Chemical, Petroleum and Environmental Engineering

Advanced Oxidation of Antibiotics Polluted Water Using Titanium Dioxide in Solar Photocatalysis Reactor

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ABSTRACT
The aim of this study was to investigate antibiotic amoxicillin removal from synthetic pharmaceutical wastewater. Titanium dioxide (TiO$_2$) was used in photocatalysis treatment method under natural solar irradiation in a tubular reactor. The photocatalytic removal efficiency was evaluated by the reduction in amoxicillin concentration. The effects of antibiotics concentration, TiO$_2$ dose, irradiation time and the effect of pH were studied. The optimum conditions were found to be irradiation time 5 hr, catalyst dosage 0.6 g/L, flow rate 1 L/min and pH 5. The photocatalytic treatment was able to destruct the amoxicillin in 5 hr and induced an amoxicillin reduction of about 10% with 141.8 kJ/L accumulated solar energy per liter of solution.

Keywords: Synthetic wastewater; Amoxicillin; Photo catalyst; Solar energy; Titanium dioxide; Advanced oxidation
1. INTRODUCTION

Through the last decades, antibiotics have been widely utilized for disease treatment (Heberer, et al., 1997). Previous studies had discovered pharmaceutical substances existence in the normal ecosystems, which resulted in contamination to the origins of drinking water, surface water, and groundwater, (Putschew et al., 2000; Sacher et al., 2001; and Anderson et al., 2004). The origins of such substances always arrive from the expelling of human’s waste, where the managed as pharmaceutical substances cross through the human body unchanged, i.e., as parent substance or metabolite, into feces and urine. (Ternes, 1996). Three of them are quite often discovered in the aqueous surrounding are carbamazepine (CBZ), amoxicillin (AMX) and diclofenac (DCF), (Ortiz et al., 2013).

Amoxicillin (AMX) Fig. 1 is an antibiotic that belongs to penicillin’s group. The amoxicillin chemical structure composed of “d-4-hydroxyphenylglycine” side chain linked to 6-aminopenicillanic acid (6-APA) moiety. From the other side, Amoxicillin is a wide spectrum antibiotic utilized for treating the infections of bacterial resulted via sensitive microorganisms, (Chatterjee et al., 2014). This drug includes capsules, tablets, powder, and injections as well as in combination with other ingredients. Because of antibiotics less bio-degradability, they’re partially eliminated in the traditional wastewater processing plants, by that means, giving a great contamination danger into the bodies that receive water. (Papageorgiou et al., 2016 and Luo et al., 2014).

It has been reported in the literature that antibiotics can exist in water bodies at different concentrations due to the discharge of the untreated pharmaceutical wastewater, Omar et al., 2016. For example, in Australia the concentration of the antibiotics in the wastewater was recorded as 3.8 μg L⁻¹, (Watkinson et al., 2007). The concentration of AMX in Iraq was reported as from 0.6 to 24.0 μg L⁻¹, (Omar et al., 2016) which is much higher than that reported in other countries such as in Italy (Castiglioni et al., 2004). These substances can harm both humans and animals and cause serious toxicological risks to the aquatic environment, (Kostich et al., 2014). In Iraq, there are no specific management recommendations for antibiotics in the environment. Pharmaceuticals are easily obtainable to everyone without any control and regulation or even without prescription.

![Molecular structure of amoxicillin](image)

Figure 1. Molecular structure of amoxicillin.

There are several technologies for amoxicillin elimination as well as filtration, biological processes, coagulation, flocculation, sedimentation, (Homem and Santos, 2011) ozonation, ion-exchange, membrane and adsorption, (Chatterjee et al., 2014). The sustainable and influential processing of pharmaceutical factory and hospital wastewater that contains a high level of these substances introducing an essential challenge to the engineers of wastewater and environment all over the world. “Advanced oxidation processes”, AOPs, have introduced more capability for contaminants elimination from the wastewater. The contaminants elimination from wastewater via AOPs depends upon the procreation of hydroxyl radicals, which have the ability to oxidize the inorganic and organic intricate substances, (Murgolo et al., 2014).
Advanced oxidation put forward potential treatment for treatment of hazardous effluents from hospitals, (Deegan et al., 2006), textile dyeing, (Bantu et al., 2008) and pharmaceutical industry, (Klavaroti et al., 2009); tertiary treatment of municipal wastewater, (Augugliaro et al., 2005) and disinfection, (Agullo et al., 2013), especially effluents containing pathogens resistant to chlorination, (Dominguez et al., 2013); wastewater effluents containing chlorophenols, phenols, herbicides and pesticides, (Torbina et al., 2015). Titanium dioxide is the most widely used semiconductor photocatalyst in water treatment due to its low cost, chemical stability, and abundance (Gaya and Abdullah, 2008). A broad extension of contaminants of organic could be oxidized via the light having bandgap energy of ($\lambda < 400$ nm) in the TiO$_2$ catalyst existence (Suvarna and Chandana, 2016). The TiO$_2$ catalyst nature (surface area with effective site) acts a significant function in the whole pollutants degrading rates. The bandgap energy of TiO$_2$ has (3.02 eV), that means the irradiation optimum wavelength is about (400 nm), (Deegan et al., 2006).

