

# Nanostructured Catalysts for Photo-oxidation of Endocrine Disrupting Chemicals

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Removal of four Endocrine disrupting chemicals (EDCs) Estrone (E1), 17- $\beta$ -estradiol (E2), Estriol (E3) and 17- $\alpha$ -ethynylestradiol (EE2) were investigated using UV oxidation and combined with Nafion/iron catalyst. Immobilization of iron on the perfluorosulfonic polymer, Nafion®, has been investigated as a carrier for the oxidation of pollutants by hydroxyl radicals (heterogenous photo-Fenton mechanism). However, the low surface area of Nafion, less than 0.2 m<sup>2</sup>/g, usually results in low pollutant degradation rates. Sol-gel technology was used to produce a high surface area poly(dimethylsiloxane) (PDMS) modified Nafion/silica composite suitable for catalysis of the photo-Fenton reaction without significant leaching of iron. The incorporation of Nafion into silica greatly increases the accessibility of Nafion/iron loaded active site. PDMS reinforces the structure of silica and maintains the transparency of the composite, which is essential for efficient Photo-Fenton reactions. These composites were utilized for the decomposition of estrogens which are Estrone (E1), 17- $\beta$ -estradiol (E2), Estriol (E3) and 17- $\alpha$ -ethynylestradiol (EE2). In consequence, it is clear that the composite effectively catalyses the photo-Fenton reaction to remove estrone. The presence of iron through the use of the catalyst leads to rapid degradation of the estrone compared to just H<sub>2</sub>O<sub>2</sub> and UV light alone. It was found that the addition of only 8.5 mg/L H<sub>2</sub>O<sub>2</sub> produced more than %90 conversion of estrogens within 60 minutes.

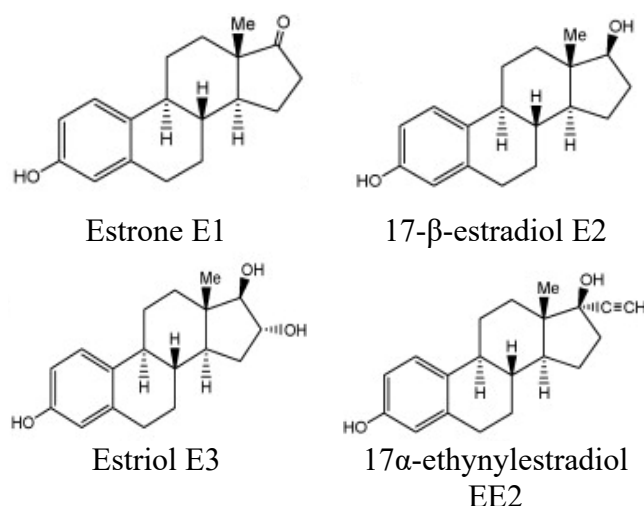
**Keywords:** EDC's, Nafion/iron catalyst, UV-oxidation.

## 1. Introduction

Endocrine Disrupting Chemicals (EDCs) are environmental contaminants that interfere with endocrine system function [1]. Estrogens are a group of steroid chemicals functioning as the primary female sex hormone and are defined by their effects within the estrous cycle [2, 3]. By imitating the hormonal system and altering the endocrine system function, estrogens act as EDCs and induce an adverse effect on the natural environment [4]. This impact is seen in animal populations due to the EDCs interference in reproductive and development cycles [5, 6]. The past two decades have seen extensive research conducted highlighting how influential environmental chemicals, such as estrogens, are at interrupting the endocrine system causing reproductive abnormalities in wildlife [7]. Although natural hormones have always been present in the natural water system, the increasing use of both natural and artificial estrogens for both medicine (i.e. oral contraceptive pills, treatment of cancers and hormone replacement therapy) and animal farming have contributed to a substantial rise in their presence and subsequent pollution within the aquatic environment [8].

These EDCs are excreted and reach the aquatic environment mainly via Waste-Water Treatment Plants (WWTPs). WWTPs receive a broad range of molecules, including estrogens, that are not entirely removed during the treatment processes meaning that the discharges from WWTPs are considered to be a major source of estrogenic water pollution [1]. With worldwide reuse of surface water increasing and the potential for EDCs to bio-accumulate, the treatment and removal of estrogens from wastewater is becoming increasingly important [8].

Natural estrogens such as Estrone, Estriol and 17- $\beta$ -estradiol and synthetic estrogens such as 17- $\alpha$ -ethynylestradiol (the main hormone within the oral contraceptive pill) are shown in Figure 1 and display the strongest estrogenic effects presenting a significant cause for concern [5, 7, 8].



**Figure 1: Molecular structures of estrogens**

The concern surrounding EDCs began in the 1980s when deformities in UK fish were discovered along stretches of river [9]. Abnormal male development in male alligators highlighted the reproductive hazards of EDCs to wildlife in the environment [10] and that EDC contamination of a wildlife population can potentially lower its reproductive success [11].

Research in both laboratories and the natural environment has shown that exposure to these EDCs can lead to disruption of reproduction and early development in aquatic wildlife [12, 13].

There are two main methods for improving the removal of steroid estrogens: to optimise existing technology, for example activated sludge treatment, or upgrade existing WWTPs with novel end of pipe technology, including Advanced Oxidation Processes (AOPs) [8, 14]. Research has taken place into membrane bioreactors, ozonation, membrane filtration and activated carbon adsorption [8, 15]. However, these last two processes are highly energy and material intensive and currently cannot be effectively applied to a practical situation as they require relatively clean surface water or ground water with little natural organic matter [16].

AOPs and ozonation have been highlighted as more appropriate waste water treatment processes for pharmaceuticals, including contraceptive compounds, and for the oxidation of organic pollutants. These treatment processes can degrade pollutants through mineralisation or alter them to products that are less harmful to wildlife and the aquatic environment [24]. AOPs are characterized by the generation of hydroxyl radicals that involve different chemical agent combinations [6]. Example AOP combinations include O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>), photo- and electro-Fenton, chelating agent assisted Fenton/photo-Fenton, heterogeneous photo oxidation using titanium dioxide (TiO<sub>2</sub>/hν), γ-radiolysis, and sonolysis [16, 17].

