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Removal of endocrine disrupting chemicals in wastewater treatment applications

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Removal of Endocrine Disrupting Chemicals in Wastewater Treatment Applications

By

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by Portfolio

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I am grateful to God Almighty for his strength and infinite mercies during this period. To my wife, Lucia and kids Sharon, James and Elliot thank you for your understanding when work kept me away.

I would like to thank Severn Trent Water for the opportunity and support I received from them throughout the research and to my former colleagues in T&D particularly John Churchly my R&D Manager.

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Dedication

I wish to dedicate this work to the memory of my late father who passed away to the great beyond on Monday 25th March 2013.

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Chapter One

Introduction

1.1 Background

This critical overview document (COD) presents, discusses and brings together the selected portfolio of publications that the author believes make a significant contribution to the field of wastewater treatment, focusing on the removal of endocrine disrupting chemicals (EDCs) in wastewater treatment applications.

There have been concerns by the scientific community of the effects of EDCs in the environment (Desbrow *et al*., 1998; Snyder *et al*., 2001). EDCs are compounds that mimic normal hormonal functions when absorbed into the body. They can induce aquatic toxicity at parts per trillion levels (ng/l). The Organisation of Economic and Corporative Development (OECD) defined EDCs as "exogenous substances that alter the function of the endocrine system and consequently causes adverse health effects in an intact organism or its progeny". They enter the water environment mainly through industrial and wastewater discharges. Their occurrence in wastewater treatment plant (WWTP) effluents is well documented worldwide (Reddy *et al*., 2005; Nakada *et al*., 2006; Gomez *et al.,* 2007; Miege *et al*., 2009; Gabet-Giraud *et al*., 2010; Plosz *et al*., 2010; Rosal *et al*., 2010; Ifelebuegu, 2011). Effluent discharges from WWTPs can produce 'feminising' effects or estrogenic responses in fish (Jobling *et al*., 1998a). Vitellogenin, an egg yolk protein produced and found in the blood of sexually matured female fish, have been found in male fish exposed to effluent discharges of WWTPs (Purdom *et al*., 1994; Sumpter and Jobling, 1995; Jobling *et al*., 1998a, b).

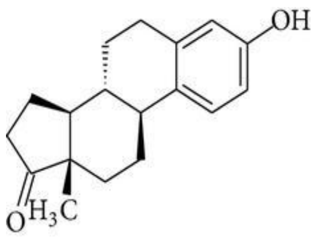
The natural steroid hormones estrone (E1), 17-beta-estradiol (E2) and estriol (E3) are responsible for the development and functioning of female sex organs. They are secreted naturally by females primarily in urine in conjugated form as estrogen glucuronides, sulphates and sulfonides, making them initially inactive as hormones (Guengerich, 1990). They are, however, deconjugated and released as free hormones due to microbial activity in sewers and wastewater treatment plants (Ternes *et al*., 1999a, b; Panter *et al*., 1999). The synthetic steroid hormone 17-alpha ethinylestradiol (EE2) is used in female contraceptives and in hormone replacement therapy. It is also regularly found in wastewater effluent. The steroid hormones (natural and synthetic) have been reported to be the most potent of the EDCs (Desbrow *et al*., 1998; Jobling *et al*., 1998a; Birkett and Lester, 2003). EE2 has been found to have the greatest impact in terms of feminisation of fishes even though it is usually found in the lowest concentration in wastewater effluent among the steroid estrogens (Jurgen *et al*., 2002). E2 is next to EE2 in estrongenicity, closely followed by E1, with E3 being less potent and less of a problem to aquatic organisms (Baronti *et al*., 2000: Metcalfe *et al*., 2001).

Alkyphenols polyethoxylates and their metabolites are another class of EDCs known to cause endocrine disruption in aquatic organisms. They are non ionic surfactants that get into the environment through domestic and industrial discharges. The most widely used ethoxylate derivatives are nonylphenol (NP), and octylphenol (OP). They are active ingredients in detergents, pesticides, wetting agents, emulsifiers, lubricants and many cosmetic products.

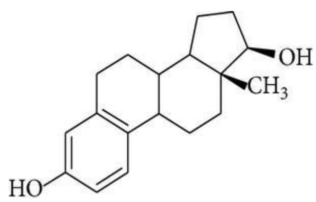
1.2 Research Context

This work represents the author's research interest over an eight years period mainly shaped by his experience in the water industry and in academia. As part of the author's industry experiences, he was involved in designing and operating the pilot and small scale EDCs treatment plants in Ilkeston, Derbyshire, UK, which were part of DEFRA's £40 million National Demonstration Programme (NDP) on EDCs removal in wastewater treatment plants in England and Wales between 2005 and 2008. The author also led various sampling campaigns for EDCs monitoring in the West Midlands, UK. The research papers presented in this portfolio were shaped by the experiences and expertise acquired during the Ilkeston NDP and West Midlands sampling campaigns.

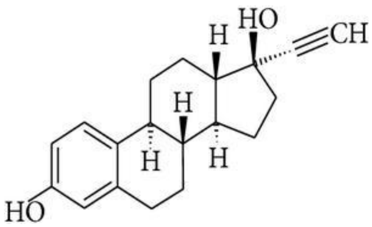
The papers in this portfolio are focused on the steroid hormones (E1, E2 and EE2) and alkylphenols (NP). Their chemical structures are shown in Figure 1. These EDCs are known to be recalcitrant to conventional wastewater treatment processes that are typically used for the removal of sanitary parameters such as BOD, chemical oxygen demand, solids and ammonia (Ternes *et al*., 2002). Due to the public concerns and increasing evidence of the health implications of EDCs on aquatic organism and humans, the EU has proposed to regulate the discharge of these chemicals into environmental waters through the Water Framework Directive 2000/60/EC, which establishes a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater. EU Member States are required to take action to prevent human exposure to priority hazardous substances, particularly the EDCs (Annex VIII-group 4). Also the US Environmental Protection Agency since 1985 has classified EDCs as Contaminants of Emerging Concern.



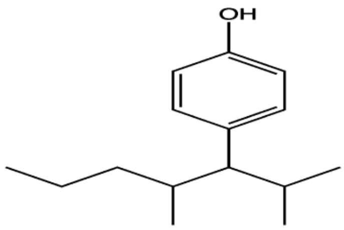
(a) Estrone (E1)



(b) 17-beta-estradiol (E2)



(c)17-alpha ethinylestrodiol (EE2)



(d) Nonylphenol (NP)

Figure 1- Chemical Structures of E1, E2, EE2 and NP (Sigma Aldrich)

The water industry is thus faced with the challenge to better understand the mechanisms and methods of removal of EDCs to be able to proffer cost effective solutions for their removal in wastewater treatment. The research papers included in this portfolio investigated the behaviour and fate of selected EDCs in the wastewater and sludge treatment applications to offer a better understanding of the mechanism of removal in treatment plants, which can inform decisions during process optimisation. Also included are alternative treatment methods including advanced chemical oxidation processes and activated carbon adsorption.

1.3 Research Aim and Objectives

The aim of the research within this COD was to investigate the fate, mechanisms and optimisation of EDCs removal in wastewater treatment applications.

The key objectives were to:

1. Investigate and understand the mechanisms of removal of EDCs in wastewater and sludge treatment processes.
2. Evaluate novel methods for the removal of EDCs in water and wastewater treatment applications.
3. Establish the kinetic and thermodynamic properties of the removal processes to inform process modelling of full scale design of treatment processes.

1.4 Overview of Portfolio

This portfolio is made up of six peer-reviewed journal publications (Table 1 and Appendix 3). The portfolio Outputs are linked by developing a continuing theme on the removal of EDCs in water and wastewater treatment applications by physical, chemical and biological methods. While it was important to put together a portfolio that meets the requirements, including demonstrating a significant contribution to knowledge, it was also important that the Outputs represented a coherent body of work. The body of work put together in this portfolio, is therefore, a selection of the professional and academic work that the author has been involved in over several years in both the domestic and international arena. Table 1 show all the articles contained in the portfolio and Figure 2 depicts an overview of EDCs removal methods showing the interrelationships between the Outputs.

Table 1 Outputs contained in the Portfolio

Output No	Citation
1	Ifelebuegu, A.O., Lester, J.N., Churchley, J. and Cartmell, E. (2006) Removal of an endocrine disrupting chemical (17alpha-ethinyloestradiol) from wastewater effluent by activated carbon adsorption: effects of activated carbon type and competitive adsorption. Journal of Environmental Technology, 27, 1343-1349.
2	Ifelebuegu, A. O., Theophilus, S. C., and Bateman, M. J. (2010) Mechanistic evaluation of the sorption properties of endocrine disrupting chemicals in sewage sludge. International Journal of Environmental Science and Technology, 7(4), 617-622.
3	Ifelebuegu, A.O. (2011) The fate and behaviour of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes. International Journal of Environmental Science and Technology, 8(2), 245-254.
4	Ifelebuegu, A. O., and Ezenwa, P. C. (2011) Removal of endocrine disrupting chemicals in wastewater treatment by Fenton-Like Oxidation. Water, Air and Soil Pollution, 217, 213 -220.
5	Ifelebuegu, A. O. (2012) Removal of endocrine disrupters by activated carbon adsorption; Kinetic and thermodynamic studies- Journal of Environmental Protection, 3, 469 - 475
6	Ifelebuegu, A. O., Onubogu' J., Joyce, E., Mason, T. (2013) Sonochemical degradation of endocrine disrupting chemicals 17β-estradiol and 17α-ethinylestradiol in water and wastewater International Journal of Environmental Science and Technology, DOI: 10.1007/s13762-013-0365-2