Solar photo catalysis is an energy efficient technique for degrading the organic pollutants within water without utilizing lamps but only sun light (Agullo et al., 2013; Dominguez et al., 2013 and Seck et al., 2013).

Catalyst being a semi-conductor that absorbs the apparent light (320-750 nm) desired photons transformed energy into the carriers of charge, (Alrousan et al., 2012). Accordingly, the reactors of solar photo-catalytic have taken a significant concern. The reactor design is greatly significant to secure the effective change of incidental solar radiation to the carriers of charge, (Bahnemann et al., 1991).

Various reactor shapes were utilized for degrading different kinds of pollutants employing the solar light or the artificial light that simulates the sunlight. The four often utilized reactor shapes are parabolic double-skin sheet reactor, DSSR; compound parabolic collector, CPC; thin-film fixed bed reactor, TFFBR; and parabolic trough reactor, PTR, (Bahnemann et al., 1991 and Goswami, 1997). Tubular reactors are a variation of other reactors types like (CPC); the discrepancy is the reflector absence that permits (CPC) to possess a small factor of concentration. However, the tubular reactors are subjected to the optical losses owing to the absorbance of (UV) via the tube and the material of reflector. The additional feature is the aging of glass tubes, which is recognized as “UV-solarization”. The more prolonged solar radiation exposure causes additional decrease of the tubes (UV) transmittance that impairs the efficiency of processing and incurs further costs for the regular substitution of tubes.

The objective of the present study is to evaluate the antibiotic amoxicillin elimination from synthetic wastewater using a tubular photoreactor model under the natural solar irradiation and assess the possibility of such technique for water reclamation.

2. MATERIAL AND PROCEDURES

2.1. Chemicals

Amoxicillin AMX (C$_{16}$H$_{19}$N$_3$C$_5$S) with a molecular weight of 365.4 g/mol was taken from Samarra Pharmaceutical State Company. Sodium hydroxide NaOH, Sulfuric acid H$_2$SO$_4$ (these chemicals were used to change the pH value) (Sigma–Aldrich) and Titanium dioxide TiO$_2$ photocatalytic were provided by HIMEDIA Company (India), (purity more than 99.0%) with a molecular weight of 79.87 g/mol.

2.2. Setup of TiO$_2$ solar photocatalytic reactor system

Experiments were: conducted in a reactor of eight tubular glass pipes connected with each other by PVC joints. The dimensions of each tube were 0.55 m long and 0.022 m inside diameter. The glass pipes are placed on a steel construction shielded via a fine surface fabricated from Aluminum foil. The reactor configuration possesses the benefit of the consistent upward blending with a circulating
flow (ranging from 1 to 6 L/min) that was supplied via a pump to provide a regulated circulating flow in the glass tubes. The pilot plant was fixed and tilted at an angle of 45°. The synthetic wastewater was prepared in a glass tank. For reaching the uniform states within this tank, a mechanical blender was utilized. The experimental diagram of the solar photocatalytic reactor system concept and the actual photo of the experimental setup are illustrated in Fig. 2 and Fig. 3, respectively.

![Diagram](image)

**Figure 2.** Schematic diagram of the solar photocatalytic reactor system concept.

![Photo](image)

**Figure 3.** Photograph of the experimental setup.

### 2.3. Solar Experiments
The synthetic pharmaceutical wastewater (5, 7.5 and 10 mg/l of AMX) was mixed with a proper quantity of TiO₂ (100 to 1000 mg/l) and then conveyed to the reactor that is exposed to natural sunlight. The processed water that comes out of this reactor is blended with the water in the tank of containment. This treatment proceeds until the blended concentration in the tank of containment attains a maximum removal. The whole experiments were carried out in the sunny days of July and August 2018. The states of climate (solar irradiance and surrounding temperature) were usual in such period of year at such site. The measurement of the (UVA) radiation was conducted at the “Center of
Solar Energy Research - Ministry of Science and Technology” utilizing “Davis 6152 C Vantage Pro 2 Weather Station radiometer”. This device supplies the information in terms of the incident (UVA-W/m²): the mean solar irradiance for the whole experiments was (763 W/m²) during the interval (8:30-1:30) local time, with a peak magnitude of (905 W/m²) recorded during the period from 9:00 am to 1:00 pm. The water specimen’s temperature and pH within the solar experiments were from (40°C ± 1.6) to (43°C ±3.8) by using thermometer (Hanna instruments, Spain) and pH meter (multi720, WTW, Germany).