This study will concentrate on the photo-Fenton reaction since Fenton-type processes have been found to be more effective than ozonation alone [16]. The Fenton reaction provides a powerful oxidant for contaminants through a reagent involving a mixture of ferrous iron (catalyst) and hydrogen peroxide (oxidising agent). The photo-Fenton process involves hydroxyl radical formation through photolysis of the hydrogen peroxide and Fenton reaction [18]. Given that the Fenton reaction is accelerated by light, the photo-Fenton reaction provides faster rates and potential for higher amounts of pollutant mineralisation [19]. This irradiation with UV light of the Fe<sup>3+</sup> ions (produced by the Fenton reaction, as shown in equation [1] in the presence of H<sub>2</sub>O<sub>2</sub> forms Fe<sup>2+</sup> ions with a hydroxyl radical as shown in equation [2] [20, 21, 22 ]. A continuous cycle between the Fe<sup>2+</sup> and Fe<sup>3+</sup> species is generated.

The use of UV light in the presence of hydrogen peroxide and an iron based catalyst would eliminate the need for continuous addition of iron. Although the Photo-Fenton reaction is a popular choice for pollutant mineralisation, its application requires a pH of less than 4 otherwise a reduction in the amount of iron in the system occurs as it is precipitated out producing an iron sludge.



Fenton Reaction



Photo-reduction of Fe<sup>3+</sup> ions



Oxidation of organic species RH

The organic ion exchange resin, Nafion, has been tested as an immobilisation technique or carrier for the iron and is also known to catalyse a wide range of reactions [23, 24]. Nafion is chemically inert and a realistic option for use in WWTPs, unlike strong homogeneous acid

catalysts [24, 25]. Its resistance to oxidative conditions and ability to form stable complexes with both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  prevents precipitation (leading to the iron sludge) at pHs higher than 4 and allows the Fenton reaction to occur at pH 7 (closer to that of WWTPs). Nafion is also transparent for UV radiation and is therefore suitable for use with the photo-Fenton reaction [26].

One disadvantage of Nafion is its low surface area. Several studies have shown the success of developing a new kind of solid Nafion catalyst by entrapping the resin particles in a highly porous silica matrix [23, 25, 27, 28]. The use of silica provides a large inter-surface for the catalytic reaction and better accessibility of the catalytically active acid sites by making the catalyst more porous [23, 29].

A previous study showed that using the sol-gel technique to produce the catalyst is most effective at optimising the materials listed above to create a catalyst suitable for xenobiotic chemicals with readily available active sites [25]. The sol-gel method used here follows previous studies [24, 28] and employs a gelation agent, the hydrolysis and polycondensation of alkoxides to form the gel, followed by aging and drying to give the solid catalyst. The two-step process reported by Kim *et al.* [28] refers to the acidic and alkaline environments being separated to allow more control of the reflux reaction [24]. PDMS acts as the gelation agent and has previously shown to add toughness and flexibility to the catalyst [30] by having a positive effect on the structural stability.

In this study, sol-gel technology will be used to produce a high surface area PDMS modified Nafion/silica composite suitable for catalysis of the photo-Fenton reaction without significant leaching of iron. One aim of this research is to develop a catalyst that did not produce an iron sludge from the photo-Fenton AOP and to see if that is reproducible for use in wastewater treatment. Therefore, the catalysts apply to degrade Estrone, 17- $\beta$ -estradiol, Estriol, and 17 $\alpha$ -ethynylestradiol.

## 2. Materials and Methods

### 2.1 Materials

All chemicals were used as received without further purification. The chemical reagents used for synthesis of the poly(dimethylsiloxane) modified Nafion/silica composite: Tetraethoxysilane (TEOS) (Fisher Scientific) was used as a precursor of silica. Hydroxy terminated poly(dimethylsiloxane) (PDMS) (Sigma-Aldrich) with average molecular weight of 550 was used as a structure modifier, elastomer. Nafion oligomer (5 wt. % in lower aliphatic alcohols and water, contains 15-20% water) (Sigma-Aldrich) was used as an iron species carrier for Photo-Fenton reaction. Iron (II) chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) (Laboratory FSA Supplies) was used as a source of iron species. Isopropanol (IPA) and tetrahydrofuran (THF) were used as mutual solvents for dissolving TESO, PDMS and Nafion polymers. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for catalysing hydrolysis and condensation, respectively.

Estrone (E1), 17 $\beta$ -estradiol (E2), estriol (E3) (purity $\geq$ 97%) and 17- $\alpha$ -ethynylestradiol (EE2) (purity $\geq$ 98%) were obtained from Sigma-Aldrich. For the HPLC analyses acetonitrile (E Chromasolv<sup>®</sup> for HPLC, far UV) was supplied by Riedel-de Haën. Ultra high purity water for all experiments and analyses was produced by a NANOpure Diamond UV water purification

system that provides bacteria free water of  $18.2\Omega\text{cm}^{-1}$  resistivity with less than 1 ppb total organic carbon.

### 2.1.1 Synthesis of Catalyst

The uses of each chemical in the production of the catalyst and its source are listed below: Hydroxyl terminated Polydimethylsiloxane (PDMS) (average Mr 550): Used as a structure modifier. Tetraethylorthosilicate (TEOS): Used as a soluble silica precursor/to form silica in the catalyst [23, 31]. Tetrahydrofuran (THF) and Isopropanol/propan-2-ol (IPA): Mutual solvents for dissolving the polymers Nafion, PDMS and TEOS. Hydrochloric Acid (HCl): Catalysed hydrolysis Sodium Hydroxide (NaOH): Catalysed condensation leading to gelation [25]. Anhydrous iron chloride ( $\text{FeCl}_2$ ): A source of iron species. Nafion: To support the iron species and act as an iron species carrier for the Photo-Fenton reaction [31]. All the chemicals required for the catalyst synthesis were used as received. The following method and molar ratios were based on the previous work to produce a poly(dimethylsiloxane) modified Nafion/silica sol-gel composite catalyst for the removal of pesticides and the degradation of azo-indigo carmine solution. Fixed molar ratio of TEOS:THF:IPA:HCl = 1:1:4:0.03,  $\text{SiO}_2$ :PDMS = 9:1, Nafion:Fe = 1:1.5, NaOH:THF = 0.15:1 and TEOS:THF:H<sub>2</sub>O = 1:1:3 were used.

