Degradation of Endocrine Disrupting Chemicals in Aqueous Phase by Photolysis and Hydrogen Peroxide

Dr.Khaled M. Mezughi[1]*, Dr.Mawaheb M. Derdar*[2]*, Asia A. Meshrghi*[3]
1 Chemical Engineering, Faculty of Petroleum and Gas, Zawia University
2,3. Chemical Engineering, Faculty of Engineering, Tripoli University

Abstract:

Due to the ever increasing concerns about pollutants and contaminants found in water, new treatment technologies have been studied. In this article, photocatalytic degradation was explored for the removal of reactive three endocrine disrupting compounds (EDCs) (estrone, 17β-estradiol and 17α-ethinylestradiol) from synthetic effluents. The major factors affecting the photocatalytic processes including the initial concentration of the target compounds, the amount of catalyst, the *light intensity, the type of catalyst, the electron acceptor, the irradiation time and the pH were studied. Complete degradation of all the three EDCs was achieved with* UV/H_2O_2 *in 60 minutes at catalyst concentration of* $(2.94\times10^{-2}\ M)$.

Keywords: *Endocrine disrupting chemicals (estrone, 17β-estradiol, and 17α-ethinylestradiol); photocatalytic degradation;* (H_2O_2, UV)*; Aqueous phase.*

1. Introduction

During, the photocatalytic process, the illumination of the semiconductor photocatalyst with ultraviolet radiation activates the catalyst, establishing a redox environment in the aqueous solution (Zhang et al., 1994). The energy difference between the valence and conduction band is called the band gap energy (Hoffmann et al., 1995).

The semiconductor photocatalyst absorbs impinging photons with energies equal to or higher than its band-gap or threshold energy. Each photon of the required energy that hits an electron in the occupied outer orbital of the valence band of the semiconductor atom can elevate that electron to the unoccupied conduction band leading to an excited state conduction band electrons and positive valence band holes as shown in Figure 1 (Schiavello and Sclafani, 1989).

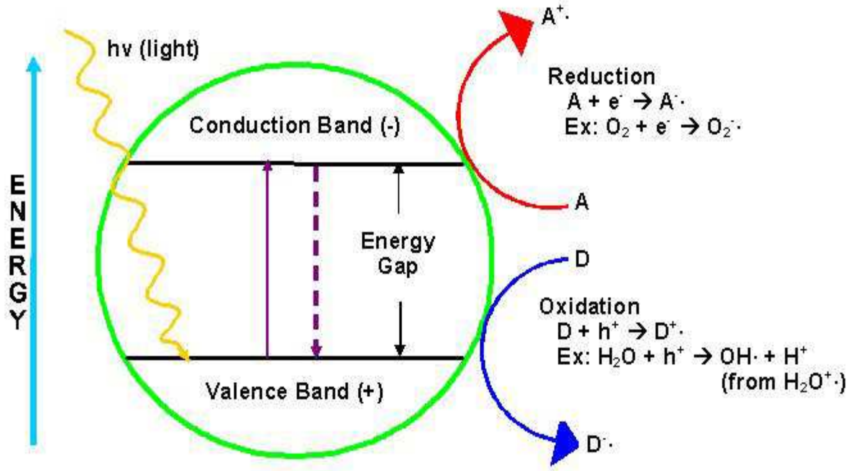

Figure 1: Schematic of an irradiated TiO_2 particle.

There are several sources and pathways for the exposure of EDCs to the environment, for example, wastewaters from production of synthetic EDCs in the pharmaceutical industry and runoff waters from agriculture (Ying et al., 2004). Intensive farming with both natural and synthetic EDCs in its runoff waters also acts as a steroid estrogens contributor to environmental contamination with EDCs. However, the most important source of EDCs in the environment is domestic sewage. Natural EDCs together with the residues of synthetic ones, originating from contraceptives and other pharmaceuticals, are excreted by humans mainly through urine. The increasing amount of EDCs in domestic sewage is due to the growing world population and the increasing urbanisation and consequently consumption of synthetic EDCs. The effects of EDCs on the endocrine system can result in health changes of the organism itself or might not be seen until the next generation. The development of embryos and foetuses are especially sensitive to disruption. Although trace amounts of EDCs do not affect adults, they can have a crucial impact on the developing embryo. The time of exposure is assumed to be more important than the dose (Ying et al., 2004). The observed impacts of EDCs on wildlife include hermaphrodite fish and polar bears, reproductive failure in birds and abnormalities in the reproductive organs of reptiles, amphibians and non-vertebrates (Jobling et al., 1998; Ahmed, 2000). The health effects on humans include reproductive abnormalities, effects on male to female ratio, decreased sperm counts and quality, both male and female fertility problems (reproductive function, miscarriage, ectopic pregnancy, stillbirth, premature birth), and an increase in certain types of male and female cancers (testicular cancer, prostate cancer, breast cancer), effects on brain and behaviour (Mendes, 2002;Ferguson, 2002).

