

## DEGRADATION OF ENDOCRINE DISRUPTING COMPOUNDS BY OZONE IN SYNTHETIC WATER

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### Abstract

In this research paper, ozone technology is used to eliminate pollutants in water and in wastewater treatment processes. The ozone reactions with the endocrine disrupters were studied at different gas flow rates, initial concentrations of endocrine disrupters, ozone concentrations and pH. The degradation of 17 $\beta$ -estradiol (E2) as single compound was the fastest reaching about 90% removal in almost 5 minutes. However, estrone (E1) degradation was the lowest reaching about 70% removal at the same time. The degradation of mixtures of the endocrine disruptors was found to proceed to lower percentages than individual components at the same conditions. During the multicomponent ozonation of the endocrine disruptors, it was found that 17 $\beta$ -estradiol (E2) converted to estrone (E1) at the beginning of the reaction.

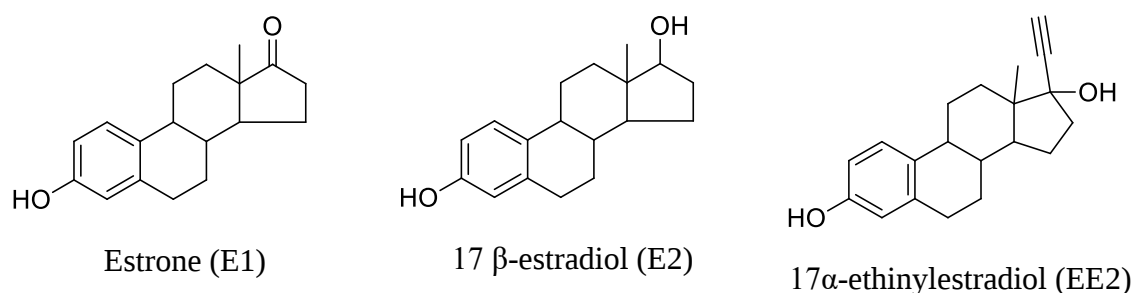
**Keywords:** Endocrine disrupters; Ozonation; Degradation; Synthetic water.

### Introduction

#### Endocrine Disrupting Chemicals

Environmental chemistry has recently brought increasing attention to anthropogenic substances present in the environment, one such group being endocrine disrupting compounds (EDCs). These may be in the form of pharmaceuticals, surfactants, plasticizers pesticides, industrial compounds or even hormones excreted into wastewater by humans. EDCs exposure could negatively affect growth and development and it is a potential cause or an accelerator of diseases such as cancer. Treated wastewater, surface water and groundwater are the most significant exposure pathways. EDCs may be partly removed during wastewater treatment processes. The remaining amount is discharged with the effluent consequently natural water bodies are contaminated. Animal waste is another suspected source of small quantities of EDCs in the environment. There is therefore growing concern that EDC exposure may have an adverse impact on human and environmental health and there is a need to understand and take appropriate measures to reduce EDC levels in the environment. Surfactants, plasticizers, and hormones have been found to be more widespread in environments and in higher concentrations compared to other EDCs. Steroidal estrogen hormones, such as estrone (E1),

17 $\beta$ -estradiol (E2), and 17 $\alpha$ -ethinylestradiol (EE2), excreted into wastewater form a large portion of the estrogens persistent in wastewater. Steroidal estrogens are one of the most important EDC groups in the area of risks to humans and the environment (Ning et al., 2007). In this work the three EDCs E1, E2, and EE2 were used to study the ozonation of a multicomponent mixture reacting fast with ozone (Ben Fredj et al. 2015). Figure (1) shows the structures of these EDCs.



