University of Baghdad
College of Engineering
JOURNAL OF ENGINEERING

Journal of Engineering
journal homepage: www.joe.uobaghdad.edu.iq
Number 2 Volume 26 February 2020

Chemical, Petroleum and Environmental Engineering

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

Khairi R. Kalash *
Environment and Water Directorate, Ministry of Science and Technology
Baghdad, Iraq
Email:khairirs@yahoo.com

Mustafa H. Al-Furaiji
Environment and Water Directorate, Ministry of Science and Technology
Baghdad, Iraq
Email:alfuraiji79@gmail.com

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

الاكسدة المتقدمة للمياه الملوثة بالمضادات الحيوية باستخدام اوكسيد التيتانيوم في مفاعل التحفيز الضوئي الشمسي

الخلاصة

الهدف من هذه الدراسة هو امكانية ازالة المضادات الحيوية مثل الأموكسيسيلين في مياه صرف صيدلانية محضرة مختبريا باستخدام طريقة الاكسدة المتقدمة بوجود ثنائي أكسيد التيتانيوم (TiO_2) كعامل مساعد في مفاعل التحفيزالضوئي الشمسي. تم استخدام مفاعل أنبوبي كمنظومة مختبرية للمعالجة. تم تقييم كفاءة الإزالة في مفاعل التحفيز الضوئي الشمسي من خلال تحديد الانخفاض في قيم تركيز الأموكسيسيلين. وتم دراسة تأثير تركيز المضادات الحيوية وجرعة ثنائي أكسيد التيتانيوم TiO_2 والزمن اللازم للازالة وتأثير الدالة الحامضية, وكذلك تاثير معدل الجريان في المفاعل. تم الحصول على الظروف المثلى في هذه الدراسة وبزمن 5 ساعات وكانت جرعة المحفز 0.6 غم/لتر ومعدل الجريان 1 لتر/دقيقة والدالة الحامضية 5. يمكن الاستنتاج ان عملية المعالجة باستخدام التحفيز الضوئي لها القدرة على معدل ازالة للأموكسيسيلين في 5 ساعات بنسبة انخفاض مقدارها 10٪ بطاقة متراكمة مقدارها 141.8 كيلوجول/ لتر .

الكلمات الرئيسية : مياه صرف صناعية؛ اموكسيسيلين؛ تحفيز ضوئي؛ طاقة شمسية؛ ثاني اوكسيد التيتانيوم؛ اكسدة متقدمة.

---

*Corresponding author
Peer review under the responsibility of University of Baghdad.
https://doi.org/10.31026/j.eng.2020.02.01

Article received: 19/12/2018
Article accepted: 26/3/2019
Article published: 1/2/2020

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 $\mu g\ L^{-1}$, **(Watkinson et al., 2007**). The concentration of AMX in Iraq was reported as from 0.6 to 24.0 $\mu g\ L^{-1}$, **(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.

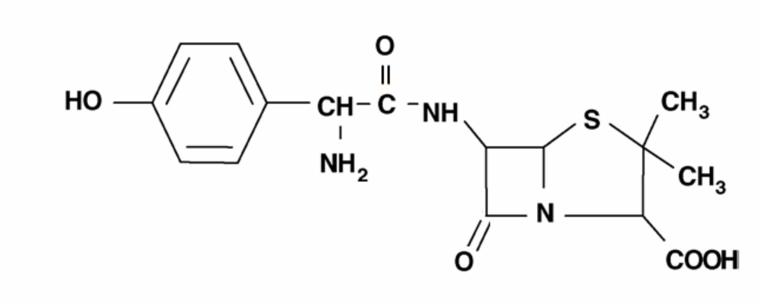

Figure1. Molecular structure of amoxicillin.

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, **(Banu et al., 2008)** and pharmaceutical industry, **(Klavarioti 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 ($C_{16}H_{19}N_3C_5S$) with a molecular weight of 365.4 g/mol was taken from Samarra Pharmaceutical State Company. Sodium hydroxide NaOH, Sulfuric acid H_2SO_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.