Materials and Methods:

Materials

Experimental setup

The mercury arc lamp was switched on and allowed to warm up for one hour. as shown in Figure 2. During this time, the power supply was monitored using the multimeter provided on the power supply, which displayed both the current drawn (amperes), and the potential applied (volts). The light source was temporarily blocked with a silvered shutter. The photocatalyst was stirred with a magnetic stirrer while the reactor was sealed with the head-space volume containing pure oxygen (or synthetic air). Then the shutter was opened to allow irradiation to begin. Liquid samples 3mL were removed at regular intervals of time and the solid titanium dioxide separated by (Millex GP 0.22µm). Analysis of the clear liquid was then performed by using HPLC for the estrogens.

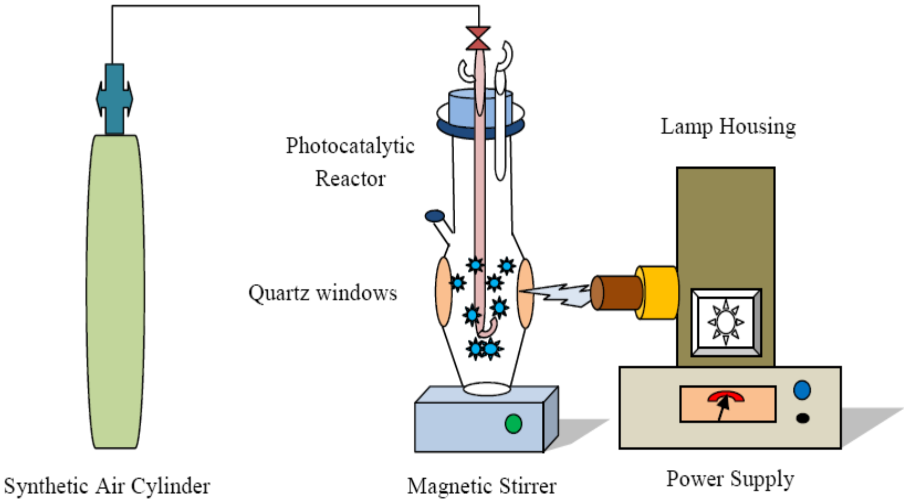

Figure 2: Schematic of the photocatalytic system.

UV/Vis Spectrum of EDCs

The analyses of EDCs were made using the HPLC/UV methodology. The maximum absorbance wavelengths of the compounds used in this study estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) were determined with the UV/Vis spectrophotometer (HP8453). Water was used as blank solution and E1, E2 and EE2 have been used at concentrations of 25 mg/L (E1= 9.25×10^{-2}, E2= 9.18×10^{-2} and EE2= 8.43×10^{-2}mM) each in water. The full spectrum for each EDC is presented in Figure 3, which shows that a wavelength of 205 nm is suitable for UV detection of the three compounds. Bila et al., (2004) used 203 nm to analyse E2. Based upon this result, subsequent analysis of E1, E2 and EE2 using the HPLC/UV detector was carried out at a wavelength of 205 nm.

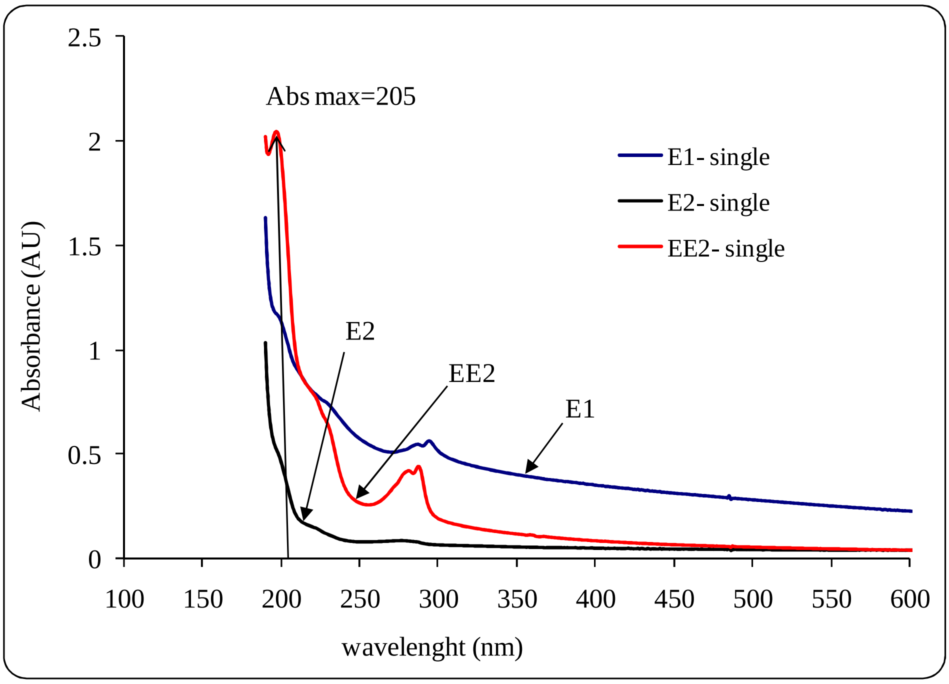

Figure 3: UV absorption spectrum of 25 mgL^{-1} E1, E2, and EE2.

