

Activity of TiO₂ Nanomaterial for Photocatalytic Ozonation Degradation of Acetaminophen

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Abstract

Acetaminophen is one the most common medicines found in cabinets of houses which is used as a painkiller. Therefore acetaminophen is usually found in household wastewater and sewage of pharmaceutical factories and as a result is found in surface water. Acetaminophen in wastewater causes pollution, so its destruction is important. In the present study acetaminophen destruction with photocatalyst ozonation and in presence of titanium dioxide and under the effect of operating conditions was investigated. The results of degradation efficiency of acetaminophen in a batch system by various advanced oxidation processes revealed the order of TiO₂/UV/O₃>TiO₂/O₃>UV/O₃>O₃>UV/TiO₂. All processes followed pseudo-first order kinetics. The influence of operational parameters such as initial pH, initial concentration of acetaminophen, ozone and catalyst dosage on the TiO₂/UV/O₃ process, which was the most significant method was investigated. The ozone dosage was found to have the noticeable impact on the process, however initial pH and TiO₂ dosage were less effective.

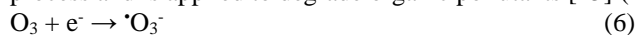
Keywords: Acetaminophen; Advanced oxidation processes; Photodegradation; Photocatalytic ozonation; nano TiO₂

Introduction

In recent years, several studies have shown interest in the degradation of pharmaceuticals, which are considered to be emerging pollutants due to the fact that they remain unregulated or are currently undergoing a regularization process [1]. These compounds can be incorporated into waterbodies from different sources, such as excretion by humans and animals [2] and the pharmaceutical industry [3]. In particular, acetaminophen (AMP), also known as paracetamol (*N*-acetyl-4-aminophenol), is a common analgesic and antipyretic drug that is widely used all over the world. AMP has attracted the interest of researchers due to its tendency to induce liver and kidney damage. Besides, there have been several reports that have supported the presence of AMP in rivers, ambient waterways, and the influents and effluents of wastewater treatment plants [4]. Additionally, several pharmaceuticals, such as AMP, are neither removed during wastewater treatment nor biodegraded in the environment [5] due to their stable chemical structure. For that reason, many researchers have focused their attention on advanced oxidation processes (AOPs), where a strongly oxidizing hydroxyl radical (OH) is created in situ. Therefore, this radical could oxidize a wide range of organic pollutants present in the water until their degradation [6]. The main oxidizing agent in these processes is hydroxyl radical ($E^0=2.8$ eV), which can be produced under ultraviolet (UV) light-catalyzed reactions [7-8]. Titanium dioxide (TiO₂) has been extensively utilized as heterogeneous catalyst in AOPs. When TiO₂ absorbs UV light photo-induced TiO₂ is generated and electrons are excited from valence band of TiO₂ to exciting band, which result in electron-hole pairs. Oxygen molecules act as electron acceptor to form superoxide ions (O₂^{•-}) and hydroxyl ions or water molecules function as electron donor to produce hydroxyl radicals [9] as follows:



Although UV/TiO₂ process can degrade contaminants in aqueous solutions, the degradation rate is not considerable [10]. High reactivity and disinfection of ozone (O₃), which is stronger oxidant than oxygen (E⁰=2.07 V) makes it suitable for application in various water treatment processes [11]. Hence, ozonation was used for treatment of wastewaters containing phenolic compounds [12]. However, it has been proven that in conventional ozonation method complete degradation of organic compounds is not achieved. The degradation efficiency of humic acid and oxalic acid was more effective by TiO₂-catalyzed ozonation (TiO₂/O₃) in comparison of ozone alone process [13]. It can be attributed to the both enhancement of ozone dissolution and decomposition in the presence of TiO₂ particles [14]. The combination of ozone with photocatalytic oxidation elicits the advantages of all above-mentioned processes. The production of extra hydroxyl radicals enhances not only by reduction of dissolved O₃ molecules with photogenerated electrons at conduction band of TiO₂, but also by absorption of UV light by ozone itself which is named as UV/O₃ process and is applied to degrade organic pollutants [15] (Eqs. (6)-(10)).