**Figure (1): Structures of E1, E2 and EE2.**

### Advanced Oxidation Processes

Advanced oxidation processes (AOPs) have been defined as processes which involve the generation of hydroxyl radicals or other highly reactive radical species, to oxidize many organic compounds (Pedit et al., 1997 and Tizaoui 2018). In advanced oxidation processes, a set of designed chemical treatment procedures are used to remove organic and inorganic materials in wastewater by oxidation. Three different reagents may be used in the oxidation process: hydrogen peroxide, ozone and ultraviolet (UV) irradiation in specific and accurately pre-programmed dosages, sequences, and combinations. Specific catalysts may also be used in combination with these procedures. AOPs have been studied by several researches (Feng et al., 2005; Lau et al., 2007; Irmak et al., 2005; Yue, 1992; Nakonechny et al., 2008; Beltran, 2004; Gottschalk et al., 2000; Langlais et al., 1991; and Crittenden et al., 2005). Ozone is widely used in Europe, Asia, Japan and United States and was first incorporated in the water treatment process in the late 1800s. Ozone is a colorless, unstable gas with similar odour to air after a major thunderstorm. It comprises of three oxygen atoms and readily converts back to oxygen. During the conversion a free oxygen atom, or free radical is formed. The free oxygen radical has high reactivity, is short lived and survives for only a fraction of a second under normal conditions. The rate of degradation of ozone is a function of pH, water chemistry and temperature, with degradation time ranging from a few seconds up to 30 minutes. Compared to chlorination, ozone is more effective in disinfection for the inactivation of bacteria and viruses in water (Tizaoui, 2018). In addition, the oxidation process can lead to reductions in the concentration of iron, manganese and sulfur and also reduces or eliminates existing problems related to taste and odor. Ozone oxidizes iron, manganese, and sulfur in the water to

form insoluble metal oxides or elemental sulfur; the oxides of which are removed by filtration (Langlais et al., 1991).