Results and discussion:

Experiments to investigate the effectiveness of UV light on the degradation of a single EDC (i.e. photolysis) were carried out at 5 mg/L (E1=1.85×10^{-2}, E2=1.84×10^{-2} and EE2=1.69×10^{-2} mM) initial concentration (power of 200 W and pH=5.8). As can be seen from Figure 4, the degradation of E1 after the first five minutes irradiation was about twice higher than the degradation of E2 and EE2. Because in E1 absorbs more light at 365 nm (a wavelength at which the UV lamp emits the highest light intensity) as compared to E2 and EE2, which explains the rapid degradation of E1 obtained in this study. After 1 hour irradiation, the measured intensities of E2, EE2 and E1 were 86.26%, 85.24% and 92.06%, based on these results which indicate a similar degradation rate. It is also important to note that after 5 minutes, the rate of degradation of E1 became slower relative to the other EDCs possibly due to the rapid reduction of E1 concentration.

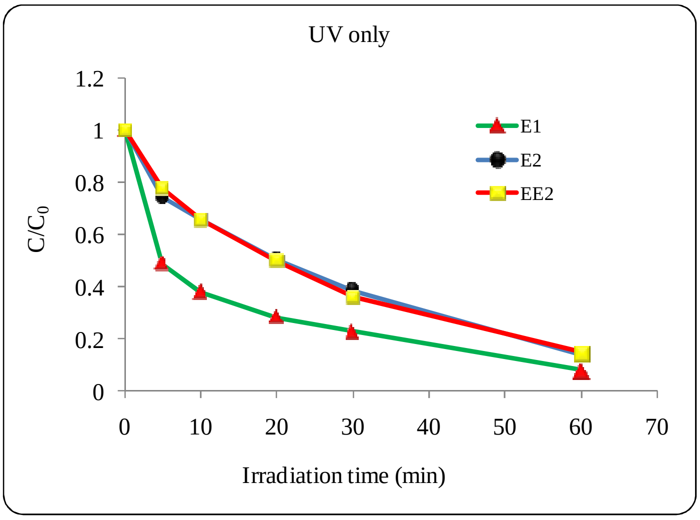

Figure 4: Effect of UV light on the degradation of single EDC

The photodegradation of mixtures of the three EDCs was also studied and the results are shown in Figure 5. Generally the pattern of degradation of the EDCs is more or less similar for single components or in mixtures. In both cases E1 was degraded faster than E2 and EE2. For the mixture of EDCs, a very rapid degradation of E1 within the first 5 minutes was observed, followed by almost nil degradation afterwards. Although this behaviour is difficult to explain, it is clear that E1 degrades rapidly either as a single component or in mixtures. The trend of degradation of E2 and EE2 is very similar, possibly due to the high similarity between their chemical structures and the fact that they represent similar light absorption properties as shown in Figure 4. If the interest is the extent of degradation at the end of the assigned time then it can be argued that the degradation efficiency was slightly better for the EDCs treated individually than for the mixed EDCs. This agrees with the fact that the amount of UV light irradiation was the same for both situations though the concentration of compounds susceptible for light absorption increased when the EDCs are mixed. As a result of the greater concentration in mixtures, two possible points should be considered. Firstly for the mixed EDCs, there is greater competition for exposure to UV light than for the less concentrated individually treated EDC. Secondly a masking effect results as a result of the greater concentration. Looking at Figure 5, the degradation of E1 was initially steeper in the mixture than for single component. This may be explained by additional reactions taking place between E1 and formed radicals as a result of the photolysis of the other EDCs. To date the photochemical behaviour and specifically the contribution of direct photolysis to the degradation of these compounds have not been deeply studied (Patrick et al., 2008). Zhang and Zhou (2008) studied the effect of UV light on the degradation of E1 and E2 and found the E1 and E2 were prone to UV photodegradation.

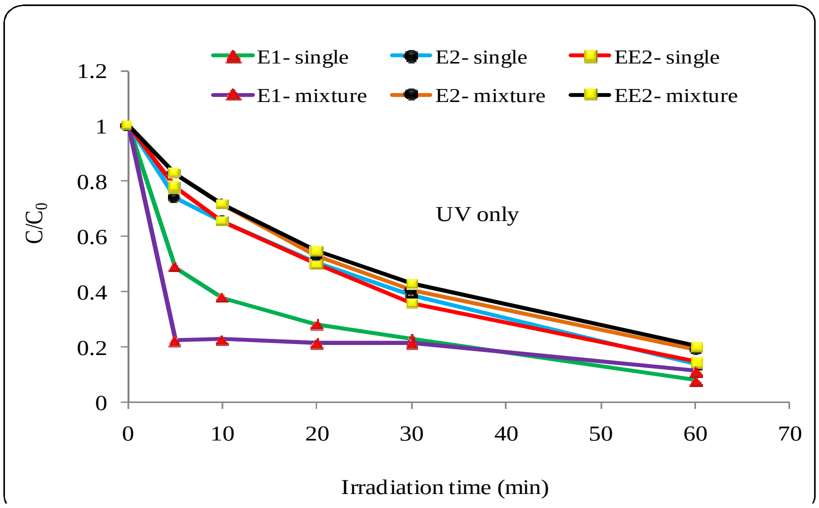

Figure 5: Effect of UV on the degradation of EDCs single and mixture [C_0=5 mgL^{-1} (E1= 1.85×10^{-2}, E2= 1.84×10^{-2} and EE2= 1.69×10^{-2}mM), pH=5.8 and Power =200 W].