The PDMS was dissolved in THF, then mixed with TEOS and heated up to 30°C for 5 minutes. Water, 1M HCl and IPA are added and the resulting solution is then brought to reflux for 60 minutes at 30°C. Anhydrous  $\text{FeCl}_2$  was mixed with 5 wt. % Nafion resin solution at 30°C for 5 minutes. An ultrasonic treatment was then performed on this solution for 30 minutes to ensure uniform dispersion of the Nafion polymer and iron. The refluxed solution was added to the ultrasonic treatment solution. This was continuously stirred whilst 5M NaOH solution was added drop by drop. The mixture soon became an off-white colour and gelled to form a solid mass. This was transferred to a watch glass and left in a fume cupboard overnight where it dried and cracked to form uneven sized, solid pellets. This was then dried in a Memmert fresh air oven at a temperature of 50°C for one hour, then at 100°C for another hour to remove any excess solvents. The catalyst was ground to powder before being used. Scanning Electron Microscope technology (SEM) and was used to analyse the catalyst morphology. Energy-Dispersive X-ray Spectroscopy (EDX) used for elemental analysis of the sample and chemical characterisation.

### 2.2. Experimental procedures

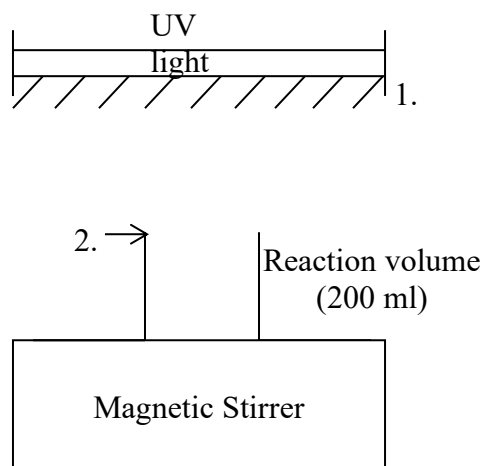
Stock solutions of E1, E2, EE2 and E3 in acetonitrile at 10mg/L were freshly prepared due to the poor solubility of the estrogens in water. They were diluted with ultrapure water to the desired concentration required for each experiment and or analysis. Estrogen experiments took place at natural pH ( $\approx 4.9$ ). Initially 0.1 mg/L estrogens were used. The amount of catalyst and H<sub>2</sub>O<sub>2</sub> were varied during experiments. Samples were taken at appropriate time intervals, solid phase extraction was used to concentrate and purify the samples so high performance liquid chromatography analysis could be used to quantify the amount of estrogen present calibration curves.

The photocatalytic reactions were set up, as shown in Figure 2, in a 100 ml reaction volume with a 2 cm stirrer. Three Phillips UV lamps were used as a light source the oxidation reaction, the measured intensities are shown in

Table 1. The UV lamps were only turned on desired of Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) had been added.

**Table 1. UV intensity**

Position	UVA intensity (W/m <sup>2</sup> )	UVC intensity (W/m <sup>2</sup> )
1	33.4	32
2	19.45	26

**Figure 2: Experimental set-up**

## 2.3 Analytical Techniques

### 2.3.1 Solid Phase Extraction (SPE)

The estrogen sample was filtered to remove any catalyst through 0.22 $\mu$ m, 33mm Millipore GP filter units. The Oasis<sup>®</sup> SPE Method for estrogens in river water (endocrine disruptors) reported by Waters was used and is shown in appendix B. OASIS<sup>®</sup> HLB, 3 cc, 200 mg cartridges were connected to Supelco visiprep<sup>™</sup> vacuum manifold system with a Gast vacuum pump, to increase the solvent flow rate via the valves. The conditioning and wash steps described by Li Puma et al. [5] were followed. The cartridges were conditioned (all solvent drawn through cartridges) with 3 mL methyl-tert-butyl-ether (MTBE). They were then washed with 3mL methanol, followed by 3 mL water. 10 mL of sample was loaded to the cartridges, the flowrate was then adjusted to one drop per second, to ensure the estrogens had as much contact time with the cartridges as possible, and a second wash step of 3 mL 5% methanol in H<sub>2</sub>O took place. The cartridges were then left to dry overnight. Elution into clean test tubes with 6mL 10% methanol in MTBE took then occurred. This elute was evaporated to dryness with nitrogen gas. After being increased to a final volume of 1 mL by 43% acetonitrile, 57% water, this was transferred to HPLC vials for analysis.

### 2.3.2 Iron detection

1,10-Phenanthroline: Reacts with ferrous ions to form a red complex to allow colorimetric detection as a method of determination of iron [32, 33]. Hydroxylamine hydrochloride: The iron must be in a ferrous state; therefore hydroxylamine hydrochloride is used as a reducing agent. Sodium acetate was used to control pH. Iron leaching from the composite was determined by colorimetric detection using the spectrophotometer at wavelength of 508nm. 1 mL hydroxylamine hydrochloride was added to 25 mL solution samples that had been filtered through a Millipore 0.22  $\mu$ m filter. 10 mL of 1,10-phenanthroline was reacted with the samples

to form a red complex and then 8 mL sodium acetate added to each. Each sample was diluted to 100 mL with distilled water and left for 10 minutes. The absorbance was then recorded and any iron concentration calculated from a calibration curve.

### 2.3.3 High Performance Liquid Chromatography

All the HPLC solvents were vacuum filtered prior to use. HPLC system (Agilent 1100 series) comprised a diode array detector a mobile phase degassing unit and an autosampler. HPLC was used to analyse the concentration of estrogen compounds and to track their degradation. The HPLC system used was a SUPELCO<sup>TM</sup> LC-8 58297-53777-05 250 mm x 4.6 mm x 5  $\mu$ m column and had an injection volume of 10  $\mu$ l. The conditions were: the mobile phase comprised 43% Water, 57% Acetonitrile; the flow rate was set at 1 mL/min; column temperature of 15°C and detector wavelengths 200 and 280nm. These parameters followed those used in multiple studies using this group of estrogens [5].

