Removal of Pharmaceuticals from Synthetic Wastewater by Ozone

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Abstract: -

The removal of the pharmaceuticals from wastewater was investigated in the present study. The degradation of 17α-ethinylestradiol(ETH) (hormone), diclofenac (DIC)(anti-inflammatory) and carbamazepine (CARB)(antiepileptic) by an advanced oxidation process (AOPs) based on ozone was studied at lab-scale in synthetic wastewater.

Pharmaceuticals have been detected at trace concentrations in the range of high ng/l or low µg/l in all influent and effluent real wastewater treatment plants which at this concentration pharmaceuticals can cause potentially adverse health effects.

The effects of operating conditions such as pH and O_3 concentration, on the degradation process were studied. The maximum degradation of pharmaceuticals dissolved in demineralized water was achieved at high pH (12) and (9 mg/l) O_3 concentration.

The effectiveness of O_3 process for treating pharmaceuticals in synthetic wastewater showed that the maximum removal of all pharmaceuticals (CARB, DIC and ETH) respectively was approximately (75.54, 77.23 and 80.68) % at O_3 concentration of 9 mg/l. A good correlations between pharmaceuticals removal and UV_{254} removal was obtained (R^2=0.9519). Also fluorescence data could be well correlated to pharmaceuticals removal with (R^2=0.9416).

Keywords: O_3; Advanced oxidation process; pharmaceuticals wastewater; GC-MS; UV-VIS; Fluorescence ;Excitation Emission Matrix.

1. Introduction

A new class of environment organic micropollutants is considered as Pharmaceuticals because of the negative influence they may have on ecosystems. Unexpected effects in

non-mammalian organisms is coming from pharmaceuticals which may lead to distribute of reproductive and hormone systems immune depression and neurobehavioral changes and also the development of resistance bacteria strains.[1]

Special attention should be given to pharmaceuticals in the aquatic environment. pharmaceuticals are trace compounds occurring at concentrations ranging from µg/l to ng/l in effluent real wastewater treatment plants, groundwater, and surface water [2], which at this concentration pharmaceuticals can cause potentially adverse health effects[3] .

Pharmaceuticals are compounds group which consist pharmaceuticals drugs, ingredients, food supplements, personal care products, and also metabolites and transformation products. Pharmaceuticals released into the environment, wastewater effluents, landfill leachate, hospitals and agriculture are the most important sources of pharmaceuticals in the environment [4],[5].

Pharmaceuticals can be classified to (analgesic, antibiotic, antiepileptic, anti-inflammatory, beta blockers, oral contraceptive) drugs, blood lipid regulators and sun screen and others[6].

For treating organic pollutants in aqueous solution the techniques available are very divers and more treatment techniques are required to degrade micropollutants. Depending on the target compound, and also on different destructive and non-destructive methods that allow the best elimination of the micro-pollutant from wastewater can be chosen, such as chemical oxidation, incineration liquid extraction, absorption and membrane process. Basically, the choice of either one of these methods depends on the cost of the process and other factors such as concentrations and volume flows of the effluent to be treated. There is a group of chemical oxidative process called advanced oxidation processes (AOPs) characterized by the generation of hydroxyl radicals. The hydroxyl radicals is the strongest known oxidant, therefore it is possible to oxidize and mineralize almost every organic molecule into CO_2 and inorganic ions[1].

A large number of organic compounds showing a high reactivity with Ozone because Ozone is an

oxidizing agent. Free hydroxyl radicals are produced due to decomposed ozone in water, hydroxyl radicals are more powerful oxidants agents than direct ozone, direct ozone can reacts selectively with certain functional groups [7]

Some authors from previous studies show that the best processes for pharmaceutical abatement from effluents can be proposed as ozonation among other different methods and also other studies demonstrated that ozone can attack pharmaceutical species which belong to different therapeutic classes [8].

In this study the degradation of pharmaceuticals using the AOP with ozone in synthetic wastewater was studied. Several parameters such as pH and O_3 concentration were investigated.

2. Materials and Methods

Ozone (O_3) was generated through using high purity oxygen by a corona discharge ozone generator (Ozomat COM-AD-02, Anseros-Germany).

Dichloromethane CH_2Cl_2 with purity > 99.8% was purchased from Carl Roth. All chemicals could be used with no any further purification. For pH adjustment, NaOH and Sodium phosphate buffer (PB) were used[9][8][7]. **Error! Reference source not found.** gives a summary of the applied pharmaceuticals used in this work (all pharmaceuticals were taken from Sigma Aldrich®.