Effect of initial concentrations of EDCs

Different initial concentrations of EDCs (mixture) with fixed catalyst concentration at 1 g/L were used to investigate the effect of initial concentrations on the degradation rates of the EDCs. From Figure 6, it can clearly be seen that low concentration of EDCs 0.5 mg/L (E1=1.85×10^{-3}, E2=1.84×10^{-3} and EE2=1.69×10^{-3}mM) resulted in higher degradation as compared to higher concentrations 1 and 5 mg/L (E1= 3.70×10^{-3}, E2= 3.67×10^{-3} and EE2=3.37×10^{-3}mM) and (E1=1.85×10^{-2}, E2=1.84×10^{-2} and EE2= 1.69×10^{-2} mM). For example at 0.5 mg/L the degradations of E2, EE2 and E1 after 10 minutes were 46.85%, 40.31% and 43.83% respectively, whereas after 60 minutes of irradiation the degradations were 100% for both EE2 and E1 and 87.27% for E2. When the initial concentration was increased to 1 mg/L EDCs, the extent of degradation reduced significantly as compared to 0.5 mg/L EDCs. For instance the degradations of E2, EE2 and E1 after 10 minutes were only

5.34%, 4.19% and 7.28% respectively, whereas after 60 minutes of irradiation the degradations increased to 36.49%, 36.13% and 46.11% respectively. The degradation rates decreased even further with increasing initial EDCs concentrations to 5 mg/L EDCs. At 5 mg/L EDCs and after 10 minutes of irradiation, the degradations of E2, EE2 and E1 were 4.05%, 3.26% and 4.66% respectively. The degradation increased slightly to 9.54%, 10.75% and 13.12% for E2, EE2 and E1 respectively after 60 minutes. These results clearly indicate that the initial concentration of EDCs has a significant effect on the extent of degradation of these compounds. For a fixed concentration of catalyst, the higher the concentration of EDCs, the lower the degradation efficiency. Knowing that in real wastewaters, the concentrations of these compounds are very low (~ng/L), hence a photocatalytic system seems suitable for their removal.

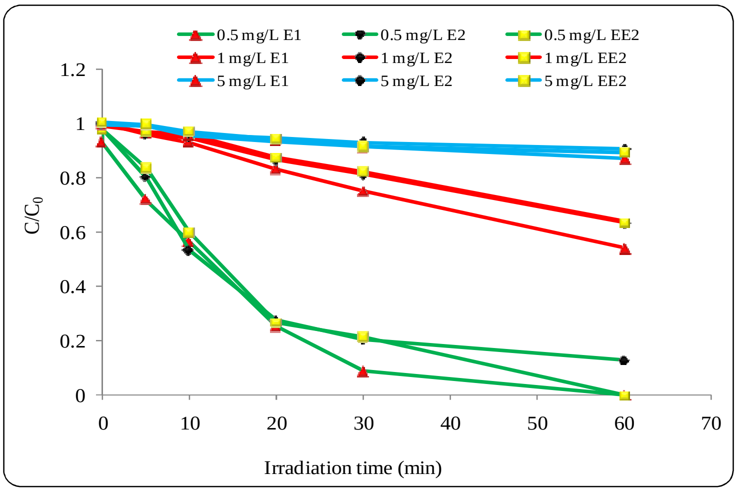

Figure 6: Effect of initial concentrations of EDCs (mixture) on the degradation rate [C $_{\text{Degussa P25}}$=1 gL^{-1}, pH=5.8 and Power=200 W].

Photodegradation of EDCs with UV/ H_2O_2

The degradation of E1, E2 and EE2 as single components and in mixtures was studied using the UV/H_2O_2 system. The initial concentration of each EDC was 20 mg/L (E1= 7.40×10^{-2}, E2=7.34×10^{-2} and EE2=6.75×10^{-2} mM) and that of H_2O_2 was 1g/L (2.94×10^{-2} M). The power of the UV light was 200 W.

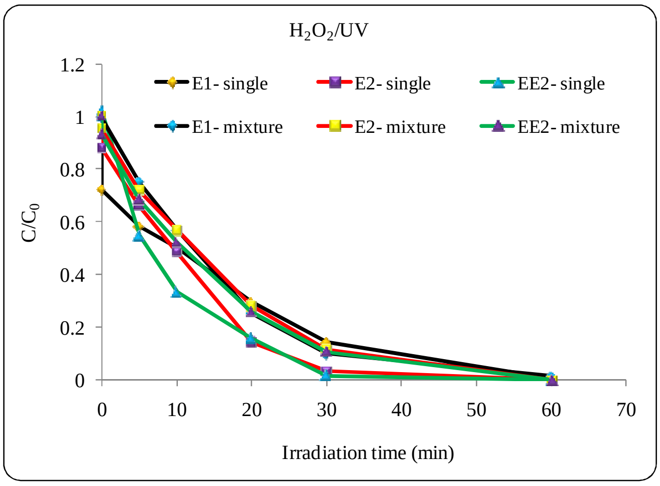

Figure 7: Effect of H_2O_2/UV on the degradation of EDCs single and mixture EDCs [CH_2O_2=1 gL^{-1} (2.94×10^{-2} M), C_0=20 mgL^{-1} (E1= 7.40×10^{-2}, E2=7.34×10^{-2} and EE2=6.75×10^{-2}mM), pH=5.8 and Power=200 W].