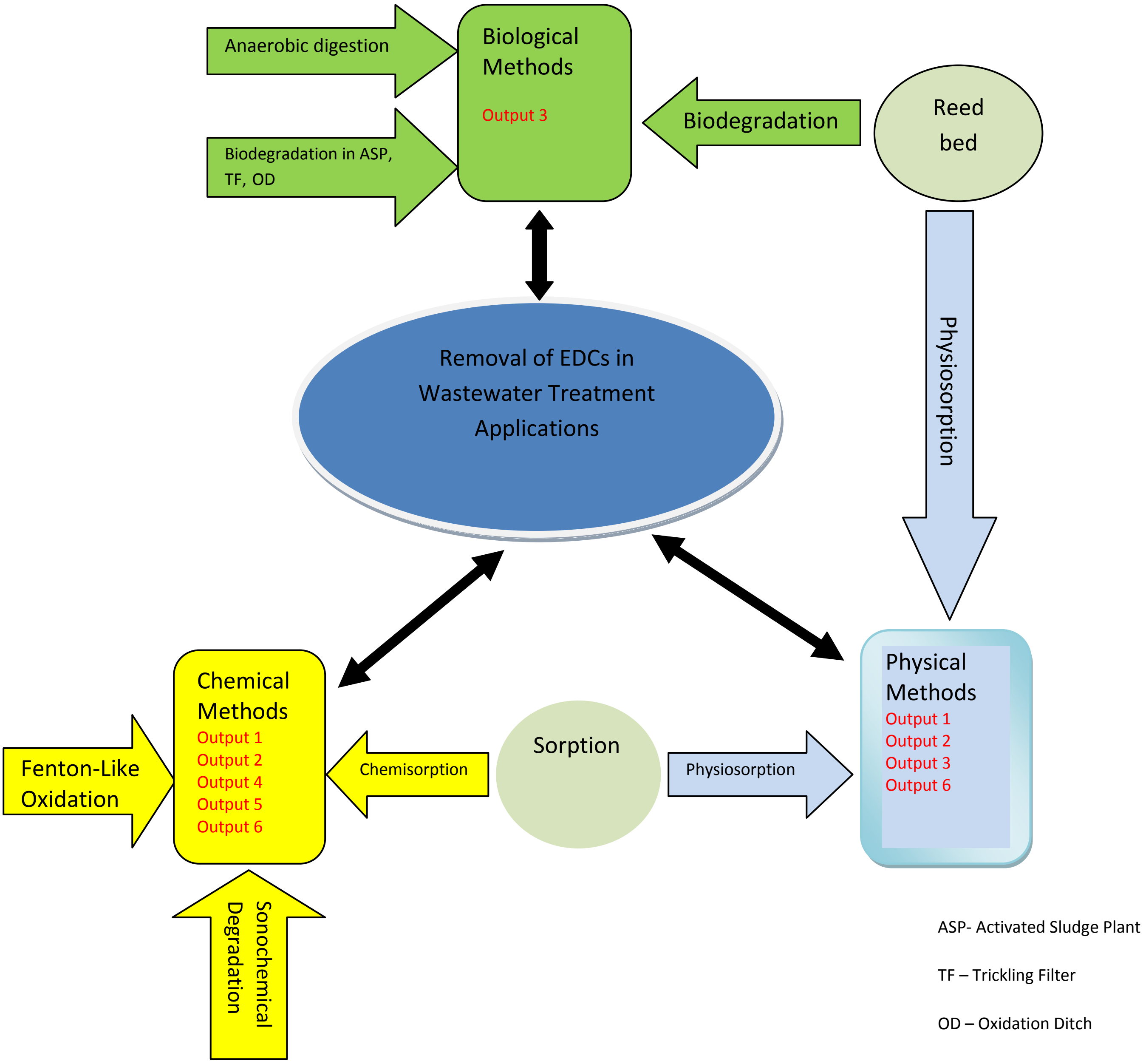


Figure 2 - Overview of EDCs Removal Methods and Interrelationships between the Different Portfolio Outputs

The work is presented in three key themes, each of which has significant relevance in understanding the fate, behaviour and removal mechanism of EDCs in water and wastewater using different methods and technologies. They are namely:

Theme 1 – Biological Removal of EDCs in Wastewater Treatment

Theme 2 – Chemical Removal of EDCs in Wastewater Treatment

Theme 3 – Physical Removal of EDCs in Wastewater Treatment

The next three chapters discuss each of the three themes outlined above. The chapters bring together the fundamental theories of the themes and outline the findings from the Outputs related to the specific theme. Chapter 5 discussed the methodological approaches used in the various Outputs, reflecting on method development, quality control and reasons for the various approaches. Chapter 6 discussed in details the findings highlighted in chapters 2 to 4 while chapter 7 highlighted some of the contribution made to knowledge using a matrix.

1.5 Collaborative Work

The author was the lead author for all the papers contained in this portfolio. However, some of the papers were co-authored. About 90% of the work in the portfolio (initial ideas, planning, sampling, laboratory work, data analysis and write-up) were carried out by the author. Details of the contributions made by the other co-authors are described in Appendix 1.

Chapter 2

Biological Removal of EDCs in Wastewater

EDCs are detectable in the final effluent of WWTPs after biological treatment. The biological treatment process, which is typically the secondary stage of a multistage treatment process in a WWTP, is designed to remove dissolved organic matter from wastewater. Steroid estrogens, which are the most potent EDCs, get into WWTPs through human excretions and agricultural runoffs. They are excreted mainly as inactive glucuronides and sulphate conjugates which are rapidly deconjugated to active hormones in sewer and during biological treatment. It is believed to be due to the activity of beta-glucuronidase, an enzyme present in bacteria found in WWTPs (Belfriod *et al*., 1999; Wegener *et al*., 2001). Various studies carried out worldwide, have reported varying capacities of conventional biological methods to remove estrogens. They vary from as low as 10% to as high as 95% removal (Joss *et al*., 2004; Liu *et al*., 2009).

Alkylphenols and alkylphenol ethoxylates (APEOs) are biodegraded by the rapid and stepwise removal of ethylene oxides groups to form lower APEO congeners. Under aerobic conditions, they can further be degraded to the corresponding carboxylic acid groups and nonyphenol/octylphenols. (Lee and Peart, 1998; Bennie, 1999; Maguire, 1999). In a laboratory scale experiment Jonkers *et al*. (2001) proposed that during the biodegradation of APEOs, the ethoxylate groups are converted to carboxylates. Work by DiCorcia *et al*. (1998) suggested that both the ethoxylate and alkyl chains are oxidised to form carboxyalkylphenoxy ethoxycarboxylates metabolites, which are recalcitrant to further biodegradation.

There are three main approaches for biological removal of dissolved organics namely suspended growth systems, attached growth systems and lagoon systems. The suspended growth systems include the activated sludge systems, which include conventional activated sludge plants, oxidation ditches and membrane bioreactors. The attached growth systems include trickling filter plants, submerged aerated filters and biological aerated filters. These conventional treatment processes are not effective in the removal of EDCs in WWTPs as they were primarily designed for the removal of sanitary parameters (BOD, suspended solids and ammonia), phosphorus and nitrates (Esperanza *et al*., 2007; Hashimoto *et al*., 2007; Liu *et al*., 2009).

Biological degradation of EDCs and other organics occur either aerobically as in ASPs, TFs and RBCs, or may occur under anaerobic conditions as in anaerobic sludge digesters (Langford and Lester, 2003; Moharikar *et al*., 2005). Estrogens, APEOs and their metabolites are not completely degraded in conventional WWTPs. The rate of degradation varies between different treatment plant type and the operating parameters. Due to the increasingly stringent consents for ammonia by the UK Environment Agency and US EPA, most WWTPs in the UK and US are now operated at a low loading rate and hence, high sludge ages to encourage nitrification. The high sludge ages encourages the biological transformation of EDCs (Ifelebuegu, 2011), hence increasingly EDCs are predominately removed by biological degradation in WWTPs.

The predominant WWTP types in the UK are ASPs and TF, oxidation ditches (ODs) and RBCs. The majority of the research available in the literature on EDCs is mainly for ASPs and TFs. Studies have shown that TFs are generally less effective compared to ASPs in the removal of EDCs in wastewater treatment (Svenson *et al*., 2003; Johnson and Williams, 2004). Ternes *et al*. (1999b) found elevated concentrations of EDCs in the final effluent from a TF. Turan, (1995) concluded that EDCs, particularly the synthetic estrogens, are recalcitrant to treatment by TF process. Better removals have, however, been reported for EDCs in ASPs with increased removal as the solid retention time is increased (Holbrook *et al*., 2002; Andersen *et al*., 2003).

With increasingly stringent requirements for nitrogen and phosphorus discharges through wastewater, the water industry is rebuilding or retrofitting existing WWTPs for enhanced biological nutrient removal. This involves the introduction of anaerobic zones and mixed liquor recycling (sludge recirculation), introducing both nitrifying and denitrifying reactions. These additional processes play additional roles in the biological removal of EDCs.

Several process parameters affect performance of WWTPs in the degradation of EDCs. These include retention time, sludge age, temperature and nitrification rates. These parameters are usually not captured in the majority of the research on EDCs available in the literature (Johnson & Williams, 2004). Also there are conflicting augments about the actual mechanisms of biological removal of EDCs in wastewater treatment. According to Birkett and Lester (2003), it is generally believed that the biological removal process is a combination of biodegradation and biotransformation. Ivashechkin *et al*. (2004) and Kroner *et al*. (2000) concluded that the removal process was biodegradation with no sorption to solids. Contrary to this belief, Mastrup *et al*. (2001) reported that biodegradation only accounted for 10% of the removal of estrogens during wastewater treatment, while Johnson *et al*. (2000) could not ascertain whether biodegradation or sorption was the most predominant removal mechanism. Various researchers are of the opinion that EDCs are recalcitrant to biological degradation and biological treatment processes are insufficient to reduce them to potentially no-effect concentrations.

There have been several publications on the levels of EDCs in sewage influents and effluents, using monitoring from spot/grab samples, but very little work has monitored EDCs in every unit process of the conventional treatment processes using 24 hr flow proportional composite samples. Also according to Huo and Hickley (2006), the influence of operating parameters like sludge age and hydraulic resident time are usually not capture in the majority of EDCs research available in the literature. There is, therefore, a need for further studies to investigate and understand the fate, and mechanisms of removal of EDCs in different biological treatment plant types and unit processes. Output 3 in this portfolio provides a detailed evaluation of the fate and behaviour of EDCs in various unit processes of the common and conventional wastewater treatment processes in the UK. The unit processes of ASPs, OD, TFs and RBCs were investigated to help evaluate performances of different treatment processes and also understand the mechanisms of removal. The Output demonstrated that the predominant removal mechanism for EDCs during treatment is a combination of biodegradation and sorption onto solids.