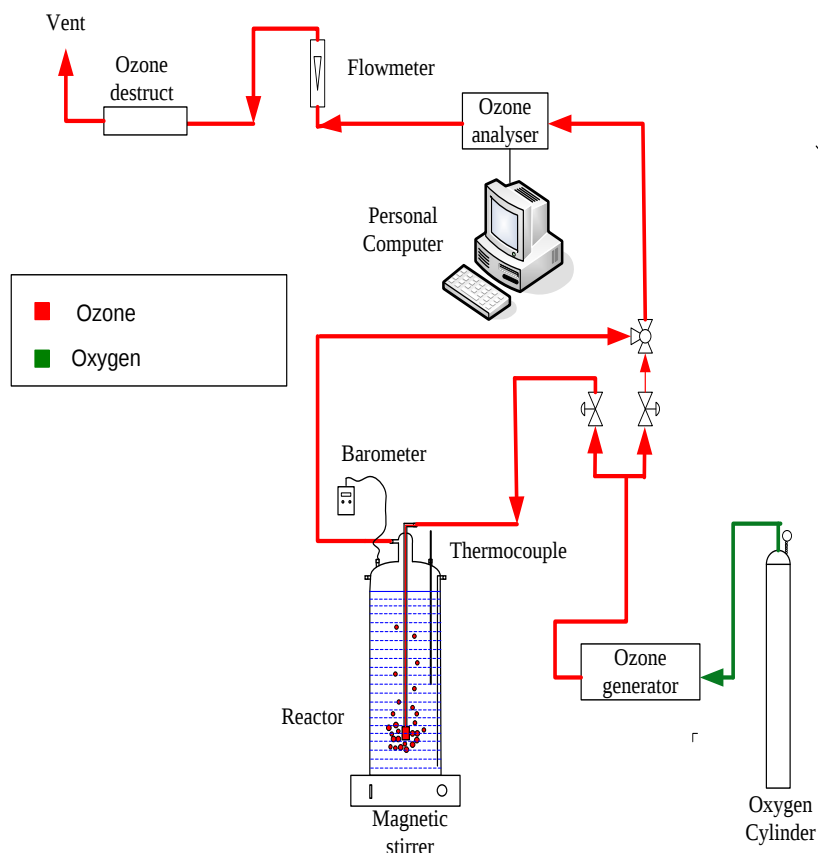
## **Materials and Methods**

### **Materials**

Cylinders of compressed gas of pure oxygen (>99%) and nitrogen were purchased from British oxygen company (BOC) and used in the experiments. Polytetrafluoroethylene (PTFE) tube of OD 3.18 mm × ID 1.6 mm (1/18"×1/16") was used for connecting the system. A fritted glass diffuser (Grade 0) was used to disperse the gas into the aqueous solutions. The ozone reactor was made of a glass bubble column having total volume of 800 mL but only 500 mL and 150 mL of the volume was used in this study as shown Figure (2). Thermocouple was fitted to the reactor for the purpose of measuring the solution temperature. A manometer model R200 UL (Digitron, England) was used for measuring gas pressure. General laboratory glassware was used. Chemicals utilized in this research work included HPLC-grade acetonitrile (99%), formic acid, obtained from Sigma Aldrich as well as endocrine disruptor chemicals (estrone (E1), 17β-estradiol (E2), and 17α-ethinylestradiol (EE2)) also purchased from Sigma Aldrich. All solutions were prepared with deionised water. pH 7 was controlled by the addition of sodium hydroxide and phosphoric acid while pH2 was adjusted by the addition of phosphoric acid. These experiments were performed in Britain at the University of Bradford in the School of Engineering.

### **Experimental Setup**

The endocrine disruptors such as E2, EE2, and E1 are immiscible compounds in water. All stock solutions were prepared in methanol initially at 1 g/L concentrations which have been kept in the freezer. Solutions at desired concentration were prepared by diluting a given volume of the stock solution with deionised water. The concentrations of each endocrine disrupters components (EDCs) sample used in this study were 25, 15, and 5 mg/L. The ozonation experiments for EDCs were carried out in the system described Figure (2). The experiments were carried out at different concentrations 25, 15, and 5 (mg/L) for E2, EE2, and E1 each, either individual or mixed together using different ozone concentration 10, 30, 60 g/m<sup>3</sup> normal temperature and pressure (NTP). The pH of the solutions were either pH 2 or 7 and the gas flow rate was fixed at 200 mL/min. Water sampling with a syringe (glass) was carried out manually at different time intervals. The content of the syringe was quickly transferred to the initially prepared vials containing a volume of 0.005 mol/L sodium thiosulfate solution to quench the aqueous ozone remaining in the solution and thus stopping the reaction before analyzing for EDCs concentration with HPLC.



**Figure (2): Schematic for Experimental Setup.**

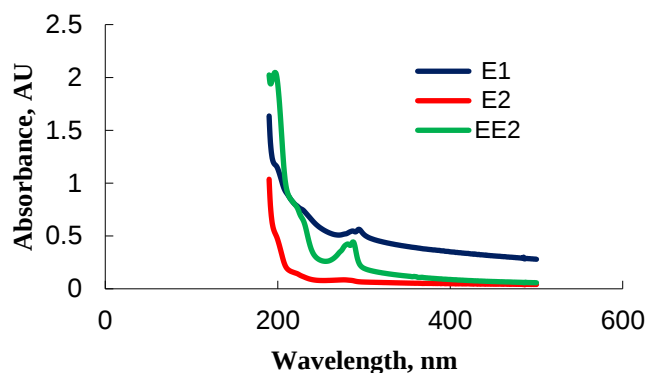
## Analyses

High performance liquid chromatography (HPLC) was used in this study to analyze endocrine disruptors. The mobile phase was made of 50% acetonitrile, 50% water and 0.1% formic acid. 50  $\mu\text{L}$  of the sample were injected at one end of the column (C18 Hypersil Gold column (150 $\times$ 4.6 mm, 5 $\mu\text{m}$  – Thermo Scientific) and carried through the column by a continuous flow of the mobile phase. HPLC (PERKIN-ELMER, Series 10 Liquid Chromatograph (A&B), and Series 10 LC Controller with UV detection (PERKIN-ELMER, LC-75), 1984, USA) was used to analyze alcohols. The mobile phase was 70% acetonitrile, 30% water and the volume of injected sample was 20  $\mu\text{L}$  at one end of the column (Hypersil 150DS, 25cm  $\times$  4.6mm, PP44398, HPLC technology).

## Results and Discussion

The analyses of endocrine disrupting were made using the HPLC/UV methodology. The maximum absorbance wavelengths of the compounds used in this study estrone (E1), 17 $\beta$ -estradiol (E2), and 17 $\alpha$ -ethinylestradiol (EE2) were determined with a UV/Vis spectrophotometer (HP8453). Water was used as blank solution and E2, EE2, and E1

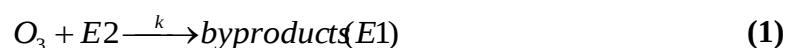
were used at a concentration of 25 mg/L each in water. The full spectrum is presented in Figure (3), the maximum absorbance for three components together occurred at almost 205 nm. Based upon this result, subsequent analysis of E2, EE2, and E1 using the HPLC/UV detector was carried out at a wavelength of 205 nm.