Figure 7 shows the effect of H_2O_2/UV on photocatalytic degradation of EDCs treated separately and as a mixture. For individual treatment, E2 degraded about 34.02% after the first five minutes of irradiation. At the same time EE2 and E1 were reduced to about half the initial concentration (45.27 and 41.01% respectively). For the mixed solutions, the degradation was lower than for individual compounds in the first five minutes of irradiation. The degradations for the three mixed EDCs after five minutes were 28.29, 31.93 and 25.15% for E2, EE2 and E1 respectively. Complete degradation of single E2 and EE2 was achieved after 30 min, but it required 60 min when a mixture was used.

On the other hand, the degradation of single E1 was more difficult and required 60 min to be almost complete. For individual treatment E2, EE2 and E1 were degraded by 100, 100 and 99.73% respectively after 60 min and for mixed treatment E2, EE2 and E1 were degraded by 100, 100 and 98.65% respectively.

Effect of UV light on the degradation of the EDCs

The effect of UV light in the presence of hydrogen peroxide was studied in experiments with and without UV light. Before UV/H_2O_2 degradation experiments, the compounds E2, EE2 and E1 were scanned in UV spectrophotometry and the results show that the 3 EDCs generally have enhanced UV absorbance at low wavelength. Their spectra indicate that E2, EE2 and E1 are prone to UV photodegradation. In the absence of UV light, a clear instantaneous drop in the concentrations of the EDCs by about 40% occurred as a result of oxidation with hydrogen peroxide Figure (6). The concentration then remains constant throughout the remaining time. The most likely explanation for this inference is the high concentration of H_2O_2 used (~ 0.03M). Bledzka et al. (2010) found insignificant result of photodegradation of EDCs with only H_2O_2 (0.01M). Xianghua et al. (2005) studied the degradation of E2 with only H_2O_2. These authors found the increase of H_2O_2 concentration resulted in the increase in the degradation of E2. This could be explained by Equation (1). H_2O_2 can also become a scavenger of $^{\bullet}OH$, when present at high concentration (Daneshvar et al., 2003).

$$H_2O_2 + {}^{\bullet}OH + h\nu \rightarrow H_2O + {}^{\bullet}HO_2 \qquad (1)$$

The degradation of the EDCs using UV light only Figure 5 resulted in better efficiency than using 1g/L H_2O_2 (2.94×10^{-2} M). On the other hand coupling H_2O_2 with UV light Figure 8 resulted in better degradation efficiency than using only H_2O_2 or only UV light. For instance E2 degraded 100% after 10 minutes irradiation, while EE2 and E1 were degraded 89.95 and 93.24% after 10 minutes respectively when UV/H_2O_2 system was used as compared to 28.36, 28.23 and 77.27% after 10 min when only UV was used. The effectiveness of the UV/H_2O_2 is due to the production of hydroxyl radicals at significant amounts following the photolysis of hydrogen peroxide (Equation 2).

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \qquad (2)$$

The rate constants obtained with UV/H_2O_2 were 2.49×10^{-1}, 2.02×10^{-1} and 2.03×10^{-1} min^{-1} for E1, E2 and EE2 respectively.

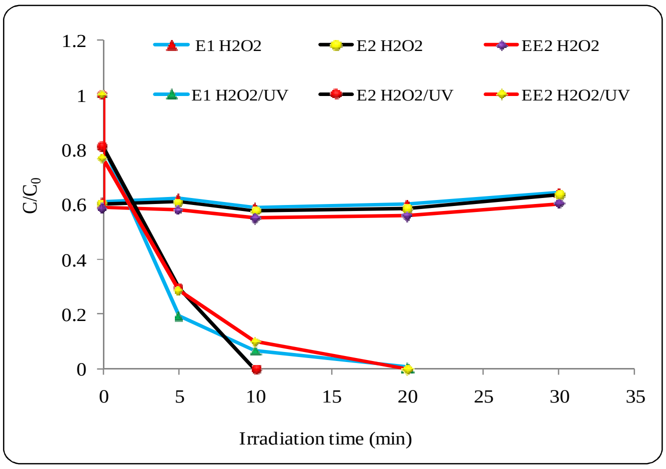

Figure 8: Effect of H_2O_2 on the degradation of mixed EDCs without UV and with UV [CH_2O_2=1 gL^{-1} (2.94×10^{-2} M), C_0=5 mgL^{-1} (E1= 1.85×10^{-2}, E2= 1.84×10^{-2} and EE2= 1.69×10^{-2} mM), pH=5.8 and Power=200 W].