Chapter 3

Chemical Removal of EDCs in Wastewater

Some researchers have concluded that existing biological treatment methods cannot reduce the concentrations of EDCs in wastewater to levels below their potentially non-effect concentrations (PNEC) (Ternes *et al*., 2003; Esplugas *et al*., 2007) and are therefore looking at other "end of pipe" alternatives. Some of the alternatives are the use of activated carbon adsorption and chemical methods including advanced oxidation processes (AOPs).

AOPs have been used in potable water applications for many years but are relatively new in wastewater applications. Various AOPs that have been used for wastewater treatment include ozonation (Baron *et al*., 2006; Ermawati *et al*., 2007; Zhang *et al*., 2008), Fenton oxidation (Hsueh *et al*., 2005), chlorine dioxide oxidation (Deborde and von Guten, 2008), ultrasound (Suri *et al*., 2007;) UV Irradiation/H_2O_2 (Chen et *al*., 2007), Fenton/UV (Katsumata *et al*., 2004) and Fenton-like oxidation (Ifelebuegu & Ezenwa, 2011).

Ozone as an oxidant is known to selectively attack aromatic molecules and double bonds in aliphatic compounds directly as ozone or through hydroxyl radical attack (Haag and Yao, 1992; von Gunten, 2003). Ozone has been used to treat EDCs including the steroid hormones. Deborde *et al*. (2005) achieved over 95% removal of E1, E2 and EE2 in a laboratory-based experiment. Various other researchers have also reported very good removal of EDCS in water and wastewater (Nakagawa *et al*., 2002; Huber *et al*., 2003; Ternes *et al*., 2003). One of the main drawbacks of the use of ozone in wastewater treatment is the relatively high capital and operating cost as well as the potential for toxic by-products and metabolites.

Another AOP that has been reported in the literature for the removal of EDCs is UV irradiation. Various research studies have shown that estrogens are broken down under the influence of UV radiation (Synder *et al*., 2003; Liu and Liu 2004). UV has also been combined with other chemical oxidants to enhance the degradation of EDCs. The oxidants include ozone (Irmak *et al*., 2005), titanium oxide (Ohko *et al*., 2002) and hydrogen peroxide (Rosenfeldt *et al*., 2004).

Fenton oxidation (H_2O_2/Fe^{2+}) and Fenton-like oxidation (H_2O_2/Fe^{3+}) are well known methods for the oxidative degradation of organic compounds. They have been reported to be effective in the removal of organics in wastewater (Xu *et al*., 2004; Gotvajn and Zagorc-Koncan, 2005; Lucas and Peres, 2009; Mendez-Arriaga *et al*., 2010). The Fenton process involves a reaction of ferrous salt with hydrogen peroxide to produce hydroxyl radicals, reactive electrophiles which are responsible for the rapid chemical destruction of organic rich contaminants. The use of ferric salts (Fe^{3+}) or zero valence iron in Fenton-like oxidation has also been investigated for azo dyes and phenols (Yang and Long, 1999; Hsueh *et al*., 2005), and more recently steroid hormones (Ifelebuegu and Ezenwa, 2011).

Output 4 evaluated the use of Fenton-like oxidation for the mineralisation of estrogens. A limited amount of research has been conducted on the Fenton-like oxidation of organics and none to the knowledge of the author for the oxidative degradation of estrogens. The results of this Output demonstrated that E2 and EE2 are effectively degraded by Fenton-like oxidation at optimum pH 3 to less than PNEC. Relatively good removal was also achieved at pH 6.7 implying that the Fenton-like oxidation of EDCs can be carried out in treatment plants without the extra cost of pH adjustment.

One of the disadvantages of the use of AOPs in water and wastewater treatment is the formation of by-products, which could be recalcitrant to further degradation and are sometimes more toxic to the aquatic environment than the original substance. The use of ultrasound is often considered to be more environmentally friendly as it removes the problem of chemical by-products. In view of the increased demand for higher water quality standards without toxic by-product concerns, significant attention has been drawn to the use of ultrasound for treatment of pharmaceuticals and personal care products in water and wastewater (Gogate and Pandit, 2004a, b; Naddeo *et al*., 2009; Chiha *et al*., 2011). This is because the generation of hydroxyl radicals through acoustic cavitations results in oxidative degradation of contaminants (Torres *et al*., 2008). The cavitations involve the formation, growth and consequent collapse of micro bubbles, which occur in very short periods and release large amount of energy over a very small area (Gogate and Pandit, 2002). Sonochemical reactions result from the collapse of cavitation bubbles in a liquid, which leads to thermal dissociation of water vapour into hydroxyl radicals. It can also result from the interfacial sheath between the bubble and the surrounding liquid or the solution bulk (Ince *et al*., 2001; Mason and Petrier, 2004). The hydroxyl radical generated is predominantly responsible for the oxidative degradation of EDCs. Output 6 investigated the oxidative degradation of estrogens by ultrasound at the ultrasonic frequency of 850 Hz. It was found that the rate of degradation increased with increasing power density with total removal being achieved at a power of 50W. Mass degradation rates varied from 1.7 to 4 mg/KW.

Another method for the removal of EDCs in wastewater is activated carbon adsorption. Removal of EDCs by activated carbon (AC) adsorption is also well reported in literature (Choi et al., 2005; Ifelebuegu *et al*., 2006; Kiran Kumar & Mohan, 2011; Ifelebuegu, 2012). EDCs and other organics are removed by hydrophobic interaction between them and the AC surfaces. Several factors affect the efficiency of removal of EDCs by AC. They include the AC structure, pore size, aqueous solubility, pH, octanol-water partition coefficient, pore blockages and the presence of competing adsorbates like natural organic matter (Li *et al*., 2003; Westerhoff *et al*., 2005; Ifelebuegu *et al*., 2006). Outputs 1 and 5 investigated the use of GAC for the removal of EDCs. It was shown that activated carbon sourced from wood, coconut waste and coal all performed comparatively with coconut GAC showing better removal of estrogens. The mechanism of adsorption was also found to be predominantly chemisorption. The presence of other organic compounds reduced the removal efficiencies of EDCs by GAC due to the effects of competing co-present natural organic matter in wastewater.

Chapter 4

Physical Removal of EDCs

During conventional wastewater treatment, EDCs are removed by physical interaction with (sorption onto) suspended solids and sludge. Although biodegradation is believed to be the predominant removal route, sorption onto sludge remains a removal pathway (Rogers *et al*., 2000) due to the hydrophobicity of EDCs, particularly the estrogens. Although the alkylphenols are less adsorbed onto the solid phase due to their more hydrophilic nature; the carboxylic acid groups tend to be more associated with the aqueous phase than the solid phase (Ahel *et al*., 1994; Lee & Peart, 1998). The estrogens being more hydrophobic are more partitioned onto solid phase during wastewater treatment (Johnson *et al*., 2000; Clara *et al*., 2004; Feng *et al*., 2010; Ifelebuegu *et al*., 2010). EDCs can be removed by physical means during wastewater treatment by partitioning onto primary sludge and activated/humus sludge biomass in primary and secondary sedimentation tanks respectively.

The potential for EDCs to partition onto WWTPs solids are usually well predicted by the octanol water (partitioning) coefficient. Adsorption isotherms also describe the relationship between the solid and the aqueous phases from which the partitioning coefficients are determined (Abdel-Ghani and Elchaghaby, 2007; Yoochatchaval *et al.,* 2008; Abdel-Ghani *et al.,* 2009). There have been various studies that have examined partitioning coefficients of different organics including EDCs in wastewater sludge (Soltanali and Hagani, 2008; Gong *et al.,* 2009). Ternes *et al.* (2004) conducted a series of batch tests using sewage sludge to determine partitioning coefficients (Kd) for a number of pharmaceuticals and personal care products. They found that log Kd values of the compounds ranged from 0 to 2.7 with EE2 having a log Kd value of 2.5. Clara *et al.* (2004) found that the log (Kd) for steroid estrogens were in the ranges of 2.64– 2.97 and 2.71–3.00 for E2 and EE2, respectively. Andersen *et al.* (2005) determined distribution coefficients, *K*d, with activated sludge biomass for the steroid estrogens estrone, E2 and EE2 in batch experiments, and they found log *K*d values of 2.6, 2.7, 2.8, respectively. Ren *et al*. (2007) studied the adsorption of EE2 on inactivated sludge and they found that the process was spontaneous and enthalpy driven. Similar observations were also made by Feng *et al.* (2010).

Output 2 systematically evaluated the mechanics of adsorption of EDCs onto mixed sludge biomass to help provide insight into how EDCs behave during wastewater and sludge treatment. It provided empirical evidence of the nature of interactions (partitioning) between these trace compounds and blended sludge, as well as the thermodynamic properties of the adsorption of the EDCs to sludge at higher percentage dry solids similar to the ranges of solids present in the feed to anaerobic sludge digesters. The results showed that the interactions between the EDCs in mixed sludge matrix were predominantly physical attractions (physisorption). Also in Output 3 considered in Chapter 2, the removal of EDCs by physical filtration in tertiary sand filters and reed beds were significant, showing that EDCs are removed with biosolids removal.

Chapter 5

Methodological Approach

The body of work contained in this COD comprised various projects all aimed at understanding the fate, mechanism and optimisation of the removal of EDCs in conventional and novel wastewater treatment processes. Various methods were used for the various projects as described in the individual Outputs. This chapter reflects on some of the methods that have been used.

The EDCs used in the Outputs were the steroid estrogens and alkylphenols. The choices were due to the fact that they are the most potent EDCs found in wastewater. They are also the substances that top the list of EDCs in the EU list of priority hazardous substances to be potentially subject to regulatory limits under the proposed WFD.

5.1 Sampling

The wastewater and sludge samples used in the various Outputs were grab samples collected from WWTPs in the West Midlands except in Output 3, where the wastewater samples were composite samples. In the majority of research on EDCs available in the literature, samples were usually grab samples due to the difficulty in preserving EDCs samples, particularly the steroid estrogens. According to the research by Jurgen *et al*. (2002), estrogens are very unstable with various degrees of degradation from the sewer to the river with half-lives of 5 hours to 9 days.