The utilization of ozone combination with photocatalytic oxidation process for degradation of organic pollutants like monochloroacetic acid, pyridine, neonicotinoid insecticides, toluene, sulfamethoxazole and 4-chloronitrobenzene has been reported [16-21]. However, to the best of our knowledge, there is no report for degradation of AMP by this process. The aim of this study was to compare various AOPs processes including UV/TiO₂, O₃, UV/O₃, TiO₂/O₃ and TiO₂/UV/O₃ to find synergetic effect of ozonation and photocatalysis on degradation of AMP. Then, to investigate the effect operational parameters such as initial AMP concentration, initial pH, ozone and catalyst dosage in TiO₂/UV/O₃ process experiments were carried out.

2. Experimental

2.1. Materials

Acetaminophen (AMP) obtained from Retell Fine Chemical Co., Ltd. (Tianjin, China). Aqueous solution of AMP was prepared in deionized water. Titanium dioxide (Degussa P25, Germany) which has 80% anatase and 20% rutile, with average particle size of 21 nm and surface area of 50±15 m²/g was applied as catalyst. All other chemicals were purchased from Merck, Germany.

2.2. Experimental set-up and procedure

Experiments were carried out in a batch cylindrical quartz reactor with inner diameter of 50 mm and volume of 500 mL. In each experiment, 250 mL of the reaction mixture containing desired amounts of AMP and TiO₂ were poured to the reactor. The pH of solution was adjusted by adding perchloric acid or sodium hydroxide. The solution was agitated by a magnetic stirrer. Mixture of ozone-oxygen which was supplied from the ozone generator (Donali, Iran) fed to the reactor by a diffuser from its bottom. The concentration of ozone was adjusted by varying voltage and measured by KI method [22]. An UV lamp (10 W, 254 nm, GPH212T5L/4, Germany) was placed next to the reactor to provide UV irradiation. The light intensity on the outer side of the reactor was 2.3 mW/cm², which was measured by UV-Lux-IR meter (Leybold Co., Germany).

2.3. Analytical methods

High performance liquid chromatography (HPLC) (Shimadzu, SCL-6A, Japan) was applied to determination the concentration of AMP (C) in the solution. A ZOBAX column (5 μm C18) and mobile phase of methanol/water (7:3 v/v) with flow rate of 1.0 mL/min were employed in HPLC analysis. To investigate the mineralization of AMP total organic carbon (TOC) by catalytic oxidation (Shimadzu TOC-5000, Japan).

3. Results and Discussion

3.1. Comparison of various AOPs for degradation of AMP and kinetics study

The individual effect of UV irradiation and TiO₂ addition is negligible for degradation of AMP in aqueous solution. The degradation efficiency (DE%) at a certain time is defined as the percentage ratio of degraded amount (C₀-C) to its initial concentration (C₀). The decreasing order of DE% for AMP (40 mg/L) by different AOPs processes after 15 min of treatment was TiO₂/UV/O₃ (99.1%), UV/O₃ (94.5%), TiO₂/O₃ (92.8%), O₃ (91.9%) and UV/TiO₂ (14.2%) (Fig. 1a).