### 2.3.4 H<sub>2</sub>O<sub>2</sub> analysis

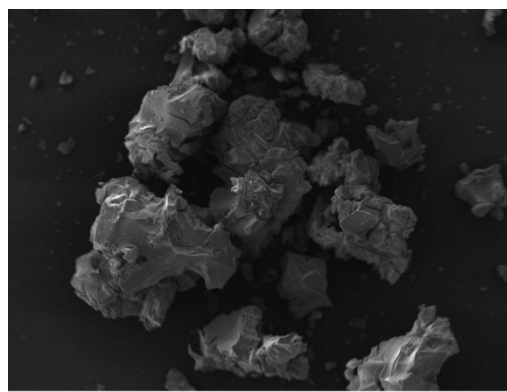
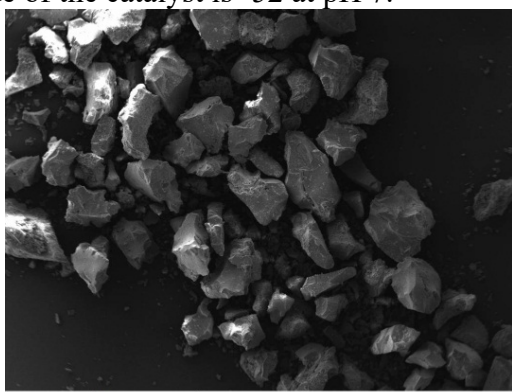
The concentration of any remaining H<sub>2</sub>O<sub>2</sub> was measured using Quantofix peroxide 25 test sticks for 0.5 – 25 mg/l H<sub>2</sub>O<sub>2</sub>, sourced from Sigma Aldrich, UK.

## 3. Results and Discussions

In the first part of the experimental study the aim was to determine characterisations of the catalyst. For this reason SEM, EDX and BET surface area and Zeta potential determinations was done.

### 3.1 Catalyst Characterisation Results

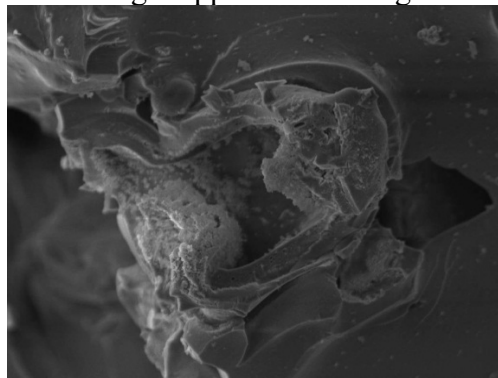
During catalyst preparation, the solution remained colourless whilst PDMS, TEOS, IPA and THF were mixed together but this clarity decreased after the addition of water due to the hydrophobic properties of both PDMS and TEOS. At the end point of the hydrolysis of TEOS however, the mixture was colourless/clear again. A brown precipitate formed when the Nafion resin solution was added to the FeCl<sub>2</sub> and after addition of this to the colourless solution, a yellowish mixture formed. Gelation began immediately after the gelating agent (NaOH) was added, forming a hard gel. After drying overnight and thermal treatment, a powdery composite that cracked into pellets, shown in Figure 3 and Figure 4, was formed. Following the method described earlier, approximately 12 g (ambient weight) of catalyst was formed each time. The BET surface area of the catalyst is 95 m<sup>2</sup>/g. According to zeta potential measurements the zeta value of the catalyst is -52 at pH 7.



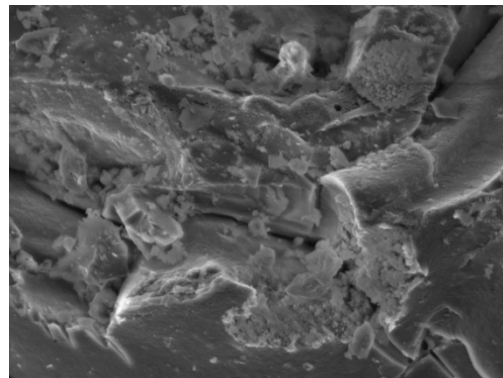
**Figure 3: SEM image of catalyst**

**Figure 4: Higher resolution SEM image of catalyst**

SEM technology showed the catalyst's characteristics and surface morphology. The catalyst was found to be very porous but did not have a very uniform morphology as can be seen by the 'areas of damage' apparent from Figure 5 and Figure 6.



**Figure 5: SEM image of damage area on catalyst**



**Figure 6: Higher resolution SEM image of damage area**

The EDX elemental analysis, seen in Table 2, estimates the weight percentage of iron in the catalyst. Although the percentage weights are extremely low, the composite was fixed at 4 wt% Nafion; the theoretical value is only 0.15% for the iron fully loaded on the Nafion oligomer in composite. The variance and lack of iron in one spectrum could be due to the iron forming as clusters on the silica supported Nafion matrix.

**Table 2. EDX results**

Element	Spectrum 1		Spectrum 2		Spectrum 3	
	Wt%	$\sigma$	Wt%	$\sigma$	Wt%	$\sigma$
O	46.5	0.4	51.9	0.4	49.6	0.5
Si	27.7	0.2	24.6	0.2	25.8	0.3
C	14.6	0.5	11.9	0.6	15.3	0.6
F	5.7	0.2	2.7	0.1	4.1	0.3
Na	3.9	0.1	7.8	0.0	3.1	0.1
Cl	1.4	0.0	1.1	0.0	2.0	0.1
Fe	0.1	0.0	-	-	0.2	0.1

## 3.2 Estrogens Experiments

### 3.2.1 Calibration curves

The analyzes retention times were 3.7 min for E3, 4.9 min for E2, 5.5 min for EE2 and 6.6 min for E1. Calibration of the HPLC chromatographic peaks against standards of the estrogens in acetonitrile resulted in a linear response in the range of concentrations investigated (0.01 – 0.1mg/L). The smallest quantifiable chromatographic peak after SPE corresponded to approximately 0.01mg/L for each estrogens. Identification of the sample was done by identifying the retention time of standard solutions. All samples injected and analyzed three times and mean values of the results were given.