In Outputs 1, 4, 5 and 6, wastewater samples were collected from an activated sludge plant and stored immediately below 4^{oC} to inhibit biological degradation prior to use for the laboratory experiments. In Output 2 sludge samples were collected from sludge thickening tanks prior to being fed to a digester, so as to have a blended sludge that is representative of the typical sludge that comes out of WWTPs after digestion. It was made up of primary sludge and thickened secondary sludge at 4.3% dry solid. This percentage dry solid is typical of the concentration at which most conventional anaerobic digesters are feed in the majority of WWTPs in the UK.

In Output 3, which was a detailed survey of the fate of EDCs in different wastewater treatment plants, a preservation method using 0.25g copper nitrate and 1 mL of hydrochloric acid was used, allowing the preservation of the samples for up to 14 days. This allowed more time for the clean-up and analytical procedures without compromising accuracy and reproducibility. This preservation method was proposed by Anglian Water, UK as part of the NDP and was validated during this research. It also allowed the use of a flow proportional composite sample providing average daily values of EDCs in the different treatment plants sampled, as EDCs concentration values are known to vary throughout the day. The samples were collected in amber coloured glass bottles pre-conditioned with copper nitrate and HCl.

Samples were collected from the various sites daily from four different treatment sites to ensure that the major conventional methods of treatment in the UK were covered. This was carried out in two sampling campaigns representative of wet and dry weathers. Crude samples were collected to enable the determination of the influent EDCs concentrations. Settled sewage samples were also collected to allow the researcher to evaluate the performance of primary sedimentation in the removal of EDCs. Also settled sewage samples mixed with liquor return from the site sludge handling process were also collected to enable the determination of the role of site sludge handling on the removal process. Further samples were collected downstream of the biological treatment and tertiary treatment process to evaluate the performance of the processes.

5.2 Sample Preparation and Clean Up

Qualitative and quantitative analysis of the EDCs covered in this portfolio was very challenging due to the very low detection limits of the target EDCs at 1 ng/L or less in a complex environmental matrix like wastewater, which usually contains various interfering compounds. This is particularly so for the analytical methods used in Outputs 1, 2 and 3.

The analysis of EDCs has been dominated by chromatographic methods, usually gas chromatography (GC) and liquid chromatography (LC). EDCs especially the steroid hormones and alkylphenols, are known to induce biological responses in aquatic organisms at parts per trillion concentration levels, most of the analytical methods used are therefore designed to be able to detect the analyte at ng/L levels.

The majority of the chromatographic equipment used are not able to detect the EDCs at this low level, hence the need for both clean-up and extraction steps to concentrate the EDCs to detectable levels. Solid phase extraction (SPE) is the most widely used extraction methods for EDCs.

After the sampling process the early phase of the sample preparation is filtration to separate the EDCs from the suspended solids and other organic materials as well as to prevent any interference with the subsequent SPE. The use of filter paper for the separation face did not affect the recovery rate as was also previously demonstrated by the work of Huang and Sedlack, 2001. The filtration steps were followed by SPE and further purification step by separating the target analyte from other molecules based on size prior to analysis. This step was accomplished by gel permeation chromatography (Ternes *et al*., 2002).

The analytical clean-up methods used in Outputs 1 and 3 are based on established methods which included SPE, gel permeation chromatography (to remove large molecular weight compounds), derivatisation (for Output 1) and a fractionation step using silica gel/alumina to separate the various compounds in the extract based on polarity (Snyder *et al*., 1999, 2001). A method modified from Patrolecco *et al*., (2004), using Tween 80 extraction was validated and used for the extraction prior to solid phase extraction for Output 2.

5.3 Quantification of EDCs

Various methods have been used to quantify EDCs especially the steroid hormones. GC and LC coupled to mass spectrometry or tandem mass spectrometry are the commonest methods (Petrovic & Barcelo, 2006: Gomez *et al*., 2006; Daughton & Ternes, 1999; Haung & Sedlack, 2001; Ternes *et al*., 2003). High performance liquid chromatography has also been used by some researchers as well as biological methods like immunoassay (Huang & Sedlack, 2001; Xin *et al*., 2009).

In Output 1, analysis was carried out using a GCMS with a derivatisation step to increase volatility of the EDCs and hence improve sensitivity during analysis. This usually more than compensates for any losses of samples that may be experienced as a result of the additional processes for sample extraction and clean-up. GC-MS/GC-MS/MS have been widely used for the analysis of EDCs, the main drawbacks being the need for derivatisation, which is time consuming, labour intensive and has the potential to introduce inaccuracies. In Output 3, LC-MS/MS was used where analytes are separated in the liquid phase.

The analysis of samples in Outputs 2, 4, 5 and 6 were carried out using HPLC with a fluorescence detector. This was based on a method developed and validated by slightly modifying the methods used by Van Emmerik *et al*. (2003). The detection limits were adequate for the concentrations at which the experiments were conducted, which were above the low level environmental concentrations. The experiments were designed at higher concentrations as the process parameters investigated, to offer insight into the mechanism of removal including the thermodynamic parameters are concentration independent (Annamalai and Puri, 2002). In trying to establish the mechanism of removal of EDCs by the various methods used in the portfolio, the principle of triangulation was used to determine the mechanisms of removal using kinetic data, isotherm data, thermodynamic data and desorption studies. These various data were used in drawing conclusions on the mechanisms of removal for the various treatment technologies considered in this portfolio.

Chapter 6

Discussion

6.1 Biological Treatment of EDCs

Output 3 investigated the fate and behaviour of selected EDCs in each unit process of the WWTPs and also, the influence of process operating parameters. The behaviours in the unit processes of wastewater and sludge treatment processes are critical in understanding options for the optimisation of the unit processes for more effective and efficient removal of EDCs in wastewater treatment.

The removal efficiencies of all the EDCs considered in this paper ranged from 81-86%, 83-97%, 41-58% and 91-100% for E1, E2, EE2 and NP respectively. E2 and NP showed the highest rates of removal with EE2 being more recalcitrant in the wastewater treatment plants. The anomalous behaviour of E1 during primary treatment that has been previously observed was confirmed with the level of E1 increasing after primary treatment (Hashimoto *et al*., 2007; Ren *et al*., 2007). This behaviour is due to the biotransformation of E2 to E1 in the primary sedimentation tanks and also during the preliminary primary sludge handling process. This observation was also supported and confirmed in the sludge treatment process as E1 had the highest concentration in the final untreated mixed sludge of 88-118 µg/kg compared to 2-16 µg/kg for E2 and 0-1.6 µg/kg for EE2. This behaviour confirmed that the interactions between the EDCs and sludge is majorly physical in nature, hence they are easily redistributed to the aqueous phase by desorption. There was no evidence of biotransformation of E1 and EE2 during the processes, suggesting that biotransformation as a removal mechanism for EDCs as reported by Birkett and Lester (2003) is only limited to E2.

Suspended growth processes including ASPs and oxidation ditches were found to be more efficient than other biological treatment methods in removing EDCs. The removal efficiencies for E1, E2, EE2 and NP all increased with increasing nitrification rates and sludge ages. This supports the findings of Vader *et al*. (2000) that the degradation of EE2 is directly related to the nitrification rates. Significant removal was also observed in tertiary treatment stages of sand and reed bed filtrations demonstrating that solids removal reduces EDCs in wastewater treatment as they are adsorbed onto biosolids, contrary to the findings of Korner et al. (2000) and Ivashenchkin *et al*. (2004).

Additionally, the results demonstrated that plants configured for biological nutrient removal gave better removal performance than conventional treatment plants. The increased sludge age and solid retention times were found to be responsible for this. High retention times and sludge ages allow for the growth of diverse and slow growing microbial culture that are more effective in degrading EDCs. The evidence from this Output suggests that with optimisation of the biological processes especially the ASP process (increased sludge age and sludge recirculation), biological treatment may be sufficient to effectively remove EDCs from wastewater without the need for more expensive tertiary treatment processes, although this may involve lager footprints as a result of increased retention time and sludge age. Where space availability is a problem, variants of the ASP process with smaller footprint such a membrane bioreactors and integrated fixed film activated sludge plants may be considered.

The concentrations of the EDCs in the untreated biosolids from the treatment plants were found to range from 88-118 µg//kg for E1, 4–6 µg/kg for E2, 0-1.6 µg/kg for EE2 and 32-123 µg/kg for NP with corresponding average removal efficiencies of 23%, 25%, 13% and 46% during anaerobic sludge digestion respectively. This showed that EDCs were persistent under anaerobic conditions. This explains why estrogens are known to persist in the environment. It supported the previous findings of Lai *et al*., 2002a, b, Gomes *et al*., 2004 and Czajka & Londry, 2006 that EDCs persist in the environment and have the potential to bio-concentrate and bio-accumulate in the environment. The comparatively high level of the EDCs in the sludge also demonstrated that the sorption of EDCs onto biosolids is a significant removal mechanism. This is supported by the finding of Ifelebuegu *et al*. (2010), which demonstrated that EDCs adsorb onto biosolids spontaneously by both physical and chemical means.

Overall, the body of evidence from this Output demonstrated that the predominant removal mechanisms of EDCs during wastewater treatment are a combination of biological degradation and sorption onto solids. Also with process optimisation there is a potential for biological treatment to be sufficient to effectively remove EDCs where space and cost is not prohibitive.

6.2 Chemical Treatment of EDCs

6.2.1 Activated Carbon Adsorption

Results obtained in Outputs 1 and 6 demonstrated that the removal process of EDCs by activated carbon adsorption is predominantly by chemical adsorption; hence these Outputs are discussed in this chapter. The purpose of Output 1 was to investigate the effects of different sources of activated carbon on adsorption capacities. It was also meant to help understand the impact of other competing adsorbates on the effectiveness of the different activated carbon types to remove EDCs from wastewater effluent. The research was carried out at the preliminary stages of the NDP to decide on the best source of activated carbon to be used for the pilot trials at the Ilkeston plant in Derbyshire. Before this time, activated carbon was widely used in the adsorption of organic pollutants in potable water treatment, but its use in wastewater treatment was limited. It was shown that GAC made from coal, coconut and wood had comparable efficiencies in removing estrogens from wastewater. Removal efficiencies of 98.6%, 99.3% and 96.4% were obtained for EE2 for coal based, coconut based and wood based GACs. Coconut based GAC showed the best performance in the removal of EDCs. This contradicted the findings of Baldouf et al. (1993) that coal based GAC are better than other sources of GAC.