The initial specimen was collected, and the reactor was subjected to solar radiation. The specimens were gathered at consistent periods to obtain the change in concentrations. All experiments duration was 5 hours, starting at 8:30 am-1:30 pm local time.

Specimens of 2.5 mL were first collected at consistent intervals of time, and the adequate amoxicillin concentration was then measured via the absorbance measurements that were performed on a Spectrophotometer UV-1800 (Shimadzu Corporation, Kyoto, Japan). The removal efficiency of AMX was calculated according to the following equation:

\[
\text{Removal efficiency} = \left( \frac{C_{in} - C_{out}}{C_{in}} \right) \times 100\% \tag{1}
\]

Where

\( C_{in} \): inlet sample concentration (mg/liter),

\( C_{out} \): outlet sample concentration (mg/liter).

The quantity of energy gathered, per unit of volume, via the reactor from the test commence till every specimen composed may be obtained via Eq. 2 (Joa et al., 2014).

\[
Q_{UV} = Q_{UV_{n-1}} + \frac{\Delta t_n \cdot UV_{GN} \cdot A_{collector}}{V_{total}} \quad \tag{2}
\]

Where,

\( Q_{UV_n} \) and \( Q_{UV_{n-1}} \): The (UV) energy gathered/liter (kJ/L) at the times n and n–1.

\( UV_{GN} \): Mean incident radiation on the irradiated area

\( \Delta t_n \): The testing time of specimen

\( A_{collector} \): The collector illuminated area (m²/m³) and obtained via Equation (3)

\( V_{total} \): The whole volume of treated water (L)

\[
A_{collector} = \frac{A_r \cdot E_s \cdot t}{V_t \cdot \log \frac{C_i}{C_f}} \quad \tag{3}
\]

where

\( A_r \): actual reactor area (m²)

t: irradiance time (h)

\( E_s \): average solar irradiance (W/m²)

\( V_t \):treated volume (L)

\( C_i \) and \( C_f \): initial and final concentrations (mg/L)
Table 1. Different conditions used for amoxicillin removal by the solar photocatalytic reactor.

| Process parameters                  | conditions                                                                                       |
|-------------------------------------|-------------------------------------------------------------------------------------------------|
| Different TiO$_2$ dosages (100,200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg) | Temperature: (40 ± 3°C); flow rate: 1L/min; initial amoxicillin concentration: 7.5 mg/L; initial pH: 5; contact time: 5hr |
| Initial pH (3, 5, 7 and 9)          | Temperature: (40 ± 3°C); flow rate: 1L/min; TiO$_2$ dosage: 600 mg; initial amoxicillin concentration: 7.5 mg/L; contact time: 5hr |
| Flow rate (1, 2, 3, 4, 5 and 6 L/min) | Temperature: (40 ± 3°C); TiO$_2$ dosage: 600 mg; initial amoxicillin concentration: 5 mg/L; initial pH: 5; contact time: 5hr |
| Different amoxicillin concentrations (5, 7.5, 10 mg/L) | Temperature: (40 ± 3°C); TiO$_2$ dosage: 600 mg flow rate: 1L/min; initial pH: 5; contact time: 5hr |

3. RESULTS AND DISCUSSION

3.1. Influence of radiant flux

The variation of solar intensity with time of illumination is plotted in Fig. 4. It can be noted from this figure that the maximum solar intensity was 900 W/m$^2$ at 12 pm in July 2018, where the maximum degradation of amoxicillin can be anticipated.

![Figure 4](image)

Figure 4. Change of the solar intensity with the experimental working time at various months (2018).

The quantity of energy gathered, per unit of volume, via the reactor from the test commence till every specimen are shown in Fig. 5 which plots the change in amoxicillin concentration against the gathered solar energy/solution volume. This figure displays that the degradation of amoxicillin is positively influenced via the solar energy, because the amoxicillin oxidation is in direct proportion to the no. of light photons, which are absorbed via the solution (Colina-Marquez et al., 2015).
3.2. Effect of TiO$_2$ concentration.