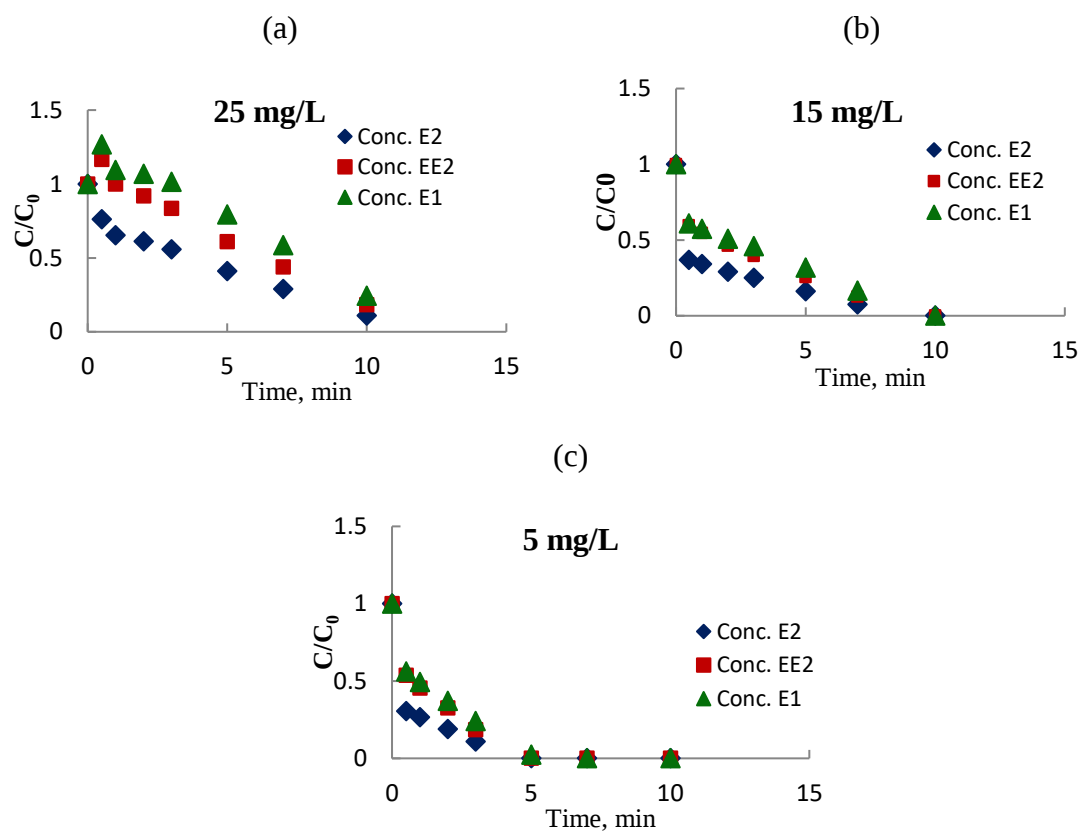


**Figure (3): UV Absorption Spectrum of Estrone (E1), 17 $\beta$ -Estradiol (E2) and 17 $\alpha$ -Ethinylestradiol (EE2).**