Table .1 Summary of pharmaceuticals.

Name Chemical	Formula	Purity
(CARB)	$C_{15}H_{12}N_2O$	99 %
(ETH)	$C_{20}H_{24}O_2$	99.8%
(DIC)	$C_{14}H_{10}C_{l2}NO_2$	99.8%

Saturated Solutions (10.3, 17.7 and 11.3) for three pharmaceuticals (CARB, ETH and DIC) respectively of different normality were prepared by adding the amount of powdered pharmaceuticals in one liter of deionized water, after added of pharmaceuticals to distilled water the pharmaceuticals will not dissolve due to the low water solubility . The stock solution of 1 mg /l was prepared by diluting the saturated solution of each pharmaceuticals after that the solutions were stirred thoroughly with a magnetic stirrer for

a minimum 3 hours, until a well-mixed solution was achieved. Finally, saturated solution were filtered with filtration paper (Rotilabo cellulose type 601) [10]. In this study, the stock solutions were further diluted to100 µg/l [10].

Finally, the removal efficiency of pharmaceuticals was calculated by using GC-MS while the surrogate parameters were done using the data of UV-VIS and fluorescence spectra.

3. Experimental procedure

The experiment was done in a circulating reactor system. The system consists of a 1l quartz glass reactor with a diameter of 80 mm and height of 160 mm which contained 1l of sample. This sample was continuously circulated with a peristaltic pump (Master Flex model 7518-00, Cole-Parmer Instrument) with a flow rate of 0.8 l/min. The reactor was connected to a flexible teflon tubing and all fittings and tubings were made of teflon as shown in **Fig. 1** Buffering the sample with sodium phosphate buffer (PB) was adjusted to pH 7.5 and for pH 12 by the drop-wise addition of NaOH.

Various concentrations of O_3 were added to the reactor at the start of every experiment

Each Experiment lasted for approximately 60 min and samples were taken every 10 minutes. All experiments were done at room temperature (20°C) and in duplicate.

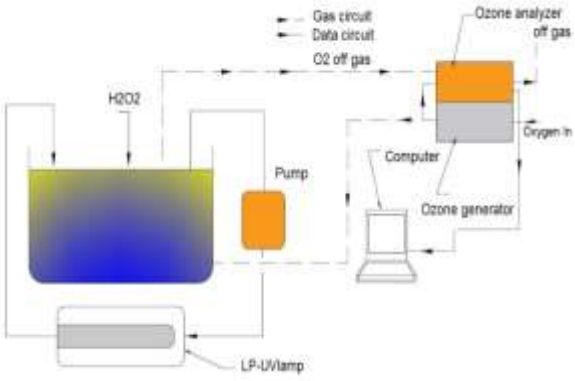

Fig. 1. Schematic of the reactor used for O_3 experiments

4. Results and Discussion

4.1 Effect of pH

The influence of pH on the removal efficiency of pharmaceuticals (CARB, ETH and DIC) at different pH values (4, 7.5, and 12) at room temperature was investigated. A dose of 9 mg/l O_3 was applied due to high removal at this dosage occurred as shown in **Fig. 2.**

As shown in **Fig. 2** the removal efficiency in basic pH is higher than

that in acidic and neutral pH, this can be related to that when pH is low (OH° is scarce), the depletion reaction is slow thus allowing for accumulation of dissolved O_3 to a high level, whereas when pH decrease (OH° is abundant), the depletion reaction is rapid thus prohibiting dissolved O_3 to accumulate [11]

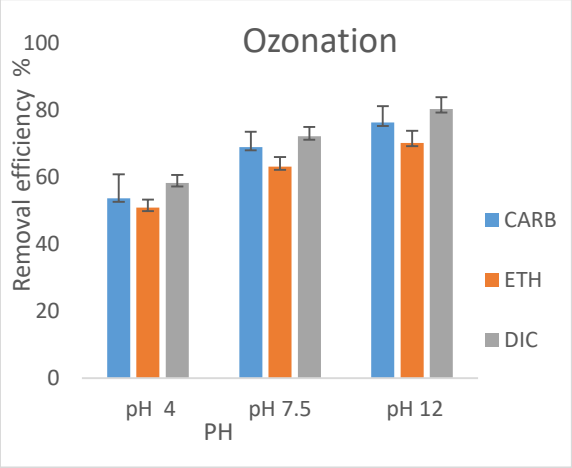

Fig. 2 Effect of pH on the three pharmaceuticals degradation efficiency, (O_3 9 mg/ l and T 20 ° C).