Coal based AC is common place in the water industry; with increasing cost and demand by both the water, energy and other industries, alternative sources of GAC are needed to meet the ever increasing demand. This paper demonstrated that GAC from coconut was as effective as the traditional coal based AC. The wood based GAC also showed relatively good removal efficiency. With the increasing cost of coal, the world market for activated carbon is predicted to expand considerably over the next few years (Freedonia, 2011). The water industry can therefore source their GAC from alternative sources. It was also demonstrated in the Output that adsorption capacities of the GACs were reduced significantly as a result of competitive adsorption from other organics in wastewater.

Output 5 was a continuation of the research carried out in Output 1. It investigated the kinetics and thermodynamics of adsorption of E2 and EE2. There have been several papers on the adsorption properties and capacities of AC to remove EDCs in water and wastewater similar to Output 1. However, there have been very few studies to investigate the mechanics of adsorption of estrogens onto AC. This is an essential research required to provide better understanding of the mechanism of adsorption and the influence of operating parameters. The effects of pH on the adsorption of E2 and EE2 were also investigated. It was shown that better adsorption capacities were obtained at acidic to neutral pH, with optimum performance achieved at around neutral pH for the coal based GAC. Typical municipal wastewater pH is around the neutral pH range. Hence the industrial scale application of the GAC adsorption of estrogens will not incur additional cost for pH adjustment. The kinetic data for the adsorption process showed a better fit to the pseudo second order kinetic model, suggesting that chemisorptions is the rate determining step. A similar conclusion was also drawn from the intra-particle kinetic model plots. The Gibbs free energy and enthalpy for the adsorption of E2 were -17 kJ/mol and 85 kJ/mol, while EE2 were -17 kJ/mol and 90 kJ/mol respectively. The thermodynamic and desorption data also confirmed that the mechanism of adsorption of the EDCs to AC is predominately chemisorptions supported by some physical/van der Waals forces.

The use of GAC adsorption for the removal of EDCs in wastewater treatment application is technically feasible. Alternative sources of GAC from coconut and wood can be used effectively. However, the presence of other organics can significantly affect the removal efficiency and hence increasing the cost of treatment due to the fact that the cost of GAC regeneration is high and energy intensive.

6.2.2 Fenton-like Oxidation

Output 4 investigated EDCs removal by Fenton-like oxidation (a modified form of the Fenton oxidation process). The Fenton-like process was effective in the removal of E2 and EE2 with efficiencies ranging from 95% to 98% at 0.003 M concentration of ferric. The thermodynamic properties of the reactions were evaluated to provide process parameters for the modelling of industrial scale applications. Arrhenius type activation energies of between 23 $kJmol^{-1}$ and 28 $kJmol^{-1}$ were obtained for E2 and EE2 showing that the Fenton-like oxidation of the EDCs involved intermediate reactions steps involving radical-molecule and ion-molecule reactions. The low activation energies also showed that the Fenton-like process is thermodynamically feasible. Furthermore, the results also demonstrated that in industrial scale applications, the highest efficiency would be achieved when applied as tertiary treatment since the dissolved organics in untreated wastewater had significant effects on the efficiency of removal. The Fenton-like process (although an AOP) was also found to enhance the biological degradation of the treated wastewater effluent. The wastewater industry uses millions of tons of ferric salts annually for the chemical removal of phosphorus in wastewater treatment. There are therefore existing facilities in those WWTPs for the storage and application of ferric. This modified Fenton process (Fenton-like oxidation) will therefore offer a potentially cost effective option for the removal of EDCs in wastewater as an “end of pipe” solution.

6.2.3 Sonochemical Degradation

Another “end of pipe” solution is the use of ultrasound for the removal of EDCs. This was investigated in Output 6. It was shown that at ultrasonic frequency of 850 kHz, the degradation rates of the EDCs increased with increasing power density with approximately 100% removal achieved at the ultrasonic power of 50 W. The mass degradation profile obtained at ultrasonic powers of 27.82 W, 16.17 W and 6.76 W ranged from 1.7 to 4.0 mg/kW and demonstrated that the degradation rates increased linearly with increases in power. This is consistent with the findings of Mendenz-Arriaga *et al*. (2008), Madhavan *et al*. (2010) and Chiha *et al*, 2011; which suggested that increased bubbles, pressure, and temperature in the bubbles are directly related to acoustic power and enhances the degradation of contaminants.

The results also showed that sonochemical degradation of steroid hormones are favoured at acidic to neutral pH but declines with alkaline pH. The reason is based on the structure of E2 and EE2 as well as their pKa values. At acidic to neutral pHs, they exist in non-ionic molecular form and can then easily diffuse into the cavity-liquid interface. Other factors that influenced the degradation include the temperature, air sparging, power intensity and the presence of organic matter.

A low activation energy of 15.21 kJ/mol was obtained for the sonochemical degradation of EE2 demonstrating that the degradation process is thermodynamically feasible and also that the ultrasonic degradation does not involve only radical reactions but also intermediate reactions steps involving radical–molecule or ion-molecule reactions and a diffusion controlled reaction (Mason 1999; Kim *et al*., 2001). It was also shown that the presence of dissolved organic matter significantly affected the efficiency of ultrasound for the oxidative reduction of EDCs. This can be attributed to the fact that a higher concentration of dissolved organics in wastewater acts as a scavenger for hydroxyl radicals and hence inhibits the hydroxide radical attack of the compounds (Torres *et al.,* 2007; Lindsey and Tarr 2000a, 2000b). This also confirms the role of free radicals in the degradation rates of E2 and EE2. It can be concluded that in wastewater treatment applications, ultrasonic treatment will only be effective at the tertiary treatment stage when most of the dissolved organics have been removed by biological means.

While this research demonstrated the technical feasibility of using ultrasound for the removal of EDCs, it seemed to appear that from the mass degradation rates and ultrasonic power, the process might be economically feasible. Further work needs to be carried out at both the laboratory and industrial scales to substantiate the economic feasibility of the process.

6.3 Physical Removal of EDCs in Wastewater

Output 2 investigated the behaviour of EDCs in sludge biomass. The average percentages of E2 and EE2 adsorbed onto the solid phase at 4.3 % dry solid were 87.2 % and 92.5 %, respectively. A similar study by Keenan *et al*. (2008) reported a > 90 % sorption rate of estrogens onto the solid phase. The high sorption rates of E2 and EE2 to the solid phase can be attributed to the high hydrophobicity of their functional group (Figure 1) and the higher % dry solid of the homogenized sludge blend. EE2 showed a higher affinity to the solid phase, this explains while EE2 is more recalcitrant compared to E2 and other natural estrogens during the biological wastewater treatment process.

The Gibbs free energy obtained showed that the sorption of E2 and EE2 to the activated sludge biomass was spontaneous. Their enthalpy changes were -45.7 kJ/mol and -43.4 kJ/mol, respectively, demonstrating that the sorption process is exothermic. The values of the enthalpy changes also showed that sorption of estrogens onto activated sludge is a combination of physical adsorption and chemisorptions with the former being predominant. The entropy changes were -105.2 J/mol/K for E2 and -96.7 J mol/K for EE2 implying that the sorption of E2 and EE2 to conventional activated sludge biomass is entropy retarded. This barrier is however, superseded by the enthalpy changes. These thermodynamic data are scare in the literature and are relevant in modelling the removal of EDCs in wastewater and sludge treatment processes. It was previously believed that only a small fraction of steroid hormones were associated with the solid phase during wastewater treatment (Williams *et al*., 2003). The findings demonstrated that adsorption on to the solid phase (sludge) is significant as the adsorption process is spontaneous. This has been supported subsequently by the findings of Horsing *et. al*. (2011) and Zhang *et al*. (2012). Also results from Output 3, which has been covered in Chapter 3, showed that physical adsorption onto sludge and removal of solids by sand filters and reed beds were significant routes for the removal of EDCs in wastewater treatment plants, although biological degradation remained dominant.

Chapter 7

Contribution to Knowledge

This chapter highlighted some of the findings of the individual Outputs and their contribution to knowledge using a matrix that was modified from the one developed by Professor Mark Jenkins of Cranfield University School of Management. The matrix was developed for use by research students and remains unpublished to the knowledge of the author to date. The matrix was used to show the contribution that the Outputs in this portfolio have made to knowledge by either confirming or replicating the finding of other researchers; contradicting or extending existing knowledge or made new contributions. A list of some of the publications around the world, where available, that have cited the Outputs in this portfolio has also been included.

7.1 Output 1

Ifelebuegu, A.O., Lester, J.N., Churchley, J. and Cartmell, E. (2006), Removal of an endocrine disrupting chemical (17alpha-ethinyloestradiol) from wastewater effluent by activated carbon adsorption: effects of activated carbon type and competitive adsorption. Journal of Environmental Technology, 27, 1343-1349.

	Confirmed/ Replicated	**Contradicted**	**Extended**	**New Contribution**
Methodology				
Empirical Results	Confirmed the finding of De Rudder et al., 2004 for EE2 adsorption	Contradicted he finding of Baldouf et al., 1993 that bituminous GAC were better than other sources		Removal of EDCs by coal based, coconut based and wood based GAC were comparable with coconut based GAC having slightly higher adsorption capacity for EE2. Impact of multi-solute adsorption in wastewater applications
Citations	Pan *et a*l., 2008; Koh *et al*., 2008, 2009; Beltran *et al*., 2009, Roswell *et al*., 2009; Filby *et al*., 2010; Gomes *et al*., 2011; Ho *et al*., 2011; Tyler & Filby, 2011; Quinn-Hosey *et al*., 2012; Han *et al.,* 2012 etc.			

In this paper we investigated the effects of activated carbon types and competing adsorbate on the adsorption capacity of GAC. We demonstrated that GAC manufactured from coal, coconut shells and wood were adequate for the removal of EDC in wastewater with coal based GAC showing better adsorption capacity. We also demonstrated that in wastewater application, adsorption is reduced to some extent due to the effects of competing adsorbates.