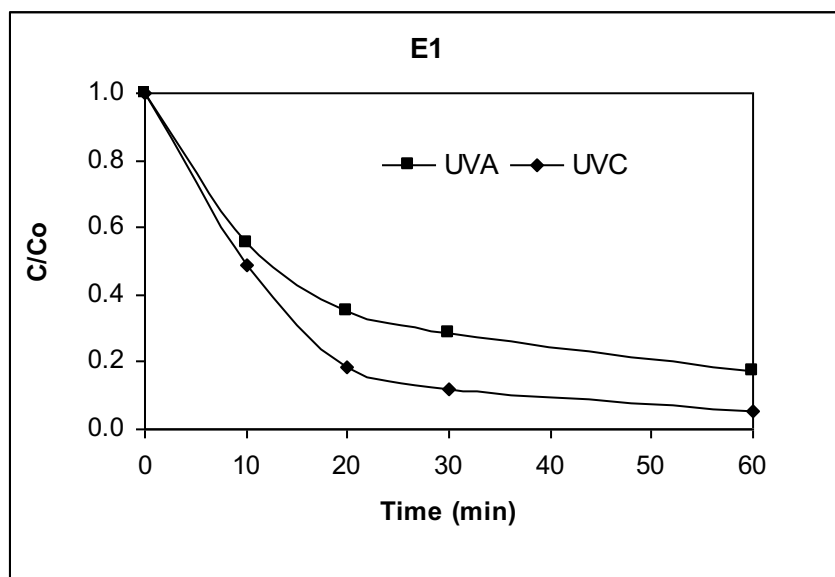


Calibration curves were plotted from integrating the peaks from chromatographs of five known concentrations of estrogens.  $R^2$  values show the accuracy of the calibration curve and therefore their reliability. The high correlation coefficient value of all the calibration curves suggests that the SPE followed by HPLC analysis is an accurate method of quantifying estrogen concentrations.  $R^2$  was 0.9931 for E1, 0.9951 for E2, 0.9845 for EE2 and 0.9813 for E3.

### 3.2.2 Degradation of EDCs

Initial experiments were done to confirm that the composite was catalysing the photo-Fenton reaction. A series of experiments were conducted to see the effect of catalyst for oxidation and adsorption. These experiments were carried out in the presence and absence of UV light. The adsorption effect was limited to 5%. All show minimal change confirming that without the presence of  $H_2O_2$  and UV light, the composite does not catalyse the photo-Fenton reaction and degrade the E1. Final experiment evaluated the ability of  $H_2O_2$  to degrade E1 which was negligible compared to with the Fenton catalyst, possibly due to the high oxidation potential of the hydroxyl radicals formed due to the iron present in the catalyst. From the results, it is clear that the composite effectively catalyses the photo-Fenton reaction to remove estrogens. The presence of iron through the use of the catalyst leads to rapid degradation of the estrogens compared to just  $H_2O_2$  and UV light alone [34].

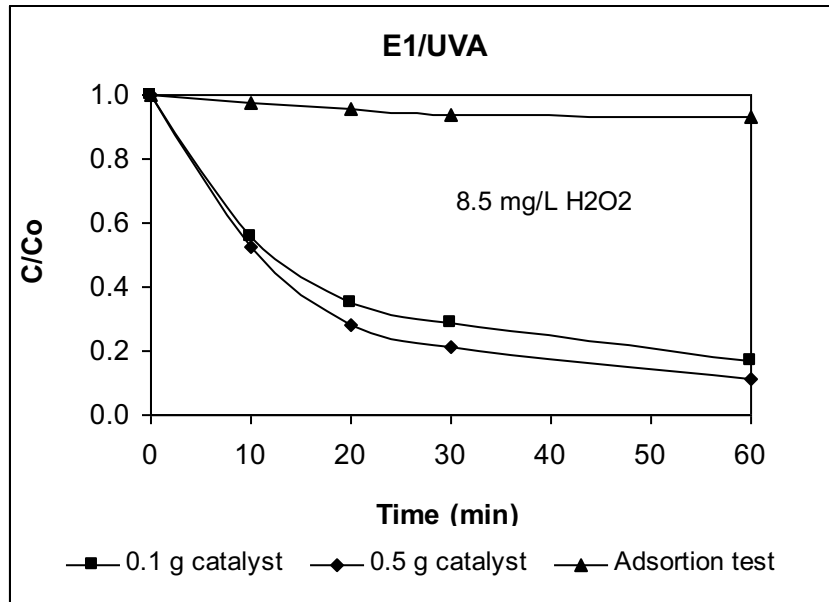
At the beginning of the degradation studies of estrogens, it was tried to find out the effects of UVA and UVC. The rates of photocatalytic degradation of the estrogens under irradiation of 0.1g catalyst and 8.5 mg/L  $H_2O_2$  with UVC were much higher than the rates under UVA photolysis (Figure 7). Therefore, UVC radiations were chosen for further studies. The faster degradation of the estrogens under UVC irradiation can be explained by their much stronger absorption of photons in the UVC region of the electromagnetic spectrum [5]. These experiments clearly demonstrated the limitation of only UV-based oxidation processes, where absorption of light is the most important step to initiate the photolysis and subsequent photooxidation [35].



**Figure 7: Degradation of 0.1mg/L E1 under UVA and UVC lights**

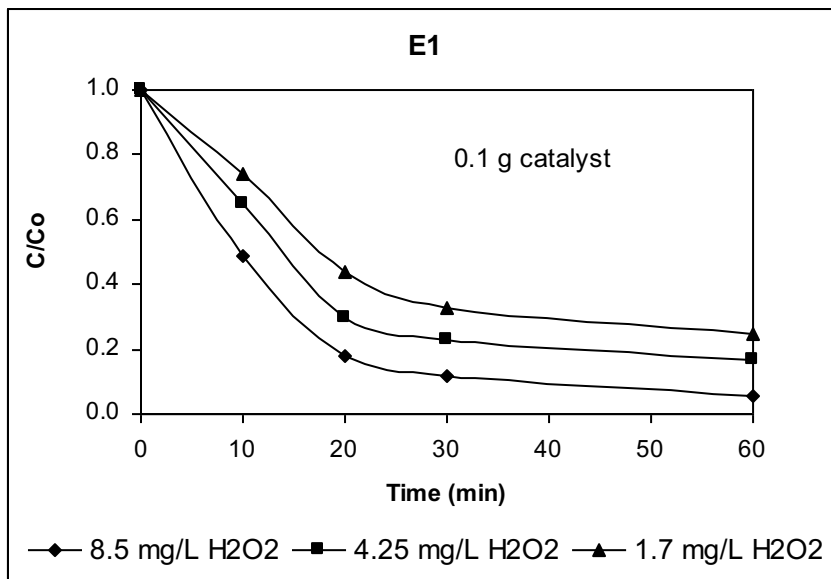
The rapid rate of degradation can be clearly seen showing that the composite effectively catalyses the photo-Fenton reaction to remove estrone. There was no significant difference

between 0.1 g and 0.5 g catalyst concentrations (Figure 8) on the removal efficiency. For this reason 0.1 g catalyst concentration was chosen as the optimum catalyst concentrations. It is clear from the similar rates of degradation that in this situation, the amount of catalyst is not the limiting factor.