Fig. 2 shows that the removal efficiencies of three pharmaceuticals at pH (4-7.5 and 12) were (53.69, 69.02, 76.32) %, (50.92, 63.19, 70.26) % and (58.25, 72.23, 80.32) % for (CARB, ETH and DIC) respectively. The results show a good reactivity of three pharmaceuticals toward ozonation, and also the difference in the removal between the pharmaceuticals is due to differences in structural , DIC contains an amino group ,CARB has a double bond and ETH contain an aniline entity, with these structure elements all compounds can react quickly with ozone, these result agreed with (Shaherstani et al., 2016 and Chys et al.,2012) [11] [12][13].

Figure 3 shows the changing in pH with time, the figure shows that pH rapidly decreases with increasing reaction time from (12, 7.5, 4) to (10.1, 6.1 and 3.1) at time 60 min respectively, this is due to that the treatment by ozonation leads to the formation of acidic byproducts [14] [9].

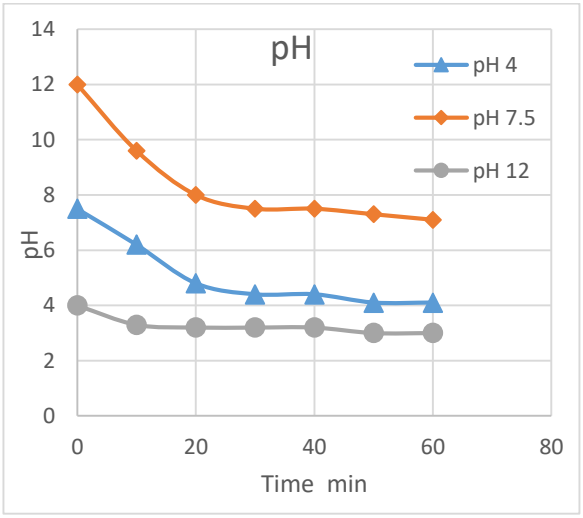

Fig. 3 Changing in pH of pharmaceuticals during O_3 process.

4.2 Effect of O_3 concentration

The effect of O_3 dosages (4.5, 7 and 9) mg/l on three pharmaceuticals degradation within 60 min with pH 12 at room temperature is shown in **Fig. 4** For initial pharmaceuticals concentration of 100µg/l. **Fig. 3** illustrates that at low concentrations of ozone 4.5 mg/l the best removal efficiency was (53.19%) whereas at 7 mg/l was equal to (68.32%) and at 9 mg/l was (80.68%). The best removal efficiency was at 9 mg/l where maximum pharmaceuticals removal is seen.

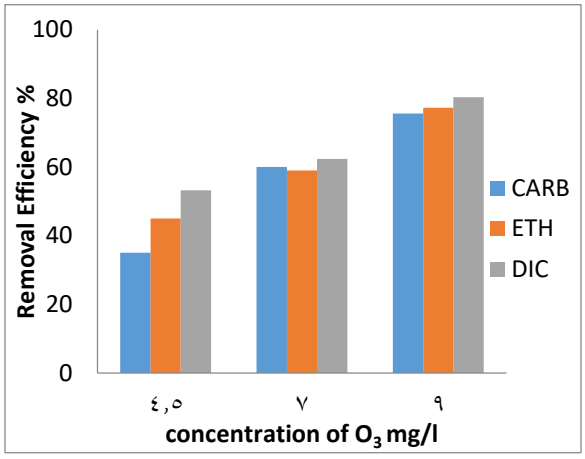

Fig. 4 Effect of O_3 dosages on the three pharmaceuticals degradation (initial concentration) 100 µg/l ,pH = 12 and t=60min

4.3 Spectral measurements

Before the treatment the absorbance of at 254 nm was 1.004 cm^{-1} , after treatment the absorbance showed a decrease in the wavelength of 254 nm, corresponding to the absorbance value was (0.562, 0.361 and 0.421) cm^{-1} for CARB, ETH and DIC respectively. The wavelength of 254 nm is a quality parameter directly referred to exist of aromatic and unsaturated structures compounds [14].The absorbance of three pharmaceuticals shows that small difference between them and the absorbance decreased after treatment. The ΔUV_{254} (difference in absorbance before and after treatment) at wave length of 254nm was measured for the three pharmaceuticals. The result of the Δ UV $_{254}$ of pharmaceuticals were (44.02, 64.04 and 58.06) % for the (CARB, ETH and DIC) respectively.