Although on the surface the research looked fundamental, it provided an understanding that GAC from other sources other than conventional coal GAC can also be used particularly at a time when the demand and cost of coal in the global market is high. It was demonstrated that estrogens can be effectively removed by coal based, coconut based and wood based GACs. The removal efficiencies were above 95% for all three types of GACs similar to the finding of De Rudder *et al*., 2004 for EE2. Coconut based GAC showed the best adsorption for EE2 contradicting an initial report of Baldouf *et al*. (1993) that coal based GACs were better than other sources of GAC for the removal of organic pesticides.

While there were a number of publications on the adsorption of EDCs using GAC, they were usually single solute adsorption. The findings of this Output showed the implications of using GAC in a multi-solute wastewater solution. The understanding from this paper informed the design and operation of the Ilkeston EDC NDP in the UK. The findings provided answers to some fundamental questions on the applications of activated carbon in wastewater cleanup. Since the publication of the paper in 2006, it has been cited more than 16 times in various journal articles from around the world as shown in the matrix above and in appendix 2.

7.2 Output 2

Ifelebuegu, A. O., Theophilus, S. C., and Bateman, M. J. (2010), Mechanistic evaluation of the sorption properties of endocrine disrupting chemicals in sewage sludge. International Journal of Environmental Science and Technology, 7(4), 617-622.

	Confirmed/ Replicated	**Contradicted**	**Extended**	**New Contribution**
Methodology	Van Emmerick *et al*, Yoon *et al*., 2003		petrolecco et al., 2004	
Empirical Results	Ternes *et al*., 2004; Adersen *et al*., 2005; Feng et al., 2010,			Thermodynamic properties (enthalpy, entropy and Gibbs free energy) of the adsorption of EDCs onto mixed primary and secondary sludge Interaction between estrogens and biosolids during wastewater treatment is predominantly physical interaction The partitioning coefficient of estrogens to biosolids decreases with temperature
Citations	Do, 2011; Horsing *et al*., 2011; Kiran Kumar & Mohan 2012; 2012; Zhang *et al*., 2012; Agarry *et al*., 2013 etc.			

In this paper we investigated the partitioning of EDCs in sludge during wastewater treatment. The understanding of this offers insight into the fate of EDCs during wastewater and sludge treatment. In carrying out this research, it was a challenge in developing analytical methods that are effective, because of the difficulty associated with the extraction and analysis of EDCs in a wastewater sludge matrix. A method modified from the work of Petrolecco *et al*. (2004) using Tween 80 extraction was used after validation. This method was therefore confirmed/replicated in this research.

The partitioning coefficient of the EDCs in mixed sludge, which is an important process design parameter was investigated. We reported values that confirmed similar values reported by Ternes *et al*. (2004) and Andersen *et al*. (2005). The effects of temperature and thermodynamic parameters were evaluated. Gibbs free energy values obtained confirmed the values previously reported by Feng *et al*. (2010) and the findings showed that the sorption of the EDCs on to the sludge biomass was spontaneous and entropy retarded. It also demonstrated that the sorption process was predominantly physical adsorption.

The outcomes of this output provided a body of new information on the thermodynamic properties and partitioning coefficient of estrogens in actual blended full-scale treatment plant biosolids as well as answers to the questions of the type of interaction between EDCs and biosolids and the effects of temperatures on the interactions. The output has since been cited in at least 7 other journal publications (see Appendix 2).

7.3 Output 3

Ifelebuegu, A.O. (2011), The fate and behaviour of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes. International Journal of Environmental Science and Technology, 8(2), 245-254.

	Confirmed/ Replicated	**Contradicted**	**Extended**	**New Contribution**
Methodology	Patrolecco *et. al*., 2004, SCA, 2005, Kanda & Churchley, 2008			24 hours flow proportional sampling with preservation for EDCs
Empirical Results	Nakada *et al.*, 2006; Zhang and Zhou, 2008; Miege *et al*., 2009; Gabet-Giraud *et al*., 2010; Zhou *et al*., 2010 Nasu et al., 2001; Jurgens et al., 2002; Hashimoto etal., 2007; Ren et al., 2007. Xu et al., 2008., Gomes *et al*., 2011	Kroner *et al*., 2000, Mastrup *et al*., 2001 Ivashechkin *et al*., 2004	Lai *et al*., 2002; Gomes *et al*., 2004; Czajka and Londry 2006. Liu *et al*., 2009 EDCs are persistent in the environment under anaerobic conditions	EDCs removal mechanism during wastewater treatment is a combination of biodegradation and sorption onto biosolids. WWTPs designed for biological nutrient removal are more efficient in removing EDCs Higher concentrations of EDCs are found in urban WWTPs compared to their rural counterpart.
Citations	Baynes *et al*., 2012; Chen *et al*., 2012; Hamid & Eskicioglu, 2012; Han *et al*., 2012; Hey *et al*., 2012; Singh, 2012; Wang *et al*., 2012; Zhang *et al*., 2012; Gianico *et al.,* 2012; Lin *et al*., 2013; Petric *et al*., 2013 and Surujlal-Nalcker, 2013 etc.			

In this Output, the author carried out an extensive sampling and survey of various treatment plants to investigate and provide an understanding of the fate and behaviour of EDCs in different types of treatment plants including activated sludge plants, trickling filters, oxidation ditches and reed beds. A flow proportional composite sample was used, as against the traditional grab sampling used due to the biological instability of the EDCs in sewage treatment plant unit processes. Methods previously used by Patrolecco *et al*. (2004), SCA, (2005) and Kanda & Churchley, (2008) were replicated with slight modifications and used with reproducible results.

The finding of this Output confirmed the finding of Nakada *et al.* (2006); Zhang and Zhou, 2008; Miege *et al*. (2009); Gabet-Giraud *et al*. (2010) and Zhou *et al*. (2010) who found comparable levels of EDCs in other WWTPs around the globe. Also the observations of Nasu *et al*. (2001), Jurgens *et al*. (2002), Hashimoto *et al*. (2007) and Ren *et al*. (2007) that E1 has an abnormal behaviour during wastewater treatment were confirmed and extended as E1 was found to increase in concentration during the initial phase of the primary treatment process, especially during primary sedimentation and dewatered sludge return liquor. This postulation was also supported and confirmed in the sludge treatment process as E1 had the highest concentration in the final untreated mixed sludge of 88-118 µg/kg compared to 2-16 µg/kg for E2 and 0-1.6 µg/kg for EE2. This behaviours confirmed that the interactions between the EDCs and sludge is majorly physical in nature, hence they are easily redistributed to the aqueous phase by desorption.

The removal of the EDCs was found to increase with increasing rate of dinitrification confirming the observation made by Vader *et al.,* 2000. Contrary to the earlier conclusions that most of the estrogenic substance were degraded and not adsorbed to solids (Kroner *et al*., 2000; Mastrup *et al*., 2001; Ivashechkin *et al*., 2004), this research demonstrated that sorption to solid is a significant mechanism of removal for the EDCs which agrees with the findings of Xu et al. (2008).

This Output is one of the detailed surveys of the fate of EDCs in the unit processes of WWTPs available in the literature. The findings provided more information on the mechanism of removal of steroid hormones in WWTPs. It also provided more insight into the behaviour of the EDCs during the different stages of treatment and the influence of operating parameters and treatment plant types. Since the publication of the paper in 2010, it has been cited more than 13 times in various journal articles from around the world as shown in the matrix above and in Appendix 2. In one of the most recent and detailed critical review of the fate of estrogens in wastewater in Water Research Journal (Hamid & Eskicioglu, 2012), the findings were cited nine times by the authors highlighting key conclusions and comparing with other findings by other authors.

7.4 Output 4

Ifelebuegu, A. O., and Ezenwa, P. C. (2011), Removal of endocrine disrupting chemicals in wastewater treatment by Fenton-Like Oxidation. Water, Air and Soil Pollution, 217, 213-220.

	Confirmed/ Replicated	**Contradicted**	**Extended**	**New Contribution**
Methodology	Van Emmerick et al, Yoon et al., 2003			
Empirical Results	Neyens and Baeyens, 2003, Christensen et al. 1993; Wang and Lemley 2002; Guedes et al. 2003; Kavitha and Palanivelu 2004 Lindsey and Tarr, 2000b			Establishment of the thermodynamic feasibility of Fenton-like degradation of estrogens in wastewater Fenton-like degradation enhances the biodegradability of the treated effluent Established of the mechanism of chemical degradation
Citation	**Xu et al., 2013; Paul Raj, 2013**			

This Output investigated the feasibility of Fenton-like oxidation for the removal of steroid hormones in wastewater treatment. Various laboratory and small-scale experiments using Fenton oxidation have been reported in the literature. However, the use of Fenton-like oxidation for the removal of estrogens was not in the literature to the knowledge of the authors. The wastewater industry uses thousands of tons of ferric salts annually for the chemical removal of phosphorus in wastewater treatment. Fenton-like oxidation will therefore offer a potentially cost effective option for the removal of EDCs in wastewater.

The finding demonstrated that the Fenton-like oxidation of estrogens is thermodynamically feasible with activation energy ranging between 23 and 28 kJ/mol for EE2 and E2. The research also established that transformation by-products which were recalcitrant to further degradation were formed during the treatment process. Also it was demonstrated that the Fenton-like treatment improved the biodegradability of the treatment wastewater effluent. The activation energies obtained were comparable to the results reported by other authors for Fenton oxidation (Christensen *et al*., 1993; Wang and Lemley, 2002; Guedes *et al*., 2003; Kavitha and Palanivelu, 2004). It was shown that the Fenton-like process was more effective in degrading estrogens at pHs 4 and below confirming the conclusions from the review by Neyens and Baeyens (2003). Additionally, the presence of DOC in wastewater was found to have significant effect on the removal efficiency which confirmed the report of Lindsey and Tarr (2000) that dissolved organics acts as a sink for hydroxyl radicals.

The outcomes of this Output delivered a body of new information on the feasibility of the removal of EDCs by Fenton-like oxidation as well as the thermodynamic properties. A claim can also be made for applied knowledge as it provided answers to the applicability and recommendation for an effective approach for industrial application of Fenton-like oxidation of EDCs in wastewater treatment.

