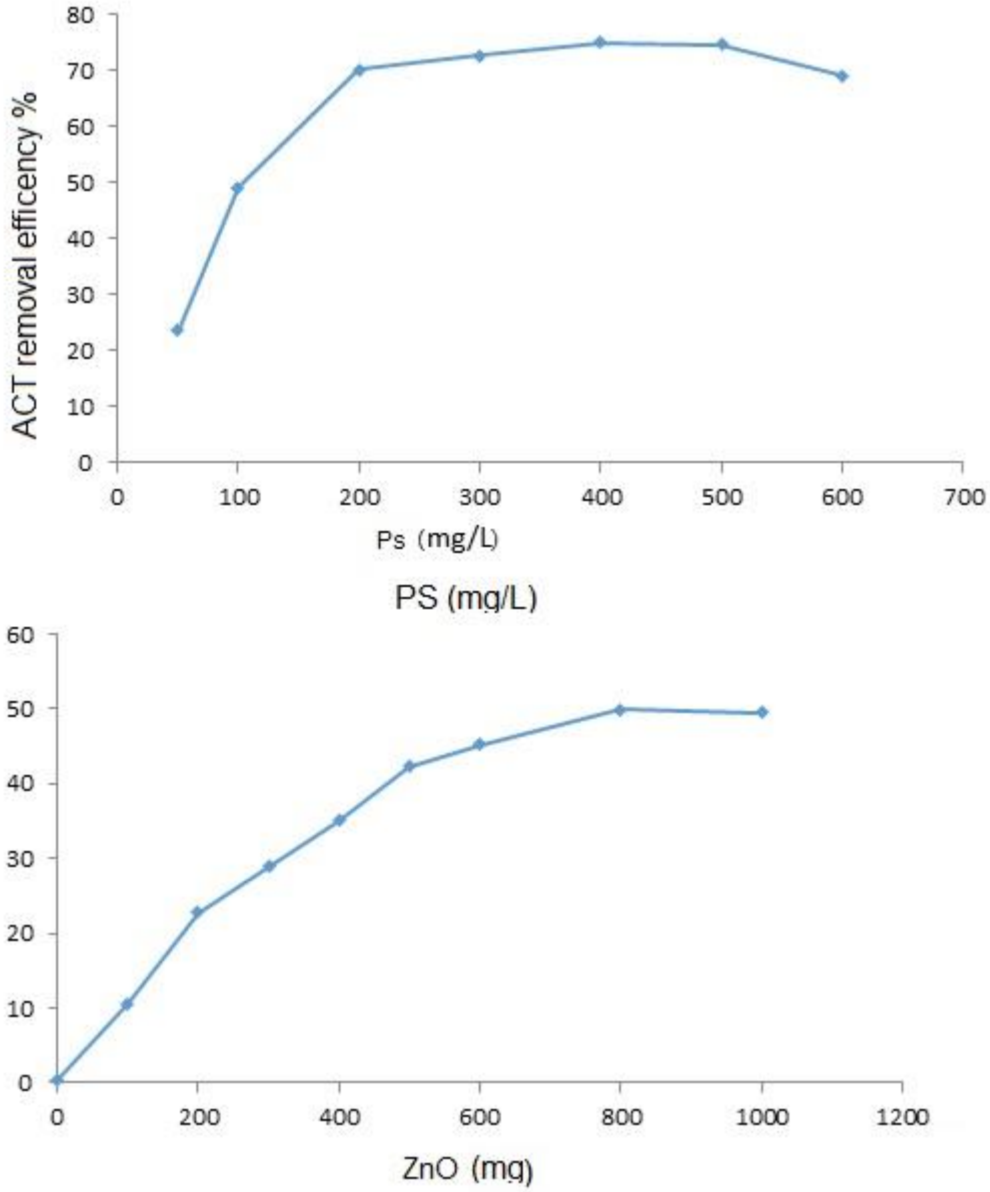

**Fig. 4.** The effect of catalyst dosage on the ACT removal efficiency% $t_{Ps}$=50 min, $t_{ZnO}$=100 min (ACT= 20mg/L, pH=3)