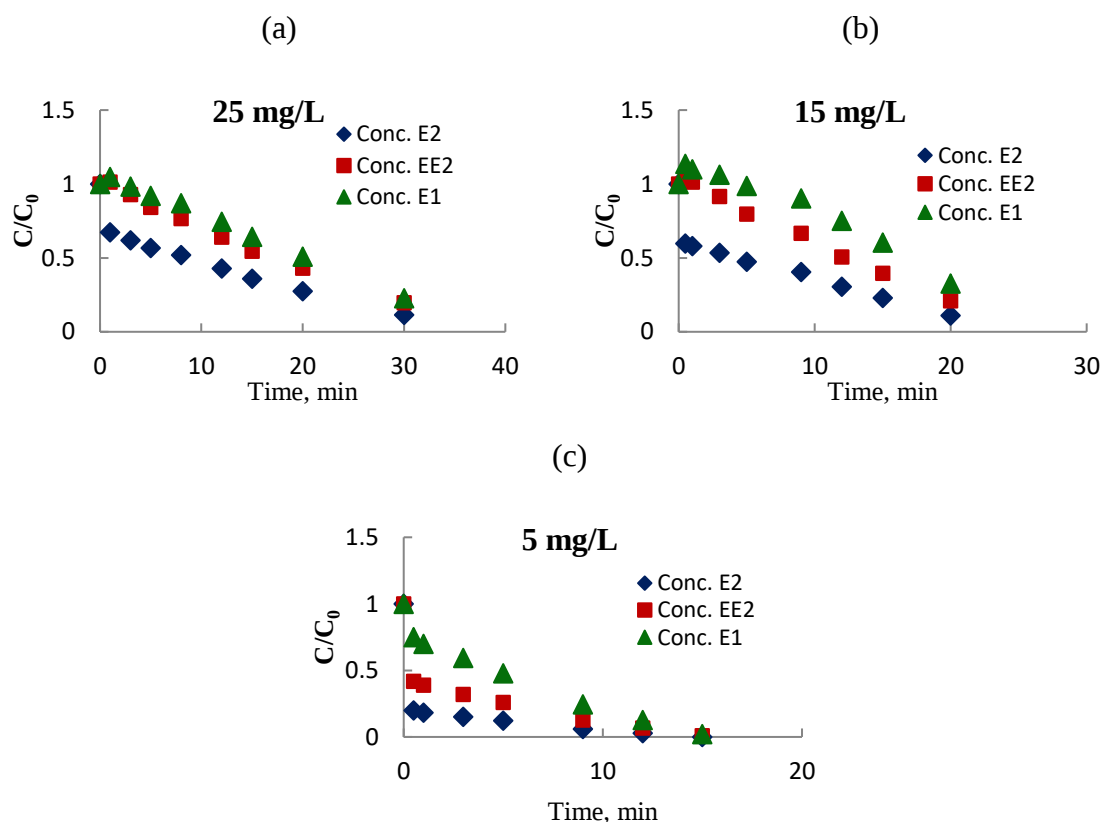
#### **Effect of (E2, EE2, and E1) Initial Concentrations on Degradation at 30 g/m<sup>3</sup> NTP Ozone Concentration and pH 7**

In order to study the effect of initial concentration of endocrine disruptors on their degradation, ozone gas at different concentration was bubbled into the multicomponent solution at different initial concentrations. The ozone concentration was 30 g/m<sup>3</sup> NTP and gas flow rate was 200 mL/min. Figure (4) shows that the degradation of multicomponent endocrine increased with decreasing the initial concentrations from 25 mg/L to 5 mg/L. From Figures (4), (a,b,c) it could be seen that when the initial concentration was 25 mg/L the time required to degrade multicomponent was around 12 minutes but when the initial concentration decreased to 5 mg/L the multicomponent degradation was very fast reaching zero in almost 5 minutes. The tests were repeated at an ozone concentration of 10 g/m<sup>3</sup> NTP, as shown in Figure (5). The degradation at lower ozone concentration (i.e. 10 g/m<sup>3</sup> NTP) took longer times to achieve a given degradation as compared with experiments at higher ozone concentration (i.e. 30 g/m<sup>3</sup> NTP). Figure (4-a) shows that the concentration of E1 increased at the start of the reaction before it started falling. This may be due to the oxidation of E2 with ozone to produce E1. Ning et al. (2007) reported that in the ozonation of E2, the overall estrogenicity increased in the first 5 minutes, then gradually decreased during the next 5 minutes, and changed little thereafter as shown Equation (1). On the other hand this behaviour was not apparent when lower concentrations were reviewed in Figure (4-b) and Figure (4-c).