Effect of initial concentration on photodegradation of EDCs

Experiments were carried out to investigate the effect of initial concentrations of mixed EDCs 5 and 20 mg/L (E1=1.85×10^{-2}, E2=1.84×10^{-2} and EE2=1.69×10^{-2} mM) and (E1=7.40×10^{-2}, E2=7.34×10^{-2} and EE2=6.75×10^{-2} mM) at fixed concentration of H_2O_2 1g/L (2.94×10^{-2} M) in the presence of UV light. It was found from the result in Figure 9 that the degradation was higher at 5 mg/L than 20 mg/L EDCs. The result indicated that the initial concentration of EDCs plays an important role in the degradation of these compounds. After 10 minutes irradiation, E2 at 5 mg/L was completely degraded but 60 minutes were required to achieve its complete degradation when its initial concentration was 20 mg/L.

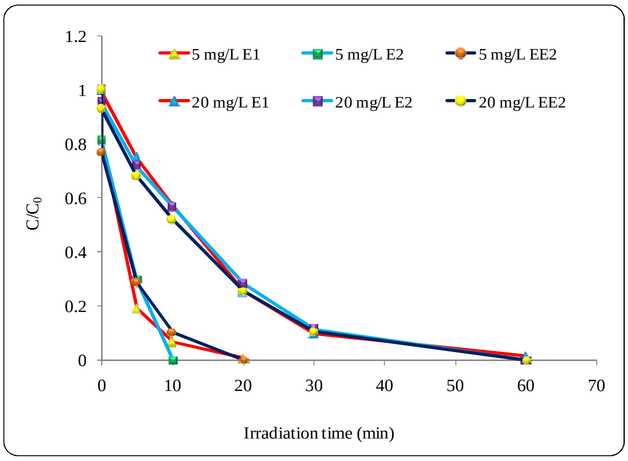

Figure 9: Effect of initial concentration of mixed EDCs [C_{H2O2}=1 gL^{-1} (2.94×10^{-2} M), pH=5.8 and Power=200 W].

Effect of H_2O_2 concentration

To investigate the effect of H_2O_2 concentration on the degradation of mixed EDCs in the presence of UV light two different concentrations of H_2O_2 were used 0.5 and 1 g/L (1.47×10^{-2} and 2.94×10^{-2} M) and the EDCs concentrations were 20 mg/L (E1=7.40×10^{-2}, E2=7.34×10^{-2} and EE2=6.75×10^{-2} mM) each. The results in Figure 10 revealed that increasing the concentration of H_2O_2 from 0.5 to 1g/L did not significantly affect the degradation rates of the EDCs. This is expected since hydrogen peroxide was added in excess.

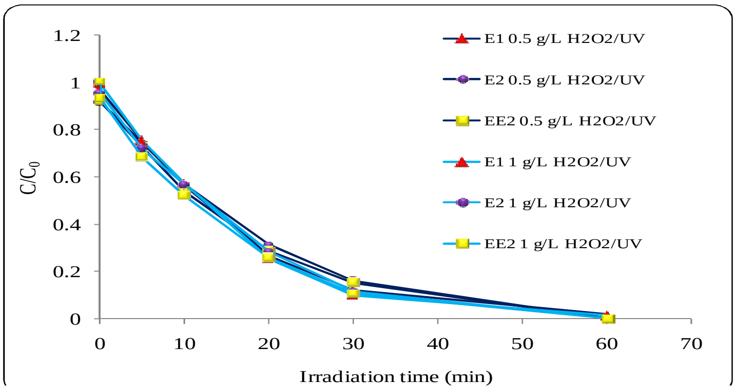

Figure 10: Effect of H_2O_2 concentration on the degradation of mixed EDCs [C_0=20 mgL^{-1} (E1=7.40×10^{-2}, E2=7.34×10^{-2} and EE2=6.75×10^{-2}mM), pH=5.8 and Power=200 W].

Effect of electron acceptors

Experiments were conducted to investigate the extent to which oxygen as electron acceptor influences the degradation of EDCs (mixed). Streams of pure oxygen, synthetic air, and nitrogen were bubbled into solution to achieve different concentrations of oxygen. These experiments revealed that no significant effect Figure 11.

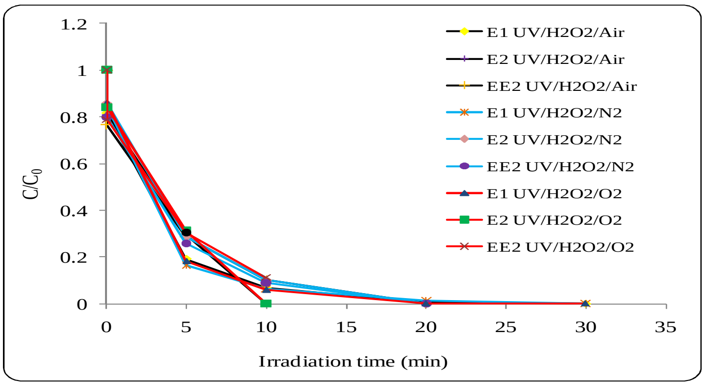

Figure 11: Effect of oxygen as electron acceptor on the degradation of mixed EDCs [C_{H2O2}=1 gL^{-1} (2.94×10^{-2} M), C_0=5 mgL^{-1} (E1=1.85×10^{-2}, E2=1.84×10^{-2} and EE2=1.69×10^{-2}mM), pH=5.8 and Power=200 W].