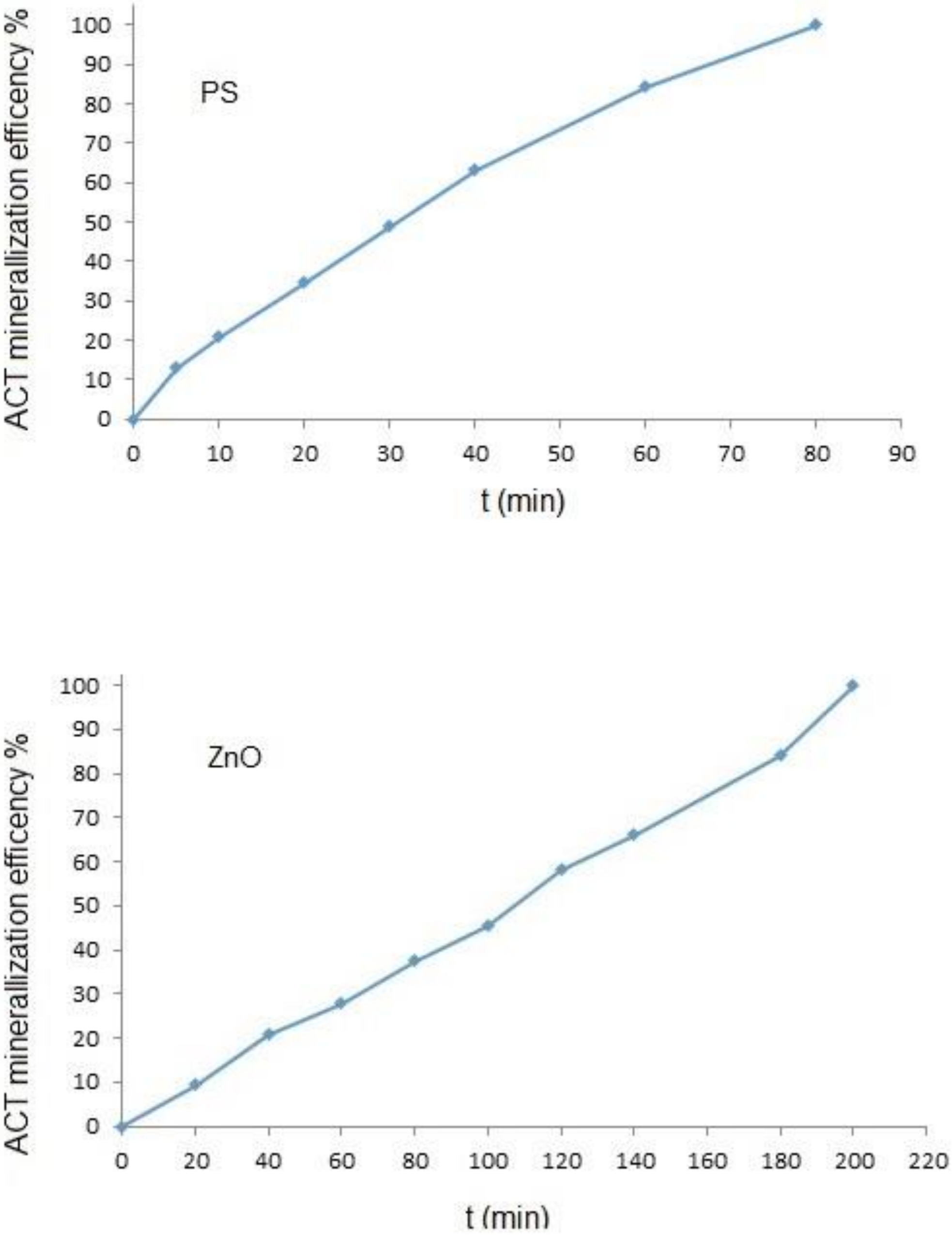

**Fig. 5.** The mineralization of ACT in UV/PS and UV/ZnO process