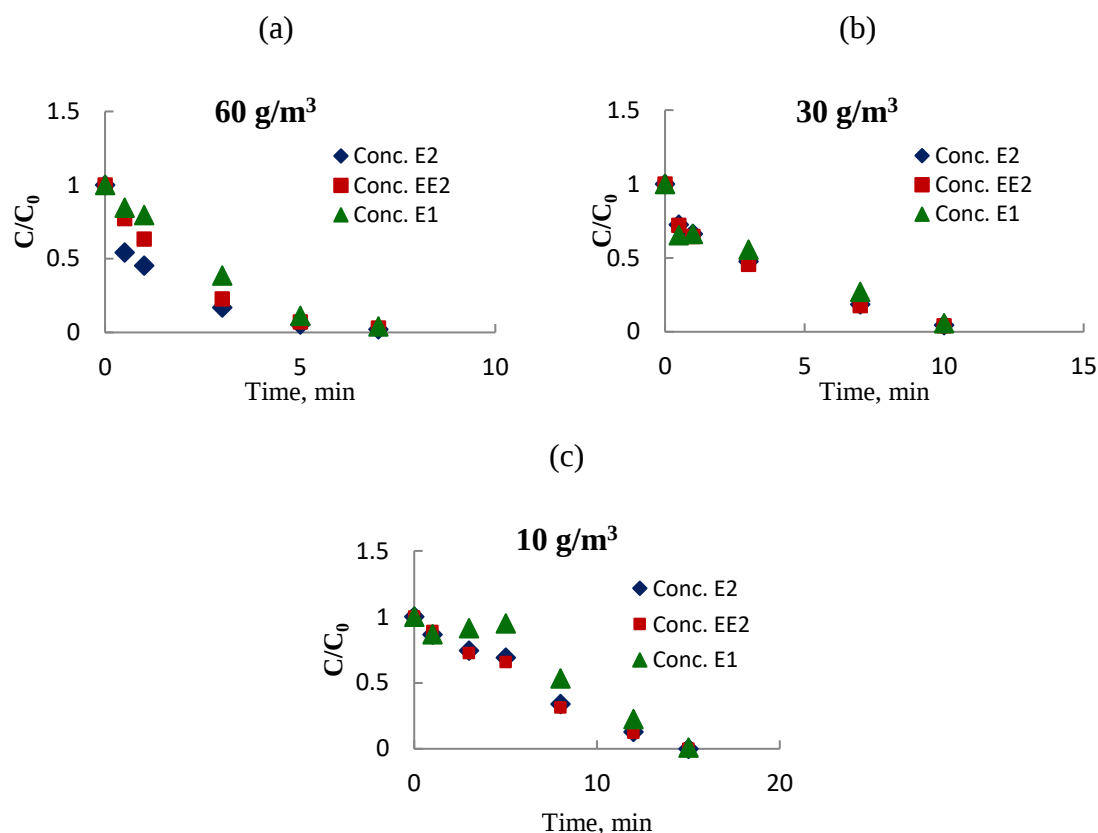
**Figure (4): Concentration Profile of E2, EE2 and E1 Solution at  $O_3$  30g/m<sup>3</sup>NTP, pH 7 and Initial Concentration (a) 25 mg/L (b) 15 mg/L (c) 5 mg/L each.**



**Figure (5): Concentration Profile of E2, EE2 and E1 Solution at  $O_3$  10g/m<sup>3</sup>, pH 7 and Initial Concentration (a) 25 mg/L (b) 15 mg/L (c) 5 mg/L each.**