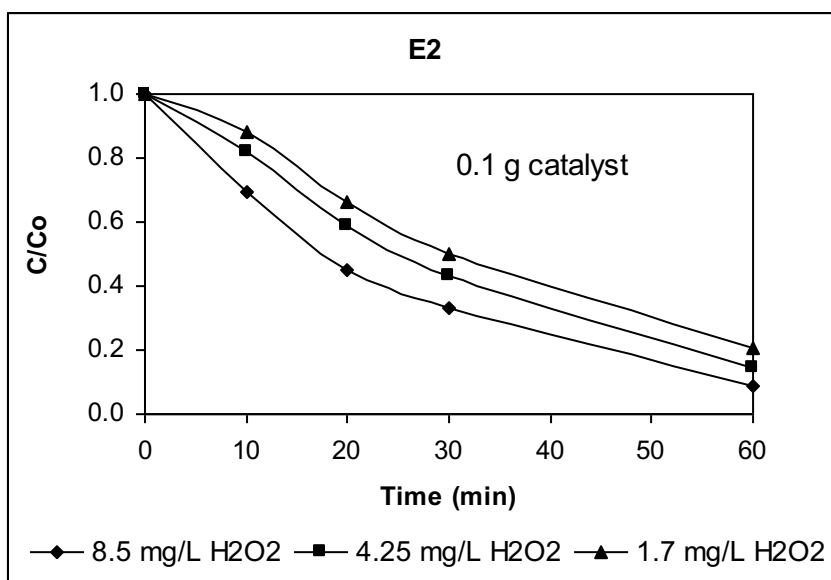
**Figure 8: Rate of degradation of E1 ( $C_0 = 0.1\text{mg/L}$ )**

Iron leaching analysis were applied after each experimental studies. Experiments shows that the leached iron is a very minimal/limited amount, the small absorbance values measured and the fact that the catalyst was able to be re-used more than once led to the conclusion that a minimal amount of iron leaches. The same experiments were repeated three times in succession to determine the availability of the catalyst and effects on the catalyst yield were observed. The catalyst used during these three experiments was filtered, dried and reused. At the end of the third experiment, the treatment yield was found to be reduced by about 20%. Non-quantifiable methods confirmed that iron leaching did occur, however, even extremely small amounts of iron are able to produce hydroxyl radicals in the presence H<sub>2</sub>O<sub>2</sub> [36] and using the calibration curve the highest iron leaching quantity was 0.4 mg/l. These experiments highlighted the improved method for producing a more effective catalyst due to much faster degradation rates. The reaction is not linear and follows previous research [5], although the degradation experienced with this catalyst is much faster.



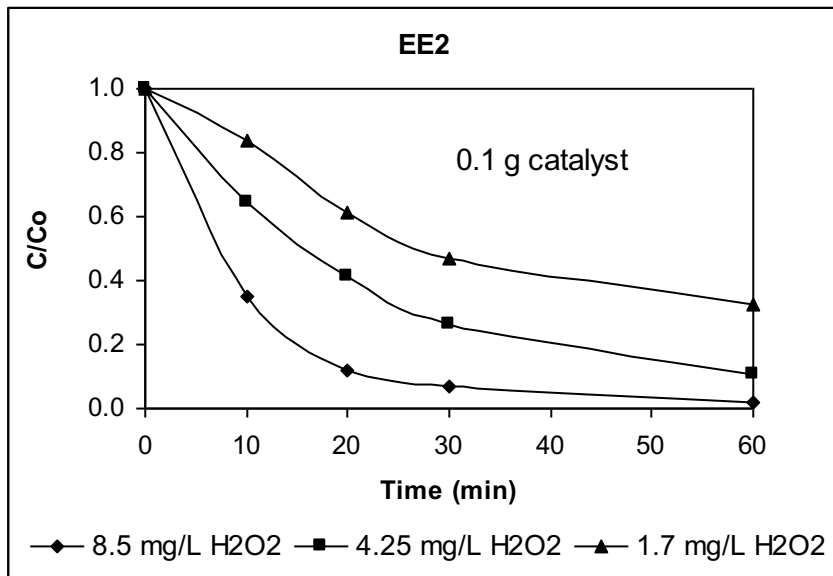
**Figure 9: Degradation changes of E1 for different H<sub>2</sub>O<sub>2</sub> concentrations under UVC light**

In order to determine the effect of H<sub>2</sub>O<sub>2</sub> on estrogen removal efficiencies three different H<sub>2</sub>O<sub>2</sub> concentrations were used with the addition of constant catalysts concentration, 0.1g. Maximum E1 removal efficiency was obtained as 95% in 60 min at a H<sub>2</sub>O<sub>2</sub> concentration of 8.5 mg/L and a catalyst concentration of 0.1g under UCV light. Figure 9 shows the degradation rates changes of E1 for different H<sub>2</sub>O<sub>2</sub> concentrations. The removal efficiency of E1 was only 70% with addition of 1.7 mg/L H<sub>2</sub>O<sub>2</sub>. It was obvious that the H<sub>2</sub>O<sub>2</sub> concentration is very effective on the removal of estrogens. The maximum E2 removal efficiency also obtained with the addition of the maximum H<sub>2</sub>O<sub>2</sub> concentration (8.5 mg/L) (Figure 10).