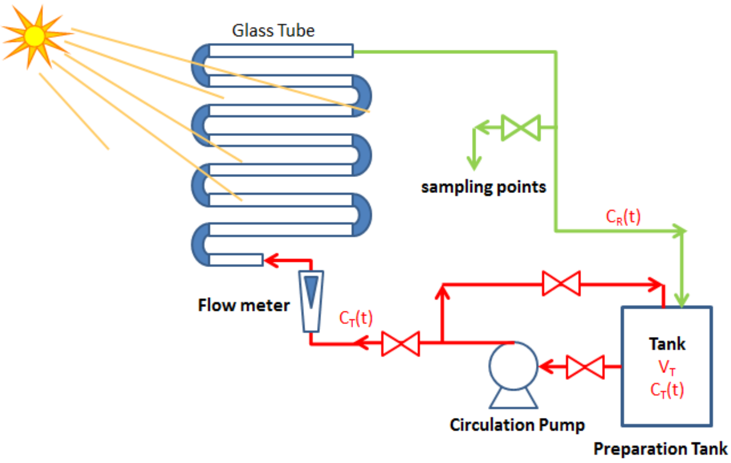

Figure 2. Schematic diagram of the solar photocatalytic reactor system concept.

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 TiO_2 (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/m^2); the mean solar irradiance for the whole experiments was (763 W/m^2) during the interval (8:30-1:30) local time, with a peak magnitude of (905 W/m^2) 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:

$$\text{Removal efficiency} = (C_{in} - C_{out} / C_{in}) * 100\% \qquad (1)$$

Where

Cin: inlet sample concentration (mg/liter),

Cout: 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)**.

$$Q_{UV_n} = Q_{\ UV_{n-1}} + \frac{\Delta t_n UV_{GN} A_{collector}}{V_{total}} \qquad (2)$$

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

Δt_n: The testing time of specimen

$A_{collector}$: The collector illuminated area (m^2/m^3) and obtained via Equation (3)

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

$$A_{collector} = \frac{A_r * E_s * t}{V_t * log \frac{C_i}{C_f}} \qquad (3)$$

where

A_r : actual reactor area (m^2)

t : irradiance time (h)

E_s : average solar irradiance (W/m^2)

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 ± 3ºC); 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 ± 3ºC); 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 ± 3ºC); 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 ± 3ºC); 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.