### **Effect of Ozone Concentration on the Degradation of (E2, EE2, And E1) at Ph 7**

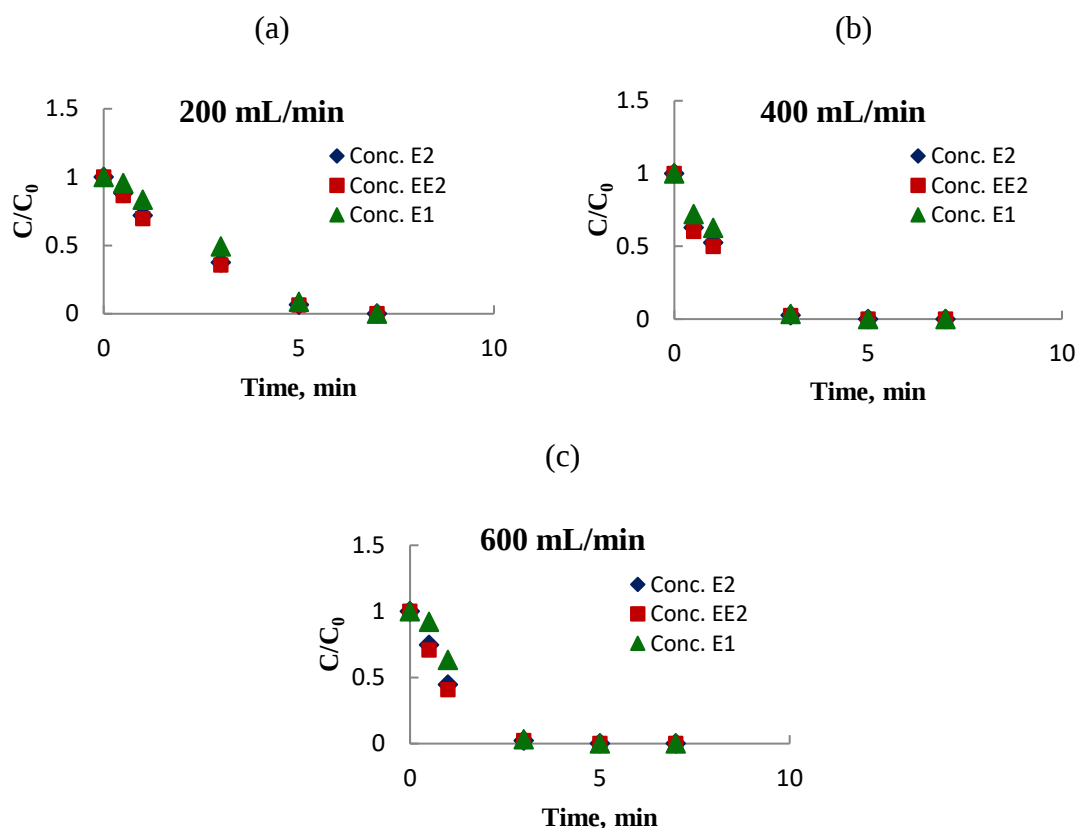
In order to study the effect of ozone concentration on endocrine disrupting degradation, ozone gas at different concentration was bubbled into the multicomponent solution at different ozone concentrations 60, 30, and 10 g/m<sup>3</sup> NTP. The gas flow rate of ozone was 200 mL/min and the initial concentrations of endocrine disruptors were 25 mg/L each. Figure (6) shows that the degradation of multicomponent endocrines increases with increasing ozone concentration from 10 to 60 g/m<sup>3</sup> NTP. Figure (6) (a,b,c) shows when the ozone concentration was 60 g/m<sup>3</sup> NTP, the time required to degrade the compounds was around 5 minutes, but when ozone concentration decreased to 10 g/m<sup>3</sup> NTP the degradation was slow and reached zero in almost 15 minutes.



**Figure (6):** Concentration profile of E2, EE2 and E1 solution at pH 7 and initial concentration 25 mg/L each, and O<sub>3</sub> concentration (a) 60 g/m<sup>3</sup> (b) 30 g/m<sup>3</sup> (c) 10 g/m<sup>3</sup>.