Effect of light intensity on photodegradation of EDCs

The effect of UV lamp power on the rate of photocatalytic degradation was investigated. An initial concentration of 20 mg/L (E1=7.40×10^{-2}, E2=7.34×10^{-2} and EE2=6.75×10^{-2} mM) of mixed EDCs with 1 g/L (2.94×10^{-2} M) H_2O_2 (pH 5.8) was used. The investigated lamp powers were 120 and 200 W. From the results in Figure 12 an increase in lamp power (by about 67%) did not result in significant increase on the EDCs degradation. This indicates that lower lamp powers may be used.

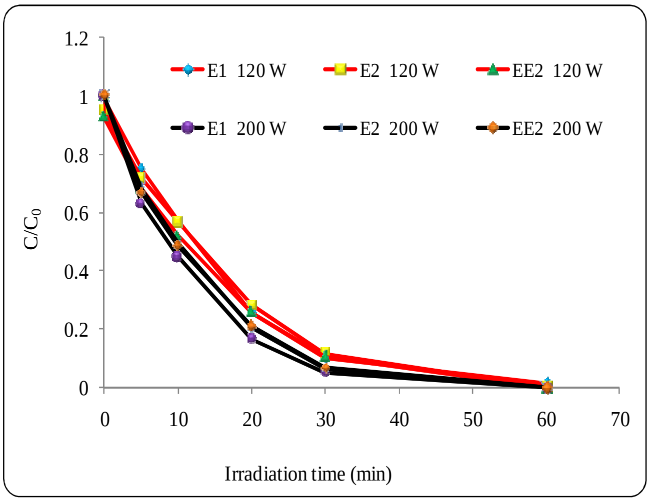

Figure 12: Effect of light intensity on the degradation of mixed EDCs [C_{H2O2}=1 gL^{-1} (2.94×10^{-2} M), C_0=20 mgL^{-1} (E1=7.40×10^{-2}, E2=7.34×10^{-2} and EE2=6.75×10^{-2}mM), pH=5.8].

Effect of pH on the degradation of EDCs with UV/H_2O_2

An important parameter in the UV/H_2O_2 reaction is the pH of the dispersion. Depending on the nature of the organic pollutant, an increase in pH will have a positive or negative effect on its degradation rate and consequently the mineralisation rate of the solution (Liu et al., 2003a). The effect of pH on the degradation of the three EDCs with UV/H_2O_2 was investigated at pH values of 3, 5, 7, 9, and 11. Figure 13 show the results of the photodegradation of 20 mg/L ($E1=7.40\times10^{-2}$, $E2=7.34\times10^{-2}$ and $EE2=6.75\times10^{-2}$ mM) EDCs as mixture using 1 g/L (2.94×10^{-2} M) H_2O_2 in the presence of UV light at the five pH values.

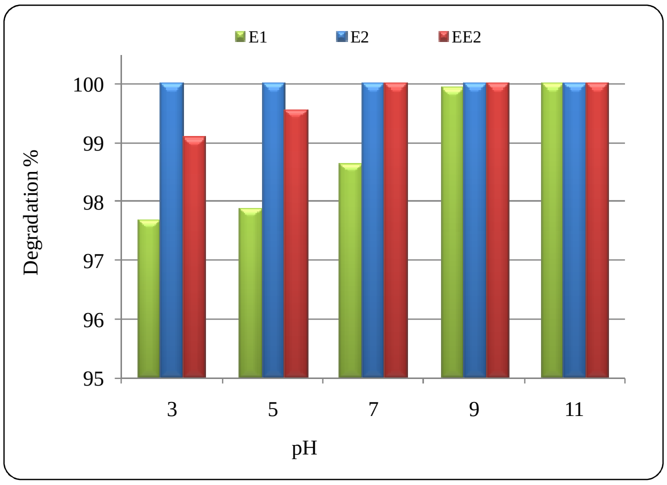

Figure 13: Effect of pH on the degradation of mixed EDCs with UV/H_2O_2 [C_{H2O2}=1 gL^{-1} (2.94×10^{-2} M), C_0=20 mgL^{-1} ($E1=7.40\times10^{-2}$, $E2=7.34\times10^{-2}$ and $EE2=6.75\times10^{-2}$mM), Irradiation time=1h and Power=200 W].

The degradation efficiency of EE2 and E1 increased with increasing the pH of the solution up to 7 and 9 respectively and then remained constant. As stated by Coleman et al., (2000) as pH increases to 11, the hydroxide ion concentration increases, thereby the generation of hydroxyl radicals will increase which increases the rate of degradation. Actually Liu et al., (2003) reported observing an increase in oxidation of EE2 with increased pH. It has been reported that photocatalytic reaction is faster in alkaline media than in acid media Doong et al., (2000). However the authors only studied EE2. In this work E1 was also found to behave in the same way. On the other hand E2 behaved differently in that its degradation, within the studied pH range, was not affected by the change of pH. The different behaviour of E2 in comparison to the other

EDCs with changing the pH is almost certainly due to differences in the effect of pH on their structures. Table 5.10 shows the values of the rate constants for E1, E2 and EE2.