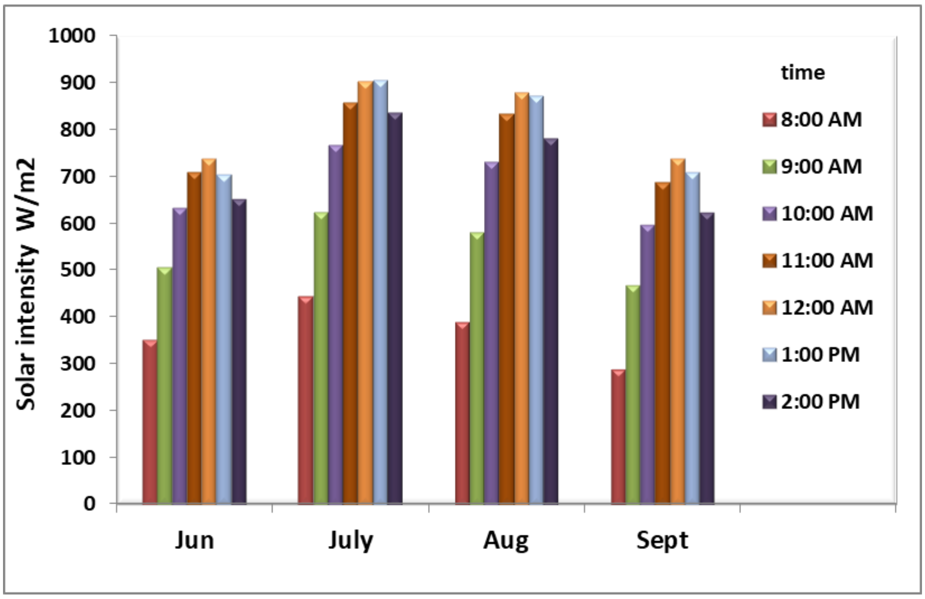

Figure 4. Change of the solar intensity with the experimental working time at various months (2018).

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)**.

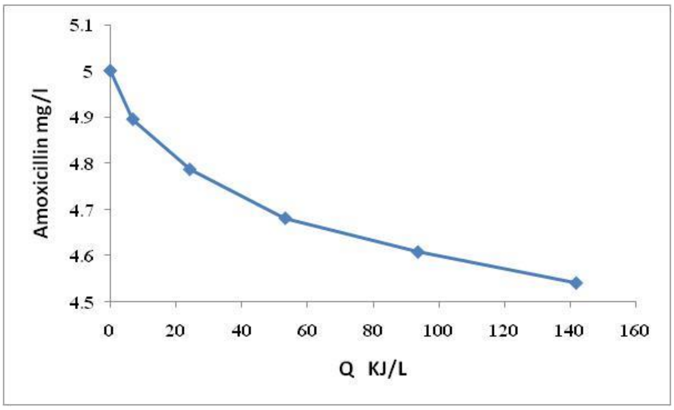

Figure 5. The change in amoxicillin concentration versus the gathered solar energy.

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).**

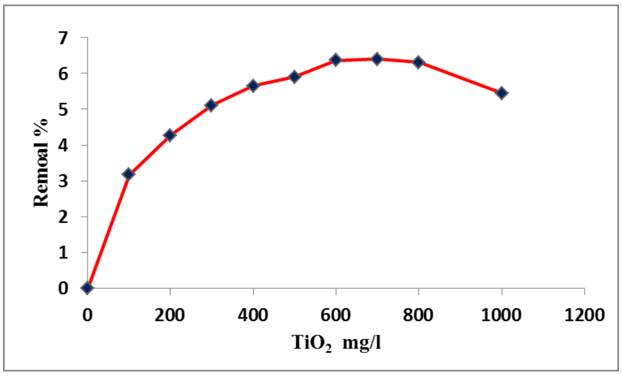

Figure 6. Removal profiles of AMX in the reactor at different concentrations of TiO_2 (AMX = 7.5 mg/l, pH = 5, Flow = 1 L/min).

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.

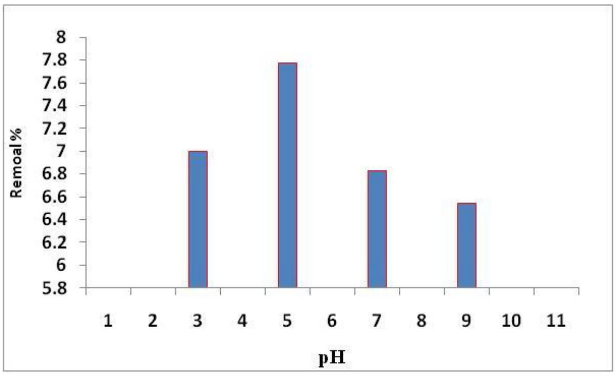

Figure 7. Effect of pH value on the amoxicillin removal (AMX = 7.5 mg/l, TiO_2 = 600 mg/l and Flow = 1 L/min).

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.