7.5 Output 5

Ifelebuegu, A. O. (2012), Removal of endocrine disrupters by activated carbon adsorption; Kinetic and thermodynamic studies- Journal of Environmental Protection, 3, 469-475.

	Confirmed/ Replicated	**Contradicted**	**Extended**	**New Contribution**
Methodology				
Empirical Results	Ho et al., 2005 Kiran Kumar et al.,2009; Mohan et al.,2007;		Ifelebuegu et al., 2006	Establishment of the thermodynamic parameters for the adsorption of estrogens to GAC. Confirmed the mechanism of adsorption of the estrogens to GAC. Confirmed the adsorption to be a boundary layer diffusion of the adsorbate to the surface of the GAC
Citation	**N/A**			

This Output, which is a continuation of Output 1, investigated the kinetics and thermodynamics of adsorption of E2 and EE2.There has been several papers on the adsorption properties and capacities of AC to remove EDCs in water and wastewater similar to Output 1. However, there have been very little work to investigate the mechanics of adsorption of estrogens onto AC. This is an essential research required to provide better understanding of the mechanism of adsorption and the influence of operating parameters.

The findings of this Output therefore extended the findings in Output 1 by confirming the mechanism of the adsorption to be predominantly chemisorptions based on the isotherm data, kinetic data, thermodynamic data and the desorption studies. This also confirmed the findings of Ho *et al*. (2005) who had suggested that chemisorption was the rate determining step for the adsorption of basic dyes to activated carbon. The Output also provided new information on the kinetics and thermodynamics properties of the adsorption of E2 and EE2 onto AC, information that is scarce in the literature. The adsorption of the EDCs onto the GAC were found to be as a result of boundary layer diffusion of the adsorbate onto the external surfaces of the GAC

7.6 Output 6

Ifelebuegu, A. O., Onubogu' J., Joyce, E., Mason, T. (2013) Sonochemical degradation of endocrine disrupting chemicals 17β-estradiol and 17α-ethinylestradiol in water and wastewater International Journal of Environmental Science and Technology, DOI: 10.1007/s13762-013-0365-2:

	Confirmed/ Replicated	**Contradicted**	**Extended**	**New Contribution**
Methodology				
Empirical Results	Gultekin and Ince, 2008; Méndez-Arriaga *et al*., 2008; Torress *et al*., 2008; Koda *et al*., 2003; Pétrier *et al*., 2007; Hameed *et al*., 2007 and Torres *et al.*, 2008			Confirmation of the mechanism and thermodynamics of the sonochemical degradations of estrogens Degradation rates per unit power were reported
Citation	**N/A**			

This Output investigated the use of ultrasound to degrade EDCs. The degradation rates were investigated at varying PHs and ultrasound power. It was found that the sonochemical degradation of the estrogens was more favourable at acidic to neutral pH with significant deterioration as alkaline pH ranges. This confirmed the findings of other researchers (Gultekin and Ince, 2008; Méndez-Arriaga *et al*., 2008; and Torres *et al*., 2008), who also reported favourable rates of degradation of other organics during sonochemical degradation. Also further finding (Koda *et al*., 2003; Pétrier *et al*., 2007; Hameed *et al*., 2007 and Torres *et al.*, 2008), were confirmed as the analysis of the rate data showed that the sonochemical degradation of EDCs can be described by both 1st and 2nd order rate equations at the different stages of the reaction process.

Furthermore in this Output we confirmed the mechanism and thermodynamics of the degradation of EDCS by ultrasound and also reported the mass degradation rates per kilowatt hour, which has not been reported elsewhere in the literature.

Chapter 8

Conclusions, Further Work and Claim for PhD

8.1 Conclusions

Our understanding of the fate and behaviour of EDCs in wastewater treatment has improved significantly over the last decade. The work contained in this portfolio has contributed to this improved knowledge. The removal, fate, behaviour and mechanism of removal of EDCs during conventional and novel treatment methods were investigated to provide further understanding of EDCs removal. Some of the key conclusions that can be drawn from this work include:

- The mechanisms of removal of EDCs during conventional wastewater treatment are mostly biodegradation and sorption onto solids through the different unit processes.
- Better removals were achieved with increasing sludge ages and nitrification rates for suspended growth treatment processes.
- Plants designed for biological nutrient removal are more effective in removing EDCs in wastewater.
- The research also demonstrated that with further optimisation of biological treatment processes like ASPs there could be a potential to efficiently and effectively eliminate EDCs biologically without the need for tertiary processes.
- EDCs are persistent under anaerobic conditions and can therefore potentially bioaccumulate in the environment
- Chemical processes are also effective in removing EDCs in wastewater treatment. Activated carbon adsorption, Fenton-like oxidation and sonochemical degradation were found to be effective for the degradation of estrogens and were all thermodynamically feasible.
- Chemical methods are significantly affected by the presence of natural organic matter and can therefore be more effective when used at the tertiary

treatment stages at the end of the conventional biological wastewater treatment processes.

- Physical methods like filtration and physical adsorption onto solids play a significant role in the removal of EDCs during wastewater treatment

8.2 Further Research

This research has demonstrated that biological treatment alone may be effective in the removal of EDCs. This needs to be further investigated to ascertain the cost implications of increasing sludge ages and nitrification rates to enhance the removal process. Also it will be beneficial to further investigate the role played by diverse microorganisms in EDCs with increased sludge ages.

Furthermore, the work has shown that alternative technologies like GAC adsorption, Fenton-like oxidation and sonochemical degradation are all technically feasible. Further investigation will be required to evaluate the commercial feasibility of these methods in full scale treatment applications.

8.3 Claim for PhD

The author believes that this COD and the portfolio demonstrate that the required academic standard and contribution to knowledge has been achieved for the award of PhD. This claim is evidenced by the following:

1. The portfolio represent a significant, continuous and coherent contribution to the subject of the removal of EDCs in wastewater treatment.
2. The Outputs in the portfolio have been cited more than 40 times by other scholars in peer reviewed journals from around the globe (see Appendix 2).
3. The research constitutes an original and independent contribution to knowledge on the removal of EDCs in wastewater treatment.
4. The research papers have been published in journal of international standard and high impact factors and meet the standards of the Research Excellence Framework of the United Kingdom.
5. The analytical methods that were chosen and used were appropriate with adequate quality controls.
6. The portfolio demonstrates the author's critical and thorough knowledge of the relevant topic and associated literatures.
7. The portfolio provides significant process data that will help design engineer to model the design of full scale treatment plants for the removal of EDCs in water and wastewater.

References

Abde-Ghani, N. and Elchaghaby, G. A., (2007), Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. *Int. J. Environ. Sci. Tech*., 4 (4), 451-456.

Abdel-Ghani, N. T., Hegazy, A. K. and El-Chaghaby, G. A. (2009), *Typha domingensis* leaf powder for decontamination of aluminium, iron, zinc and lead: Biosorption kinetics and equilibrium modeling. *Int. J. Environ. Sci. Tech*., 6 (2), 243-248.

Agarry, S. E., Owabor, C. N., & Ajani, A. O. (2013), Modified plantain peel as cellulose-based low-cost adsorbent for the removal of 2, 6–dichlorophenol from aqueous solution: adsorption isotherms, kinetic modelling and thermodynamic studies. *Chem. Eng. Commun.*, 200(8), 1121-1147.

Ahel, M., Giger, W. and Koch, M. (1994), Alkylphenol polyethoxylate surfactants in the aquatic environment – 1 Occurrences and transformation in sewage treatment. *Water Research*, 28, 1131 -1141.

Andersen, H., Siegrist, H., Halling-Sorensen, B. and Ternes, T.A. (2003), Fate of estrogens in a municipal sewage treatment plant. *Environ. Sci. Technol*., 37, 4021–4026.

Andersen, H. R., Hansen, M., Kjolholt, J., Stuer-Lauridsen, F., Ternes, T., Halling-Sorensen, B. (2005), Assessment of the importance of sorption for steroid estrogens removal during activated sludge treatment, *Chemosphere*, 61 (1), 139-146.

Annamalai, K. and Puri, K. I. (2002), Advanced Thermodynamics Engineering. Boca Raton, FL, CRC Press.

Baldouf, G., Haist-Gulde, B. and Brauch, H. J. (1993), Removal of pesticides from raw water. *Water Supply,* 11,187-1995.

Baron C.P., Refsgaard H.H., Skibsted L.H. and Andersen M.L. (*2006*), Oxidation of bovine serum albumin initiated by the Fenton reaction – effect of EDTA, tert-butylhydroperoxide and tetrahydrofuran. *Free Radic. Res.,* 40, 409–417.

Baronti, C., Curini, R., D'Ascenzo, G., Di Corcia, A. and Samperi, R. (2000), Monitoring natural and synthetic estrogens at activated sludge treatment plants and in receiving river water. *Environ. Sci. Technol*., 34, 5059-5066.

Baynes, A., Green, C., Nicol, E., Beresford, N., Kanda, R., Henshaw, A. and & Jobling, S. (2012), Additional Treatment of Wastewater Reduces Endocrine Disruption in Wild Fish A Comparative Study of Tertiary and Advanced Treatments. *Environ. Sci. Technol., 46*(10), 5565-5573.

Belfroid, A. C., Van der Horst, A., Vethaak, A.D., Schafer, A. J., and Samperi, R. (1999), Analysis and occurrence of estrogenic hormones and their glucuronides in surface water and wastewater in the Netherlands, *Sci. Total Environ.*, 225, 17 – 27.

Beltrán, F. J., Pocostales, P., Alvarez, P., & Aguinaco, A. (2009), Ozone-activated Carbon Mineralization of 17-α-Ethynylestradiol Aqueous Solutions. *Ozone Sci. Eng.*, *31*(6), 422-427.

Bennie, D.T. (1999), Review of the environmental occurrence of alkylphenols and alkylphenol ethoxylates, *Water Qual. Res. J. Can.,* 34, 79–122.

Birkett, J.W. and Lester, J.N. (2003), Endocrine Disrupters in Wastewater and Sludge Treatment Processes. CRC Press LLC, Florida.

Chen, P. J., Rosenfeldt, E. J., Kullman, S. W., Hinton, D. E., & Linden, K. G. (2007), Biological assessments of a mixture of endocrine disruptors at environmentally relevant concentrations in water following UV/H2O2 oxidation. *Sci. Total Environ., 376*(1-3), 18-26.