Conclusion"

The current research showed that the three EDCs [estrone (E1), 17β-estradiol (E2) and 17α-ethinylestradiol (EE2)] used in this study can be degraded with both photolysis and photocatalysis. E1 was found to degrade rapidly as compared to E2 and EE2 in photolysis. In photocatalysis, increasing catalyst concentration resulted in decreasing degradation of the EDCs. In addition increasing the initial concentration resulted in decreasing degradation rates of the EDCs. Near complete degradation of the EDCs (E1= 7.40×10^{-2}, E2=7.34×10^{-2} and EE2=6.75×10^{-2} mM) either as single component or in mixtures was achieved in 1 hour irradiation using UV/H_2O_2. Increasing the initial concentration of the EDCs resulted in decreased degradation rates. On the other hand the increase of H_2O_2 concentration from 2.94×10^{-2} to 5.88×10^{-2} M did not result in significant changes in the degradation rates of the EDCs. Moreover, an increase in UV power from 120 to 200 W did not affect significantly the degradation rates. The current work found no degradation of EDCs with hydrogen peroxide (H_2O_2) alone.

References:

- *Ahmed, S.A. (2000). The immune system as a potential target for the environmental estrogens endocrine disruptors: a new emerging field. Toxicol., 150, pp 191-206.*
- *Bila, D., Montalvao A.F., Azevedo D., Dezotti M., (2007). Estrogenic activity removal of 17 beta-estradiol by ozonation and identification of by-products. Chemosphere 69: pp 736-746.*

- *Bledzka, D., Gmurek, M., Gryglik, M., Olak, M., Miller, J., Ledakowicz, S. (2010). Photodegradation and advanced oxidation of endocrine disruptors in aqueous Solutions. J. Catalyst today 151: pp 125-130.*
- *Coleman HM, Eggins BR, Byrne JA, Palmer FL, King E. (2000). Photocatalytic degradation of 17β-oestradiol on immobilised* TiO_2*. ApplCatal B: Environ; 24: pp 1-5.*
- *Coleman, H.M., Routledge, E.J., Sumpter, J.P., Eggins, B.R., Byrne, J.A. (2004). Rapid loss of estrogenicity of steroid estrogens by UVA photolysis and photocatalysis over an immobilised titanium dioxide catalyst. Water research 38: pp 3233-3240.*
- *Da Silva, C.G. Faria, L., (2003). Photochemical and photocatalytic degradation of an azodye in aqueous solution by UV irradiation. J. PhotochemPhotobiol A Chem; 155: pp 133-143.*
- *Daneshvar, N., Salari, D., Khataee, A.R., (2003). Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters. J. Photochem. Photobiol.A Chem. 157: pp 111–116.*
- *Doong, R. A., Maithreepala, R. A. and Chang, S-M., (2000). Heterogeneous and homogeneous photocatalytic degradation of 2-chlorophenols in aqueous titanium dioxide and ferrous ion. Wat. Sci. Tech., vol. 42. No. 7-8, pp 253-260.*
- *Ferguson, S.A. (2002). Effects on brain and behaviour caused by developmental exposure to endocrine disrupters with estrogenic effects. Neurotoxicol. Teratol., 24, pp 1-3.*
- *Halmann, M.M. (1996). Photodegradation of water pollutants, crc press, bocaraton.*
- *Jobling, S., Nolan, M., Tyler, C.R., Brighty G., and Sumpter, J.P. (1998).Widespread sexual.*
- *Liu, B., Wu, F., Deng, N. (2003). UV-light induced photodegradation of17α-ethynylestradiol in aqueous solutions. J. Hazardous Material B98: pp 311-316.*

- *Liu, B., Wu, F., Deng, N.S., (2003a). UV-light induced photodegradation of 17α-ethynylestradiol in aqueous solutions. J. Hazard. Mater. B 98: pp 311-316.*
- *Mendes, A. (2002). The endocrine disrupters: A major medical challenge. Food Chem. Toxicol., 40, pp 781-788.*
- *Patrick Mazellier, LadjiMéité, Joseph De Laat, (2008). Photodegradation of the steroid hormones 17b-estradiol (E2) and 17a-ethinylestradiol (EE2) in dilute aqueous solution. Journal of Chemosphere 73: pp 1216-1223.*
- *Schiavello, M. Sclafani, A., (1989). Photocatalysis: Fundamentals and Applications. N. Serpone. E. Pelizzetti (Eds) John Wiley & Sons. pp 159-173.*
- *Xianghua, F., Jianfeng, Tu., Shimin, D., Feng, Wu.,Nansheng, D., (2005). Photodegradation of 17β-estradiol in water by UV-vis/Fe (III)/*H_2O_2 *system. J. Hazardous Materials B127: pp 129-133.*
- *Ying, G.G. Kookana R.S. and Waite, T.D. (2004). Endocrine disrupting chemicals (EDCs)*
- *Zhang, Y., Crittenden, J.C., Hand, D.W., Perram, D.L., (1994). Fixed-Bed Photocatalysts for Solar Decontamination of Water. Environmental Science Technology.28: pp 435-442.*
- *Zhang, Y., Zhou, J. (2008). Occurrence and removal of endocrine disrupting chemicals in wastewater. Chemosphere. 73: pp 848-853.*