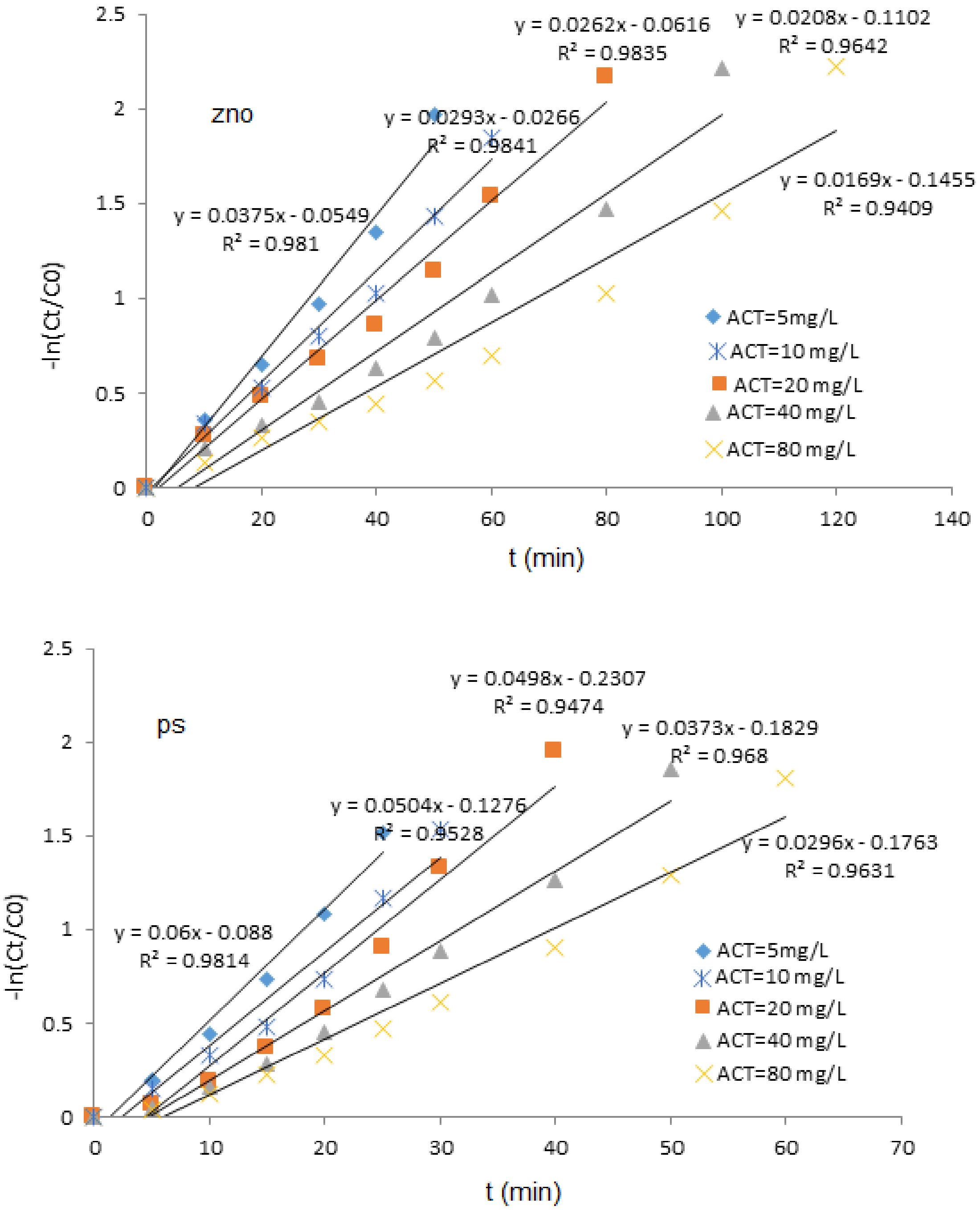

**Fig. 6.** The pseudo-first-order kinetic model of ACT removal