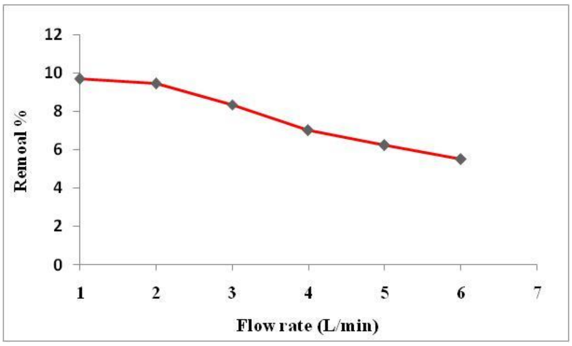

Figure 8. Change in the amoxicillin elimination with different liquid flow rates (AMX = 5 mg/l, pH = 5 and TiO_2 = 600 mg/l).

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 TiO_2 are occupied by amoxicillin molecules, then a new molecule cannot be adsorbed (**Fatemeh and Touraj, 2016; Klauson et al., 2010).**

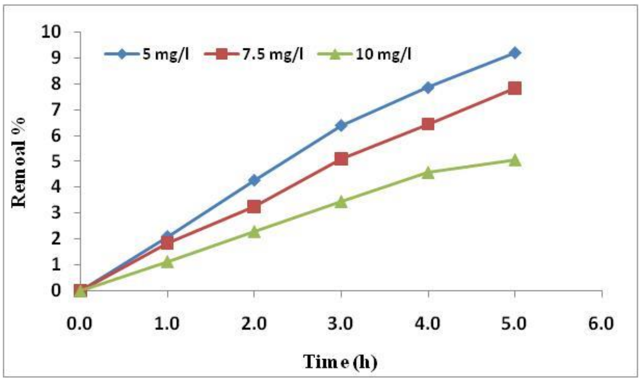

Figure 9. Profile of Amoxicillin removal efficiency at 600 mg/L TiO_2, pH= 5 and flow rate 1 L/min

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 TiO_2, 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 TiO_2 was as a feasible solar photocatalyst for the removal of Amoxicillin, using a reactor to receive the solar irradiation. TiO_2 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.

5. REFERENCES

- Agullo B., M.; Polo-Lopez, M.; Lucena, F.; Jofre, J. and Fernandez-Ibanez, P., 2013, *Solar advanced oxidation processes as disinfection tertiary treatments for real wastewater: Implications for water reclamation.* Applied Catalysis. B: Environmental, 136, 341–350.

- Alrousan D.; Polo-Lopez, M.; Dunlop, P.; Fernandez-Ibanez, P. and Byrne, J., 2012, *Solar photocatalytic disinfection of water with immobilised titanium dioxide in re-circulating flow CPC reactors.* Applied Catalysis. B: Environmental, 128, 126–134.

- Anderson P. D., D’Aco V. J., Shanahan P., Chapra S. C., Buzby M. E., Cunningham, B. M. Duplessie V. L., Hayes E. P., Mastracco F. J., Parke N. J., Rader J. C., Samuelian J. H. and Schwab B.W., 2004, *Screening analysis of human pharmaceutical compounds in US surface waters*, Environmental Science Technology, 38(3), 838–859.

- Augugliaro, V.; Gracia-Lopez, E.; Loddo, V.; Malato, S.; Maldonado, I.; Marci, G.; Molinari, R. and Palmisano, L., 2005, *Degradation of lincomycin in aqueous medium: Coupling of solar photocatalysis and membrane separation*. Solar Energy, 79, 402–408.

- Bahnemann D., Bockelmann, D., and Goslich, R., 1991, *Mechanistic Studies of Water Detoxification in Illuminated TiO_2 Suspensions,* Solar Energy Materials, 24(2), 564-583.

- Banu, J.; Anandan, S.; Kaliappan, S. and Yeom, I., 2008, *Treatment of dairy wastewater using anaerobic and solar photocatalytic methods.* Solar Energy, 82, 812–819.

- Castiglioni S., Fanelli R., Calamari D et al., 2004, *Methodological approaches for studying pharmaceuticals in the environment by comparing predicted and measured concentrations in River Po, Italy.* Regulatory Toxicology and Pharmacology, 39, 25–32.