From Fig. 6, the removal efficiency of amoxicillin after 5 hours indicates that with the TiO$_2$ dose up to about 600 mg/L, the removal increases; however, above 600 mg/L, the removal of amoxicillin decreases after the same irradiation of sunlight times. This can be explained by that the solution raised turbidity decreases the light transfer within the solution which is relevant for TiO$_2$ concentrations more than about 600 mg/L, whereas below such concentration of catalyst, it’s assumed that the surface of catalyst and the light absorption via TiO$_2$ particles are bounding (Javad and Fatemeh, 2012).

Figure 5. The change in amoxicillin concentration versus the gathered solar energy.

Figure 6. Removal profiles of AMX in the reactor at different concentrations of TiO$_2$ (AMX = 7.5 mg/l, pH = 5, Flow = 1 L/min).
3.3. Effect of pH
The outputs of changing the pH values from 3 to 9 are shown in Fig. 7, and the amoxicillin peak elimination 7.8% were performed at pH 5.

![Figure 7](image)

Figure 7. Effect of pH value on the amoxicillin removal (AMX = 7.5 mg/l, TiO$_2$ = 600 mg/l and Flow = 1 L/min).

Since TiO$_2$ has amphoteric behavior with a “zero point charge pH” of (6.25), (Saien et al., 2010), the formation of electron-hole, for adsorbing the anions, is preferred when the pH value is less than pH$_{zpc}$. At lower pH (< 5), adsorption of the existed anions generated from the decomposition of supplemented sulfuric acid decreases the opportunity of amoxicillin adsorption within the surface of catalyst, and accordingly, the oxidation rate will be decreased, (Hoffmann et al., 1995). At pH more than (5), the catalyst surface will be negatively charged and repulse the antibiotics in water, and consequently reduce the removal efficiency, (Gomathi et al., 2010).

3.4. Influence of the flow rate of liquid
Fig. 8 manifests the photocatalytic degrading efficiencies of amoxicillin at various rates of flow ranging from (1) to (6 L/min), it’s obtained that the degradation efficiency of photocatalytic at flow rate (1 L/min) gives the highest removal about round (9.6%). If the rate of flow was (> 1 L/min), the efficiency of process would decrease since the pollutants residence time within the photocatalytic reactor reduced which possesses a passive influence on the rate of amoxicillin degradation.

![Figure 8](image)

Figure 8. Change in the amoxicillin elimination with different liquid flow rates (AMX = 5 mg/l, pH = 5 and TiO$_2$ = 600 mg/l).
3.5. Influence of initial concentration of amoxicillin
The influence of initial amoxicillin concentration on the elimination efficiency was studied via changing the concentrations of amoxicillin from (5 mg/L) to (10 mg/L). Fig. 9 shows that increasing amoxicillin concentration will lead to a reduction in the elimination efficiency. The increase in amoxicillin removal at low concentrations of amoxicillin and also decrease in high concentrations may be clarified by changes in the reaction rate control mechanism. The reaction rate curb at smaller concentration when the active sites on the photocatalyst surface are partially occupied by adsorbed molecules changes to the mass transfer limitation at high AMX concentration; the active sites on TiO₂ are occupied by amoxicillin molecules, then a new molecule cannot be adsorbed (Fatemeh and Touraj, 2016; Klauson et al., 2010).

![Graph showing the influence of initial amoxicillin concentration on elimination efficiency.]

**Figure 9.** Profile of Amoxicillin removal efficiency at 600 mg/L TiO₂, pH= 5 and flow rate 1 L/min

Depending upon the all above-mentioned results; it is found that the optimum concentration of catalyst, solution flow rate and pH for the highest elimination are (600 mg/L), (1 L/min) and (5), respectively.

Also, to evaluate the antibiotic removal due to adsorption of amoxicillin into surface of TiO₂, an experiment was carried out with 10 mg/L of amoxicillin at pH = 5 in the absence of UV radiation. The reduction of AMX after 5 hours was (2%).

4. CONCLUSIONS AND RECOMMENDATIONS
The TiO₂ was as a feasible solar photocatalyst for the removal of Amoxicillin, using a reactor to receive the solar irradiation. TiO₂ concentration 600 mg/L with 5 pH and 1 L/min flow rate can be regarded as the optimum working circumstances. Through such circumstances the removal efficiency of AMX was greater than 9%. Amoxicillin degradation is positively influenced by solar energy because the amoxicillin oxidation is in direct proportionality to no. of the light photons that absorbed via the solution. The low efficiency can be explained by that the tubular reactor is a non-concentrating type, in which the water moves within the transparent pipes.
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