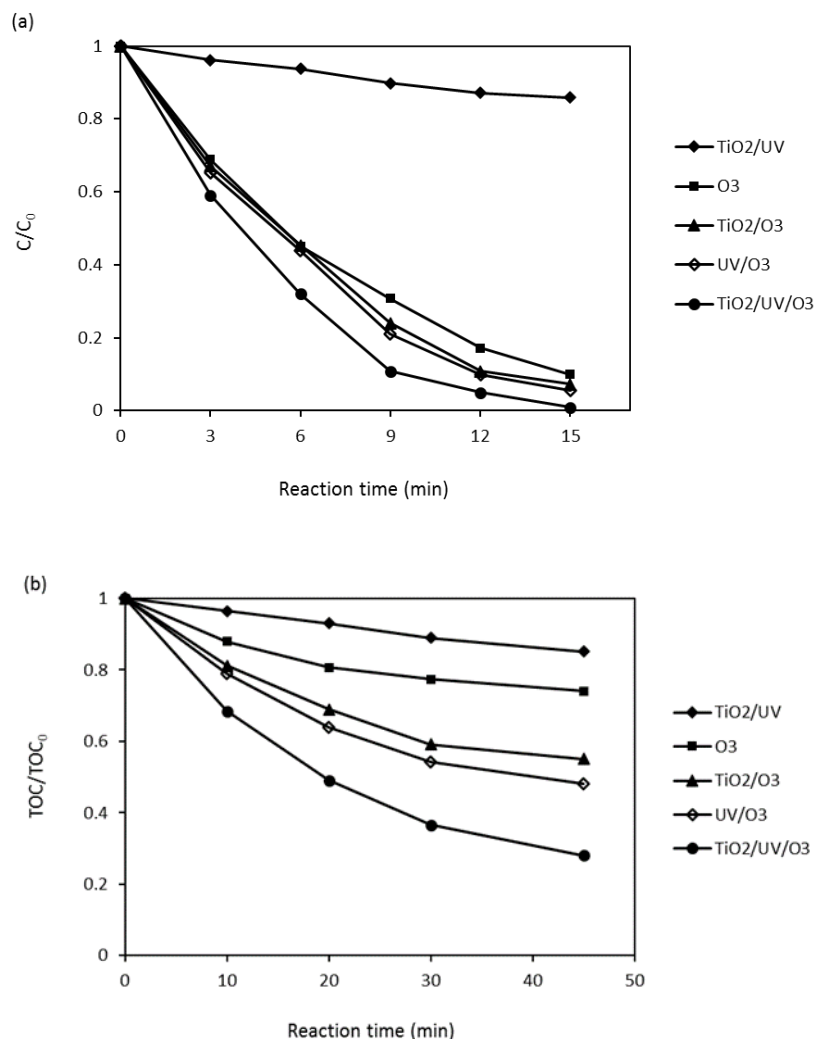


Figure 1. (a) Degradation curves of AMP by different oxidation process, (b) removal of TOC. Experimental conditions: pH= 9.5, 50 mg/L TiO₂, C₀= 40 mg/L, ozone gas concentration 5.2 mg/L.

Moreover, mineralization of AMP during above-mentioned AOPs was investigated by monitoring of TOC. Although, order of the mineralization was as same as the degradation, the significant differences for TOC removal were observed after 45 min of processes (Fig. 1b). The TiO₂/UV/O₃ process demonstrated 71.9% TOC elimination, which was 57%, 45.9%, 26.9% and 19.9% higher than that of UV/TiO₂, O₃, TiO₂/O₃ and UV/O₃ processes, respectively. The results indicate that simultaneous application of heterogeneous photocatalysis with ozone, which has high oxidative ability, is an efficient coupled process for degradation and mineralization of AMP. These findings can be explained by (i) more dissolution and decomposition of O₃ in water in the presence of TiO₂[13], and (ii) O₃ acts as electron acceptor from conduction band of TiO₂[14], preventing recombination of electron-hole pairs, and (iii) O₃ absorbs UV light(O₃/UV) [15]. All mentioned reasons cause to form extra hydroxyl radicals resulting in enhancement of DE% and mineralization of AMP.