- Chatterjee, J.; Rai, N. and Sar, S. K., 2014, *Kinetic Isotherm of Amoxicillin Antibiotic through Adsorption and its Removal by Electrocoagulation.* Chemical, 30(5), 55-68.

- Colina-Marquez, J., Machuca-Martínez, F., and Li Puma, G., 2015, *Modeling the Photocatalytic Mineralization in Water of Commercial Formulation of Estrogens 17- β Estradiol (E2) and Nomegestrol Acetate in Contraceptive Pills in a Solar Powered Compound Parabolic Collector.,* Molecules, 20(7), 13354–13373.

- Deegan A. M.; Shaik1B.; Nolan K.; Urell K.; Oelgemöller M.; Tobin J. and Morrissey A., 2006, *Treatment options for wastewater effluents from pharmaceutical companies* J. Environmental Science Technology, 8 (3), 649-666.

- Dominguez E., R.; Silva-Martinez, S.; Ortiz-Hernandez, M.; Roman-Zubillaga, J.; Guardian-Tapia, 2013, *Disinfection of municipal wastewater using TiO_2 film and Ag/TiO_2 powder under UV and solar light irradiation*. Marine Science: Research, 2(1), 60–68.

- Fatemeh S. and Touraj T., 2016, *Amoxicillin degradation from contaminated water by solar photocatalysis using response surface methodology (RSM)*, Environmental Science and Pollution Research, 23(22), 23262–23270.

- Gaya, U.; Abdullah, A., 2008, *Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress, and problems.* Photochemical Photobiology, 9 (1), 1-12.

- Gomathi D., L., and Mohan Reddy, K., 2010, *Enhanced photocatalytic activity of silver metalized TiO2 particles in the degradation of an azo dye methyl orange: Characterization and activity at different pH values*. Applied Surface Science, 256(7), 3116–3121.

- Goswami D., 1997, *A review of engineering developments of aqueous phase solar photocatalytic detoxification and disinfection processes.* Solar Energy Engineering Transactions of the ASME 119, 101-107.

- Gozlan I., Rotstein A. and Avisar D., 2010, *Investigation of an amoxicillin oxidative degradation product formed under controlled environmental conditions*. Environmental Chemical, 7, 435–442.

- Heberer, Th., Du nnbier, U., Reilich, Ch., Stan, H.J., 1997, *Detection of drugs and drug metabolites in groundwater samples of a drinking water treatment plant*. Fresenius Environmental Bulletin, 6, 438–443.

- Hoffmann M. R., Martin S. T., Choi W., and Bahnemann D. W., 1995, *Environmental applications of semiconductor photocatalysis*, Chemical Reviews, 95, 69–96.

- Homem V and Santos L., 2011, *Degradation and removal methods of antibiotics from aqueous matrices–a review*. Environmental Manage. 92(2):2304–2347.

- Javad S. and Fatemeh S., 2012, *Organic Pollutants Removal from Petroleum Refinery Wastewater with Nanotitania Photocatalyst and UV Light Emission*, International of Photoenergy, 55, 1-5.

- Joa H.O.S. Pereira, Ana C. Reis, Vera Homem, Jos'e A. Silva, Arminda Alves, Maria T. Borges, Rui A.R. Boaventura, Vı´tor J.P. Vilar, Olga C. Nunes,2014, *Solar photocatalytic oxidation of recalcitrant natural metabolic by-products of amoxicillin biodegradation.* Water Research, 65(15), 307-320.

- Klauson, D.; Babkina, J.; Stepanova, K.; Krichevskaya, M.; Prei, S., 2010, Aqueous photocatalytic oxidation of amoxicillin. Catalysis Today, 151, 39–45.

- Klavarioti, M.; Mantzavinos, D. and Kassinos, D., 2009, *Removal of residual pharamceuticals from aqueous systemsby advanced oxidation processes*. Environmental. International, 35, 402–417.