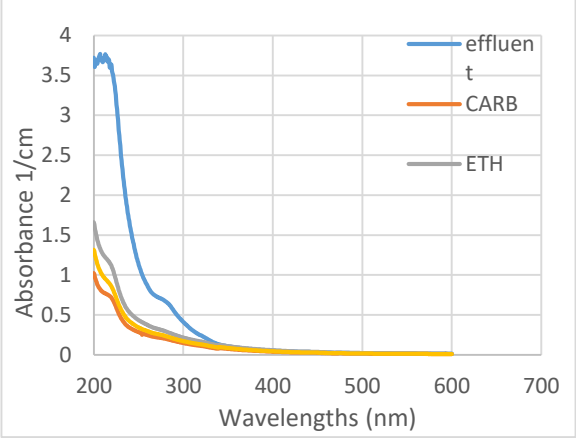

Fig. 5 Comparison of different absorbance of pharmaceuticals (100 µg/L)

4.4 Excitation-Emission Matrix Analysis (EEM)

Excitation-emission matrix of fluorescence (EEM) analysis is an additional analytical method used for the characterization of organic matter in wastewater . In synthetic water, the fluorescence was characterized by three different peaks at different EX-EM wavelength as shown in Figure 6.

The first maximum fluorescence was observed at 340 nm for the wavelength of excitation and 420 nm for the wavelength of emission (λex =340 nm; λem =420 nm) while the second maximum fluorescence peaks was observed at 250 nm for the wavelength of excitation and 420 nm for the wavelength of emission (λex =250 nm; λem =420 nm) and the third peaks at 300 nm for the wavelength of excitation and 320nm for the wavelength of emission (λex =300 nm; λem =320 nm), so the synthetic wastewater contained (microbel, protein and humic substance) fluorescence [15]. As shown in **Fig. 6**, the recorded fluorescence spectra (EEMs) for pharmaceuticals treated O_3 showed an overall intensity decrease after treatment, these results are in agreement with studies conducted previously.

The peak height of effluent wastewater was 4.5RU which had decreased after treatment to 1.244, 1.8 and 0.35 RU for the (CARB, ETH and DIC) respectively. The delta peak height had a maximum decrease 72.35, 59.5 and 92% for the (CARB, ETH and DIC) respectively.

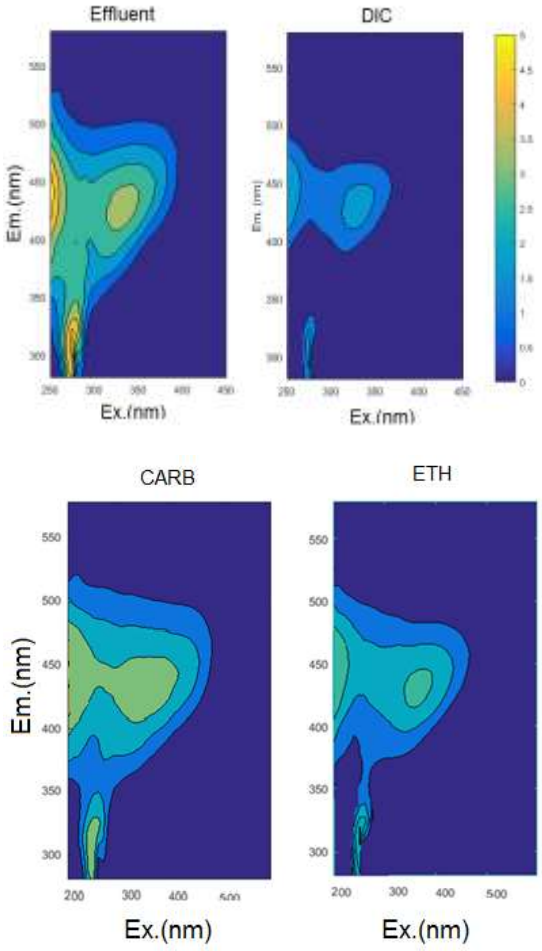

Fig. 6 EEM (Excitation Emission Matrix) of synthetic water before and

after treatment for CARB, ETH and DIC.