All applied AOPs in this study follow pseudo-first order kinetics (Fig. 2):

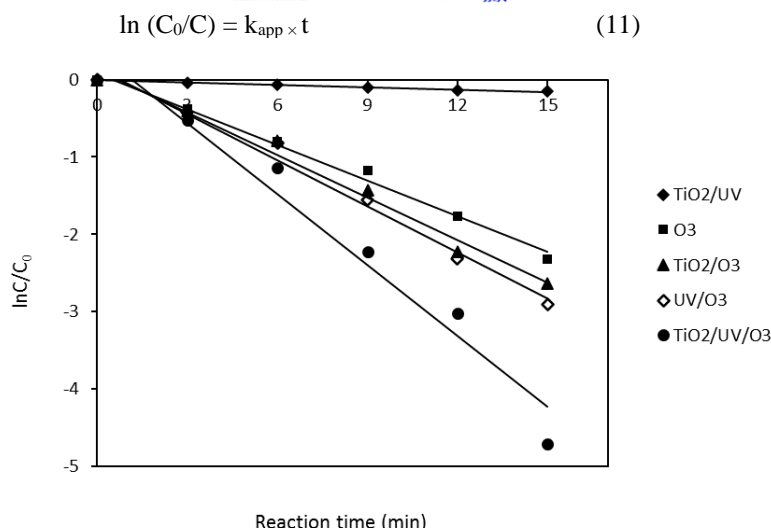


Figure 2. Kinetics of AMP degradation by various AOPs. Experimental conditions: pH= 9.5, C_0 = 40 mg/L, 50 mg/L TiO_2 , ozone gas concentration 5.2 mg/L.

Apparent pseudo-first-order reaction rate constant (k_{app}) was determined from the slope of $\ln(C_0/C)$ versus process time (t) (Table. 1). The high obtained correlation coefficients confirmed the assumed kinetics. Synergistic effect of O_3 and UV/ TiO_2 is considerable and can be measured in the apparent pseudo-first-order rate constants by following equation as 46%:

$$\text{Synergy} = (k_{TiO_2/UV/O_3} - (k_{O_3} + k_{UV/TiO_2}))/k_{TiO_2/UV/O_3} \quad (12)$$

As a result, other experiments for AMP degradation were carried out by coupled photocatalytic ozonation process.

3.2. Influence of operational parameters on photocatalytic ozonation and intermediates identification

The effects of experimental parameters including ozone and TiO_2 dosage, initial AMP concentration and pH on the degradation and mineralization of AMP were investigated. Degradation and mineralization of AMP declines by increasing of AMP concentration, because the identical amount of oxidizing species, which are generated at the same conditions, have to react with more AMP molecules and its degradation intermediates [23]. By increasing the O_3 dosage, the degradation and mineralization of AMP enhance due to formation of more oxidizing species like hydroxyl radicals [11]. However, more increase in O_3 dosage do not have remarkable effect on DE% because unreacted O_3 being released in the system [24]. The effect of TiO_2 dosage on the DE% and TOC was depicted. It can be concluded that both DE% and TOC do not vary noticeably by increasing TiO_2 dosage. This result is in consistent with degradation of 4-chloronitrobenzene by $TiO_2/UV/O_3$ process [21]. The DE% and TOC removal of AMP was studied in pH of 3.5, 6.5 and 9.5. The degradation of AMP approximately shows the same results in various pHs, but the pH of 9.5 shows the best performance for mineralization of AMP. In acidic medium (pH= 3.5), the predominant form of ozone molecule is in the solution, which can degrade organic pollutants by direct electrophilic attack [25]. In the basic medium (pH= 9.5), indirect attack of hydroxyl radicals, which were generated by O_3 decomposition [26], can degrade AMP more efficiently. Furthermore, the reaction of $\cdot OH$ with AMP might be more efficient at high pH rather than at low pH.

Conclusion

The photocatalytic ozonation process for degradation of AMP, was compared with UV/ TiO_2 , O_3 , UV/ O_3 and TiO_2/O_3 processes. All processes followed the pseudo-first order kinetics. Moreover, the operational parameters including ozone and TiO_2 dosage, initial AMP concentration and pH on the degradation and mineralization of AMP were investigated on $TiO_2/UV/O_3$ process.

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Nomenclature

AMP: Acetaminophen (*N*-acetyl-4-aminophenol)

AOPs: Advanced oxidation processes

HPLC: High performance liquid chromatography

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