### Effect of Gas Flow Rate on Degradation (E2, EE2, And E1) at Ph 7

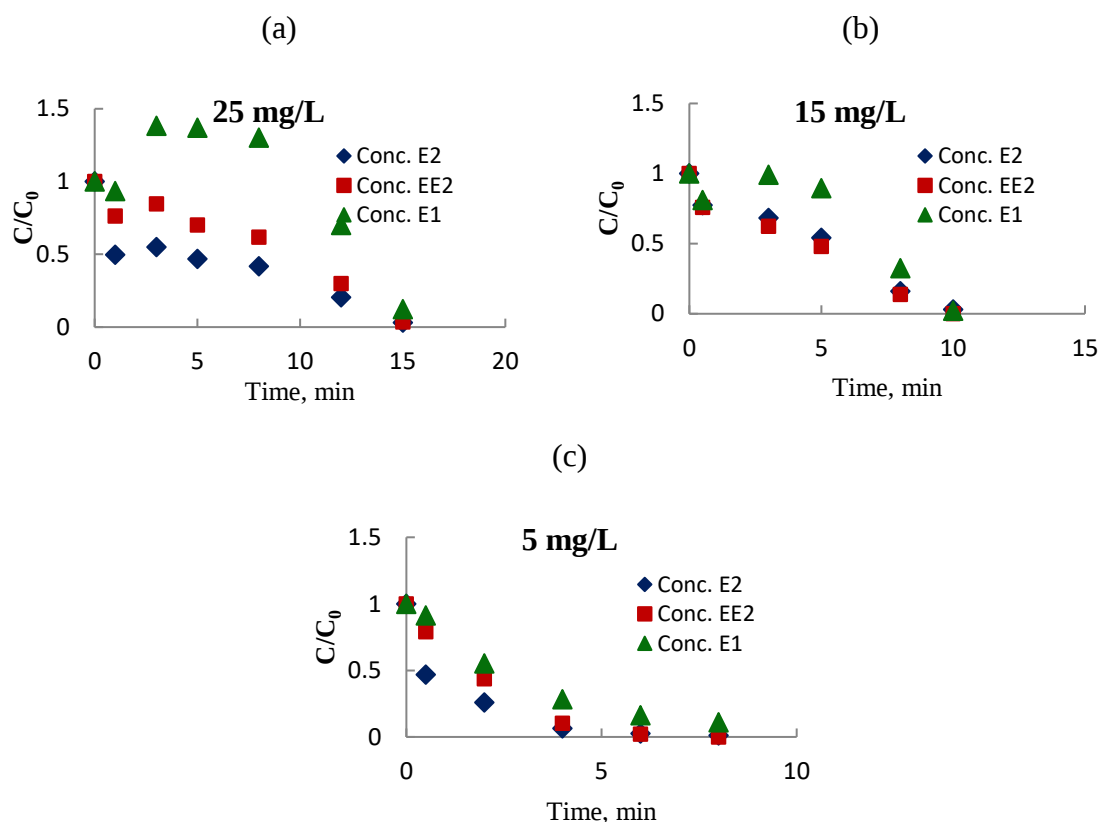
The experiments were carried out again at different gas flow rates 200, 400, and 600 mL/min, the concentration of ozone was 60 g/m<sup>3</sup> NTP and the initial concentrations were 25 mg/L each. According to Figure (7) the degradation of multicomponent endocrines increased significantly with increasing gas flow rates. This clearly indicates that the degradation is controlled by mass-transfer, which increases with increasing the gas flow rate.



**Figure (7): Concentration Profile of E2, EE2 and E1 Solution at  $O_3$  60g/Nm<sup>3</sup>, pH 7, Initial Concentration 25 mg/L each, and Gas Flow Rate (a) 200 mL/min (b) 400 mL/min (c) 600 mL/min.**

### **Effect of (E2, EE2, and E1) Initial Concentrations on Degradation at 30 g/m<sup>3</sup> (NTP) Ozone Concentration and pH 2**

In order to study the effect of pH on the degradation of the multicomponent system of E1, E2 and EE2, experiments were carried out at pH 2 in addition to the experiments that been carried out at pH 7. The concentration of solutions was 25 mg/L and the ozone concentration was 30 g/m<sup>3</sup> NTP. Figure (8) shows that the concentration of E1 increases at the beginning of the reaction at pH 2 more than at pH 7. Several literatures have mentioned the affect pH on reaction of endocrine disruptors with ozone individual (Hai-yan et al., 2006; Huber et al., 2004; Auriol et al., 2006 and Deborde et al., 2005). At higher pH and ionic strength, the main reacting route followed the radical way, and the removal rate of endocrine disruptors could be more than when they reacted with ozone through selective direct reaction at lower pH.



**Figure (8): Concentration Profile of E2, EE2 and E1 Solution at  $O_3$  30g/m<sup>3</sup> (NTP), pH 2 and Initial Concentration (a) 25 mg/L (b) 15 mg/L (c) 5 mg/L each.**

## Conclusions

Endocrine disruptor (estrone (E1), 17 $\beta$ -estradiol (E2), and 17 $\alpha$ -ethinylestradiol (EE2)) reactions with ozone were considered at different gas flow rates, ozone concentrations, initial components concentrations and pH. Almost complete degradation of the endocrine disruptors was achieved only after about 5 minutes and half hour depending on the operating conditions. It was found that estrone (E1) in the mixture at high initial concentration or low ozone concentration increases at the beginning of the reaction after that it dropped. This may be due to possible reaction between ozone and E2 which leads to the generation of E1.

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