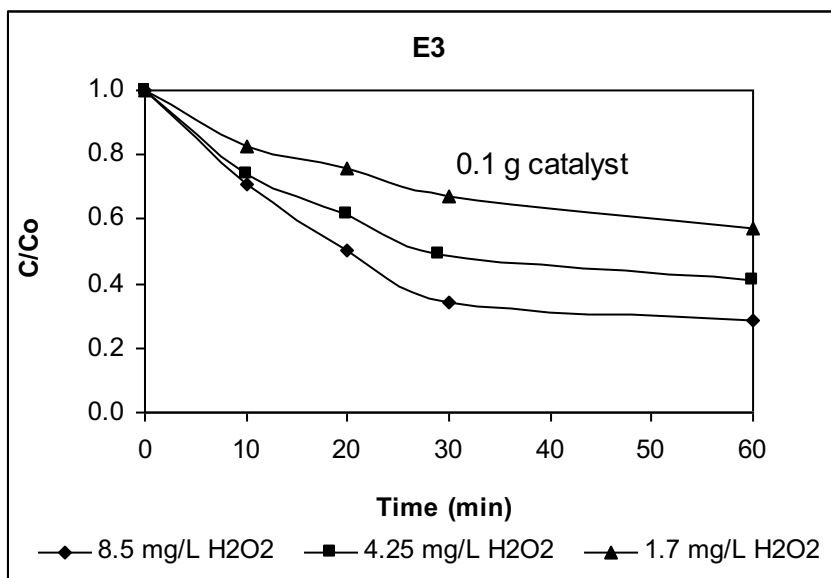
**Figure 10: Degradation changes of E2 for different H<sub>2</sub>O<sub>2</sub> concentrations under UVC light**

Figure 11 shows the degradation changes of EE2 with the addition of different H<sub>2</sub>O<sub>2</sub> concentrations. The effect of the H<sub>2</sub>O<sub>2</sub> concentrations on the removal efficiency of EE2 was higher than the E1 and E2. 98% removal efficiency was obtained with the addition of the 8.5 mg/L H<sub>2</sub>O<sub>2</sub>.



**Figure 11: Degradation changes of EE2 for different H<sub>2</sub>O<sub>2</sub> concentrations under UVC light**

The maximum removal efficiency of E3 (Figure 12) was only 70% with the highest H<sub>2</sub>O<sub>2</sub> addition. The removal efficiency of E3 is less than other estrogens. Similarly Li Puma et.al [5] was found that the degradation sequence with a multi component solution of estrogens, follows the sequence E1 > EE2 > E2 > E3.



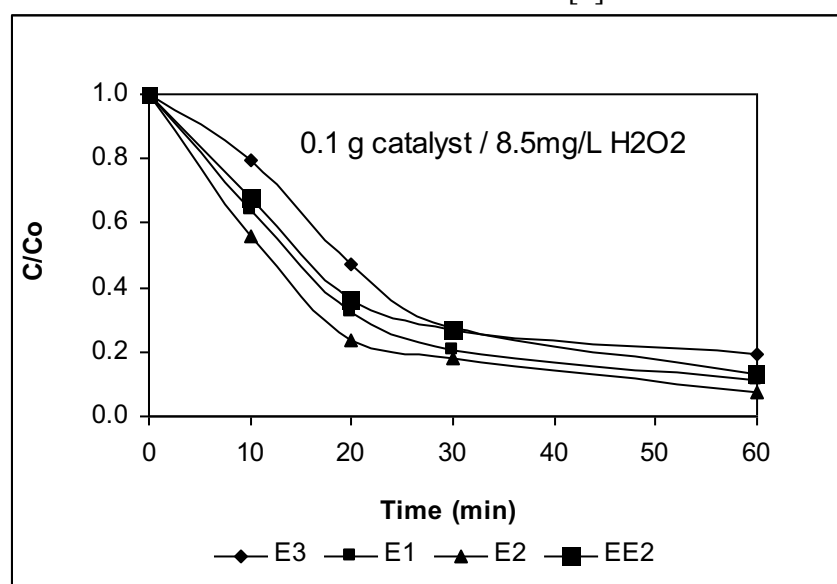
**Figure 12: Degradation changes of E3 for different H<sub>2</sub>O<sub>2</sub> concentrations under UVC light**

### 3.2.3 Degradation of Mixture of Estrogens

There is a tendency to focus solely on the primary individual usually involves multiple chemicals in EDC mixtures [37]. Mixture constituents can act via common modes of action, or by a variety of signal transduction pathways which might crosstalk or produce other matrix effects. "Combination effects" occur when synthetic EDCs interact with each other, or with

natural compounds in the environment and in the body, and they can have additive, synergistic or attenuative potential. When combined in a mixture, individual chemicals can contribute to toxicity in direct proportion to their potency and concentration, even if they are each present at a concentration below their individual effect thresholds. This phenomenon is termed “something from nothing”. Experimental evidence shows that the cumulative impact of EDCs remains poorly understood, in part because traditional dose–response testing neglects the potential mixture effects not seen in single chemical testing. Only a better understanding of real-life combined exposures can determine whether risk is amplified by exposure to mixtures. For this reason to see the combination effects on EDC oxidation, initial concentration of 0.1 mg/L of EDCs were mixed and oxidised under UVC light.

As can be seen from Figure 13 there was no significance effects of the mixture of estrogens. The maximum removal efficiency obtained for E2 and it was 92% for the mixture of EDCs. These results are much better than Li-Puma [5] obtained before.



**Figure 13: Degradation changes of mixed estrogens under UVC light**

### 3.2.4 Effect of Humic Acid

Natural organic matter (NOM) is a complex heterogeneous aggregate of organic compounds defined as decaying material from plants, animals and their degradation products in terrestrial environments as well as in aquatic systems. It has been known that NOM shows important impacts on energy and carbon dynamics [38]. Dissolved organic carbon (DOC) components in aquatic systems have display high reactivity and influence ecosystem functions over many biogeochemical reactions, with metal ions and hydrous metal oxides. In aquatic system, one of the natural DOC material is Humic substances (HSs) mainly humic acids (HAs). Natural Organic Meters has known as an oxidant scavenger. Hence it was determined the effect of the HAs.

From the literature [38] the humic acid concentrations were chosen as 10, 20, 30, 40 and 50 mg/L. But even if with the addition of 10mg/L humic acid to the mixture of estrogens the removal efficiencies decreased approximately 10-15% (Figure 14). And also,  $UV_{254}$  and  $Color_{436}$  were measured to determine the removal efficiency of the humic acid. 70%  $Color_{436}$  and 50%  $UV_{254}$  removal efficiencies were obtained. To further reduce parent compounds and oxidation by-products, biological post-filtration (sand filtration or activated carbon filtration)

can be considered [39]. It was reported that when UVC was combined with  $H_2O_2$ , natural organic matter could not be mineralized [37]. For some limited number of experiments TOC was measured after a long experimental time. It was seen that for ozonation (1.31 mg/L), TOC removal was about 85% after 500 min (8.33 h), while for UV/ $H_2O_2$  it was only 65% for the same time [42].