4.5 Surrogate analysis

Comparing both the decrease (in percentage) of UV $_{254}$ and peak height, good correlations with pharmaceuticals removal were obtained **Fig. 7** For UV_{254} a maximum decrease of 78.06 % is reached and a linear correlations (R^2=0.9519) is obtained. For peak height has a maximum decrease of 92% is reached and a linear correlations (R^2=0.9416) is obtained. The larger decrease of peak height compared to UV_{254} with the same O_3 dosage, can indicate towards the fact that peak height gives a broader range in which pharmaceuticals removal can be measured.

From previous studies, it can be demonstrated that fluorescence spectroscopy had stronger correlation with DOC removal (R^2 = 0.91) thus fluorescence spectroscopy can be a more robust quantitative method for the assessing organic material changes in drinking water systems[16] , other studies showed that reduction in UV_{254} was strongly correlated to the production of OH° for different wastewater samples by UV/ H_2O_2 [17].

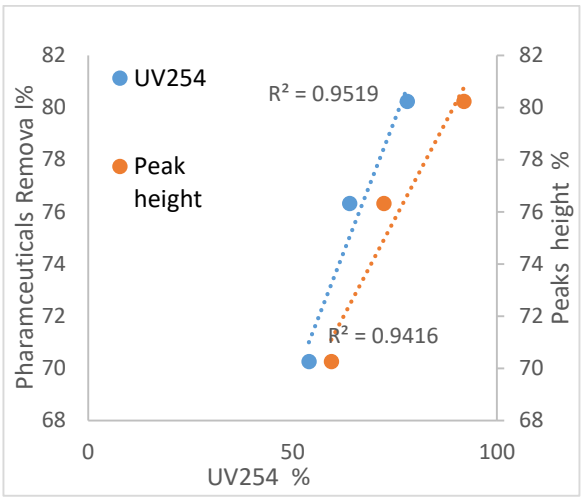

Fig. 7 Correlation between pharmaceuticals removal with ΔUV$_{254}$ and Δ peaks height.

5. Conclusions

The removal efficiency of 3 pharmaceuticals (CARB, ETH and DIC) by O_3 in synthetic wastewater was examined in this study. It was found that it is important to get the best the conditions in synthetic wastewater to give high removal efficiency, such as the concentration of ozone, since too low concentration of ozone results in decreasing the removal efficiency of pharmaceutical, while a high ozone concentration may result in increasing degradation.

Furthermore, the maximum removal efficiency of pharmaceuticals, was achieved at higher pH 12 and decreasing trend of degradation at lower pH.

Furthermore, the removal of the three pharmaceuticals was strongly correlated to the reduction of UV-VIS and fluorescence signals so the measurements of UV-VIS and fluorescence show a great beneficial for control of pharmaceuticals.

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إزالة المستحضرات الصيدلانية من المياه الصناعية بواسطة الأوزون

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الخلاصة:
بحثت هذه الدراسة في إزالة المستحضرات الصيدلانية.من المياه الصناعيه . وقد تم دراسة تحلل 17-αإثينيليستراديول (هرمون)، ديكلوفيناك (مضاد للالتهابات) و كاربامازيبين (مضاد الصرع) بواسطة عملية الأكسدة المتقدمة باستخدام الأوزون في المختبر للمياه الصناعية.
تمت دراسة تأثيرات ظروف التشغيل مثل تركيز الرقم الهيدروجيني وتركيز O_3 على عمليه التحلل .وتم تحقيق الحد الأقصى من انحلال المستحضرات الصيدلانية المذابة في الماء المعدني عند تركيز عالي بدرجة الحموضة (12) وتركيز O_3 يساوي 9 ملغم / لتر.
وأظهرت فعالية عملية O_3 في معالجة المستحضرات الصيدلانية في المياه الصناعية حيث أن التحلل الأقصى لجميع المستحضرات الصيدلانية كان حوالي 68.32٪ عند تركيز O_3 7 ملغم / لتر، بينما أدى تركيز (9) ملغم / لتر إلى إزالة أكثر من 80.68٪.
من ناحيه اخرى فان الامتصاصية (UV_{254}) قد انخفضت من المياه الصناعية مع زيادة O_3 . وتم استخدام التغير في الأشعة فوق البنفسجية وتحليل الاطياف الضوئيه لقياس التغيرات في خصائص المواد العضوية أثناء الأكسدة.
تم الحصول على علاقه جيدة بين إزالة المستحضرات الصيدلانية وإزالة UV_{254} ($R^2 = 0.9519$) وأن انخفاض في ارتفاع الاطياف الضوئيه تكون علاقه جيده لإزالة المستحضرات الصيدلانية ($R^2 = 0.9416$) .