- Kostich MS, Batt AL, Lazorchak JM, 2014, *Concentrations of prioritized pharmaceuticals in effluents from 50 large wastewater treatment plants in the US and implications for risk estimation*. Environmental Pollution, 184,354–359.

- Luo, Y.; Guo, W.; Ngo, H. H.; Nghiem, L. D.; Hai, F. I.; Zhang, J.; Liang, S. and Wang, X. C., 2014, *A review on the occurrence of micro pollutants in the aquatic environment and their fate and removal during wastewater treatment*. Science of the Total Environment, 473(4), 619–641.

- Murgolo S., Petronella F., Ciannarella R., Comparelli R., Agostiano A., Curri M. L. and Mascolo G., 2014, *UV and solar-based photocatalytic degradation of organic pollutants by Nano-sized TiO_2 grown on carbon nanotubes*", Catalysis Today, 240, 114–124.

- Omar A. Al-Khazrajy & Alistair B. A., 2016, *Box all Risk-based prioritization of pharmaceuticals in the natural environment in Iraq*. Environmental Science Pollution Research, 23, 15712–15726.

- Ortiz, S.; García, D.; Pinto, G.; García, P. and Irusta, R., 2013, *Consumption and occurrence of pharmaceutical and personal care products in the aquatic environment in Spain.* Science Total Environmental, 444(1), 451–465.

- Papageorgiou, M.; Kosma, C. and Lambropoulou, D., 2016, *Seasonal occurrence, removal, mass loading and environmental risk assessment of 55 pharmaceuticals and personal care products in a municipal wastewater treatment plant in Central Greece*. Science Total Environmental, 543(7), 547–569.

- Putschew A., Wischnack S. and Jekel M., 2000, *Occurrence of triiodinated X-ray contrast agents in the aquatic environment*, Science Total Environmental, 255(12), 129–134.

- Sacher F., Lange F. T., Brauch H. J., and Blankenhorn I., 2001, *Pharmaceuticals in groundwaters analytical methods and results of a monitoring program in Baden-Württemberg, Germany*, Chromatography, 938(4), 199–210.

- Saien J., Delavari H., and Solymani A. R., 2010, *Sono-assisted photocatalytic degradation of styrene-acrylic acid copolymer in aqueous media with nano-titania particles and kinetic studies*, Hazardous Materials, 177, 1031–1038.

- Seck, E.; Dona-Rodriguez, J.; Fernandez-Rodriguez, C.; Portillo-Carrizo, D.; Hernandez-Rodriguez, M.; Gonzalez-Diaz, O. and Perez-Pena, J., 2013, *Solar photocatalytic removal of herbicides from real wastewater by using sol-gel synthesized nano crystalline TiO_2: Operational parameters optimization and toxicity studies.* Solar Energy, 87(8), 150–157.

- Suvarna G. L. and Chandana M.V.V., 2016, *Removal of Organic Pollutants from the Pharmaceutical Effluent by Tio2 Based Photocatalysis.* International Journal of Innovative Research in Science, Engineering and Technology,5(8), 15831.

- Ternes T. A., 1998, *Occurrence of drugs in German sewage treatment plants and rivers*, Water Research, 32 (7), 3245–3260.

- Torbina, V.; Vodyankin, A.; Ivanchikova, I.; Kholdeeva, O. and Vodyankina, O., 2015, *Support pretreatment effect on the catalytic properties and reusability of silica-supported Titania catalysts in 2, 3, 6-Trimethylphenoloxidation with Hydrogen peroxide*. Kinetics and Catalysis, 56, 369–374.

- Watkinson AJ, Murby EJ, Costanzo SD., 2007, *Removalofantibiotics in conventional and advanced wastewater treatment: implications for environmental discharge and wastewater recycling*. Water Research, 41, 4164–4176.