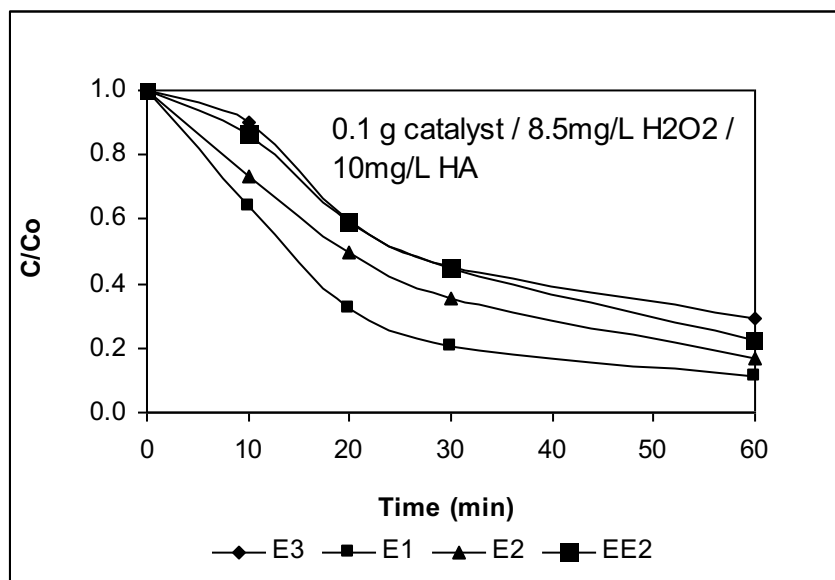


Figure 14: Effect of Humic Acid

### 3.2.5 Effect of Radical Scavengers

Wastewaters and natural water systems contain a variety of organic and inorganic contaminants that inhibit with oxidation reactions of ( $\bullet OH$ ) Hydroxyl radicals. The inorganic anions such as carbonate, bicarbonate and chloride are known as  $\bullet OH$  scavengers. Carbonate and bicarbonate ions are commonly exists in natural waters whereas chloride founds in high concentrations in some industrial wastewaters (such as; tannery and dye manufacturing wastewaters).

Carbonate, bicarbonate and chloride are known as hydroxyl radical scavengers; consequently, their excess concentration is expected to adversely affect AOP treatment efficiency. And also, the presence of  $CO_3^{2-}$  and  $HCO_3^-$  in solution also interferes with  $H_2O_2$  for UV light, decreasing the fraction it normally absorbs. This causes, in turn slows down the rate of hydroxyl radical generation. It was observable from the literature [40, 41]  $CO_3^{2-}$  is 45 times more reactive with  $\bullet OH$  than  $HCO_3^-$ , therefore is more important retardant of the oxidation process. Considering this information we have just examined the effect of  $CO_3^{2-}$  on the removal of estrogens mixtures. It was found that higher content of carbonate ions led to higher residuals of estrogens in the effluent. When 1, 2.5, 5, and 10mM  $CO_3^{2-}$  were added to the solution, the removal efficiencies of estrogens decreased between 10% and 40%.

### 3.2.6 Degradation kinetics of estrogens

The degradation of estrogens follows apparent first-order kinetics. Under UVC irradiation, the rate of degradation of estrogens in the mixture increased significantly. The faster degradation

of the estrogens under UVC irradiation can be explained by their much stronger absorption of photons in the UVC region of the electromagnetic spectrum.

**Table 3. Reaction rate constants of estrogens photooxidation in the presence of catalyst**

	E1	E2	EE2	E3
R <sup>2</sup>	0.904	0.998	0.936	0.911
k <sub>1</sub> (min <sup>-1</sup> )	0.048	0.041	0.064	0.022

According to the first order reaction rate constants EE2 degradation was faster than the others EE2 > E1 > E2 > E3 and also removal efficiency of EE2 (%98) was higher than the other estrogens (Table 3). Similarly, in another work with immobilized TiO<sub>2</sub> on titanium alloy in which mass-transfer limitations may have occurred, the degradation rate under UVA photolysis was found to be EE2 > E1 > E2 [5]. In another study, the treatment of EE2 using commercially available TiO<sub>2</sub> suspensions (P25) with a conventional UV lamp was used. EE2 removals using P25 suspensions indicate first-order kinetics with rate constant corresponding to 62 × 10<sup>-3</sup> 1/min [43]. This results is almost the same rate with our study.

In the literature, comparing with UV treatment alone, UV and H<sub>2</sub>O<sub>2</sub> (50 mg/L) exhibited elevated transformation (a total degradation of 81%) of the micropollutants [41]. After 30 min of UV/H<sub>2</sub>O<sub>2</sub>, the transformation increased further up to 97%. Fenton process (5 mg/L Fe<sup>2+</sup>,<sup>3+</sup>/50 mg/L H<sub>2</sub>O<sub>2</sub>) achieved 31% degradation. It was able to completely eliminate only one of the micropollutants, norfloxacin, after 30 min, and the concentrations of ten compounds were reduced by less than 15%. When UV was applied to the Fenton process (under the same conditions mentioned above), significantly increased global degradation (97%) was observed. For the photo-Fenton process, either increased H<sub>2</sub>O<sub>2</sub> dosage or extended reaction time was found to have positive impact on the global degradation [41]. In our study, we used far less than from the literature H<sub>2</sub>O<sub>2</sub> and catalyst concentration.

#### 4. Conclusion and Comments

One aim of this research was to develop a catalyst that did not produce an iron sludge from the photo-Fenton AOP and that was reproducible for use in wastewater treatment. The catalyst under UV irradiation were tested for their ability to photocatalytically degrade target estrogenic compounds. Experiments shows that the leached iron is a very minimal/limited amount, the small absorbance values measured and the fact that the catalyst was able to be re-used more than once led to the conclusion that a minimal amount of iron leaches. The same experiments were repeated three times in succession to determine the availability of the catalyst and effects on the catalyst yield were observed. Another aim was to discover the ability of the Poly(dimethylsiloxane) modified Nafion/Silica composite to catalyse a reaction to degrade estrogens. It was found that near 90% complete degradation of this environmentally significant pollutant was possible within 60 minutes. The study showed that the UV irradiated catalyst with H<sub>2</sub>O<sub>2</sub> have the potential for treatment (removal) of these compounds. The data shows that the addition of only 0.1 g catalyst and 8.5 mg/L H<sub>2</sub>O<sub>2</sub> produced greatest conversion of estrogens within 60 minutes.

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