Chen, Y., Zhang, X. X., Wu, B., Liu, B., Xiao, L., Li, A., & Cheng, S. (2012), Semivolatile organic compounds removal and health risk reduction in drinking water treatment biofilters applying different backwashing strategies. *Inter. J. Environ. Sci. Technol. 9*(4), 661-670.

Chiha M., Hamdaoui O., Baup S., Gondrexon N. (2011), Sonolytic degradation of endocrine disrupting chemical 4-cumylphenol in water. Ultrasonics Sonochem., 18 (5), 943 – 950.

Choi, K. J., Kim, S. G., Kim, C. W. and Kim, S. H. (2005), Effects of Activated Carbon Types and Service Life on the Re-moval of Endocrine Disrupting Chemicals: Amitrol, Nonylphenol and Bisphenol-A. *Chemosphere,* 58,(11), 1535-1545.

Clara, M., Strenn, B., Saracevic, E., Kreuzinger, N. (2004) Adsorption of bisphenol-A, 17â-estradiol and 17á-ethinylestradiol to sewage sludge, *Chemosphere,* 56 (9), 843-851.

Christensen, H., Sehestedand, K., and Logager, T. (1993), The reaction of hydrogen peroxide with Fe(II) ions at elevated temperatures, *Radiat. Phys. Chem.,* 41(3), 575–578.

Czajka, C.P. and Londry, K.L. (2006), Anaerobic biotransformation of estrogens, Sci. *Total Environ.*, 367 (2–3), 932–941.

Daughton, C.G. and Ternes, T.A. (1999), Pharmaceuticals and personal care products in the environment: Agents of subtle change? *Environ. Health Persp.,* 107, 907-938.

Deborde, M., Rabouan, S., Duguet, J.P. and Legube, B. (2005), Kinetics of aqueous ozone-induced oxidation of some endocrine disruptors. *Environ. Sci. Technol.,* 39, 6086-6092.

Deborde M. and von Gunten, U. (2008), Reactions of chlorine with inorganic and organic compounds during water treatment-kinetic and mechanisms: A critical review. *Water Research,* 42 (1-2), 13-51.

De Rudder, J., Van de Wiele, T., Dhooge W., Comhaire F. and Verstraete W. (2004), Advanced water treatment with manganese oxide for the removal of 17-ethynylestradiol. *Water Res*., 38, 184 – 192 (2004).

Desbrow, C., Routledge, E.J., Brighty, G.C., Sumpter, J.P. and Waldock, M. (1998), Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and in vitro biological screening. *Environ. Sci. Technol.,* 32, 1549-1558.

Di Corcia, A., Constantino, A., Crescenzi, C., Marinoni, E. and Samperi, R. (1998), Charaterisation of recalcitrant intermediates from Biotransformation of branched alkyl side chain of nonylphenol ethoxylates surfactants, *Environmental Science and Technology*. 32, 2401 – 2409.

Do, A. T. (2011), *Anaerobic Membrane Bioreactor (AnMBR) for Treatment of Landfill Leachate and Removal of Micropollutants* (Doctoral dissertation, University of South Florida).

Ermawati, R., Morimura, S., Tang Y., Liu, K., and Kida, K. (2007), Degradation and behaviour of natural steroid hormones in cow manure waste during biological treatments and ozone oxidation. *J. Bioresour. Bioeng.,* 103 (1), 27 – 31.

Esperanza, M., Suidan, M.T., Marfil-Vega, R., Gonzalez, C., Sorial, G.A., McCauley P., and Brenner, R. (2007), Fate of sex hormones in two pilot-scale municipal wastewater treatment plants: conventional treatment, *Chemosphere* 66 (8), 1535 – 1544.

Esplugas S, Bila DM, Krause LGT, Dezotti M (2007), Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. J. Hazard. Mater., 149, 631–642.

Feng, Y., Zhang, Z., Gao, P., Su, H., Yu, Y., Ren, N. (2010), Adsorption behaviour of EE2 (17α-ethinylestradiol) onto the inactivated sewage sludge: Kinetics, thermodynamics and influence factors. *J. Hazard. Mater.,* 175 (1-3), 970-976.

Filby, A.L., Shears, J.A., Drage, B.E., Churchley, J.H. and Tyler, C.R. (2010), Effects of advanced treatment of wastewater effluents on estrogenic and reproductive health impacts in fish. *Environ. Sci. Technol.*, *44* (11), 4348-4354.

Fredonia Group 2011. “World Activated Carbon” Industry forecast for 2012 & 2017. Available online from http://www.freedoniagroup.com/brochure/23xx/2363smwe.pdf accessed 25/04/2013.

Gabet-Giraud, V., Miege, C., Choubert, J.M., Martin Ruel S. and Coquery M. (2010), Occurrence and removal of estrogens and beta blockers by various processes in wastewater treatment plants. *Sci. Total Environ.,* 408(19), 4257 – 4269.

Gianico, A., Braguglia, C. M., Mascolo, G., & Mininni, G. (2013), Partitioning of nutrients and micropollutants along the sludge treatment line: a case study. *Enviro. Sc. Poll. Res.,* 1-10.

Gogate, P. R. (2002), Cavitation: an auxiliary technique in wastewater treatment schemes. *Adv. Environ. Res.*, *6*(3), 335-358.

Gogate, P. R., & Pandit, A. B. (2004a), A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Adv. Environ. Res., 8*(3), 501-551.

Gogate, P. R., & Pandit, A. B. (2004b), A review of imperative technologies for wastewater treatment II: hybrid methods. *Adv. Environ. Res., 8*(3), 553-597.

Gomes, R.L., Deacon, H.E., Lai, K.M., Birkett, J.W., Scrimshaw, M.D. and Lester, J.N. (2004), An assessment of the bioaccumulation of estrone in Daphnia magna. *Environ. Toxicol. Chem*., 23 (1), 105-108.

Gomes, R.L., Scrimshaw, M. D., Cartmell, E., & Lester, J. N. (2011), The fate of steroid estrogens: partitioning during wastewater treatment and onto river sediments. *Environ. monitor. Assess.*, *175*(1-4), 431-441.

Gomez, M.J., Petrovic, M., Fernandez-Alba, A.R. and Barcelo, D. (2006), Determination of pharmaceuticals of various therapeutic classes by solid-phase extraction and liquid chromatography-tandem mass spectrometry analysis in hospital effluent wastewaters. *J. Chromatogr., A,* 1114 (2), 224-233.

Gomez, M.J., Martinez Bueno, M.J., Lacorte, S., Fernandez-Alba, A.R. and Aguera, A. (2007), Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. *Chemosphere*, 66 (6), 993 – 1002.

Gong, R., Liang, J., Chen, J., Huang, F. (2009), Removal of bisphenol A from aqueous solution by hydrophobic sorption of hemimicelles. *Int. J. Environ. Sci. Tech.*, 6 (4), 539-544.

Gotvajn, A. Z., and Zagorc-Končan, J. (2005), Combination of Fenton and biological oxidation for treatment of heavily polluted fermentation waste broth. *Acta Chimica Slovenica,* 52, 131–137.

Guedes, A.M.F.M.,. Madeira, L.M.P. Boaventura, R.A.R. and Costa C.A.V. (2003), Fenton oxidation of cork cooking wastewater—overall kinetic analysis Water Research, 37,3061–3069.

Guengerich, F. P. (1990), Metabolism of 17α-ethynylestradiol in humans. *Life Sciences*, 47, 1981 – 1988.

Gultekin, I. and Ince, N. (2008), Ultrasonic destruction of bisphenol-A: the operating parameters, *Ultrason. Sonochem.* 15 (4), 524-529.

Haag, W.R. and Yao, C.C.D. (1992), Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. Technol*., 26, 1005-1013.

Hamid, H., & Eskicioglu, C. (2012), Fate of estrogenic hormones in wastewater and sludge treatment: A review of properties and analytical detection techniques in sludge matrix. *Water Res., 46(18), 5813-5833.*

Hameed, B.H., Ahmad, A., Aziz, N. (2007), Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash. *Chem. Eng. J.,* 133(1-3), 195-203.

Han, J., Qiu, W., Meng, S., and Gao, W. (2012), Removal of ethinylestradiol (EE2) from water via adsorption on aliphatic polyamides. *Water Res., 46(17), 5715-5744.*

Hashimoto, T., Onda, K., Nakamura, Y., Tada, K., Miya, A. and Murakami, T. (2007), Comparison of natural estrogen removal efficiency in the conventional activated sludge process and the oxidation ditch process. *Water Res.,* 41 (10), 2117 -2126.

Hey, G., Grabic, R., Ledin, A., la Cour Jansen, J., & Andersen, H. R. (2012), Oxidation of pharmaceuticals by chlorine dioxide in biologically treated wastewater. *Chem. Eng. J., 185*, 236-242.

Ho, L., Grasset, C., Hoefel, D., Dixon, M. B., Leusch, F. D., Newcombe, G. & Brookes, J. D. (2011), Assessing granular media filtration for the removal of chemical contaminants from wastewater. *Water Res., 45*(11), 3461-3472.

Ho, Y. S. Chiu W. T. and Wang, C. C. (2005), Regression Analysis for the Sorption Isotherms of Basic Dyes on Sugar-cane Dust. *Bioresour. Technol.*, 96, 1285-1291.

Holbrook, R.D., Novak, J.T., Grizzard, T.J. and Love, N.G. (2002), Estrogen receptor agonist fate during wastewater and biosolids treatment processes: A mass balance analysis. *Environ. Sci. Technol*., 36, 4533–4539.

Hörsing, M. Ledin, A. Grabic, R. Fick, J. Tysklind, M. la Cour Jansen, J. and Andersen H.R. (2011), Determination of sorption of seventy-five pharmaceuticals in sewage sludge. *Water Res.,* 45, 4470–4482.

Huang, C. H.and Sedlak, D. L. (2001), Analysis of estrogenic hormones in municipal wastewater effluent and surface water using enzyme-linked immunosorbent assay and gas chromatography/tandem mass spectroscopy. Environ. Toxicol. Chem., 20 (1), 133-139.

Huber, M.M., Canonica, S., Park, G.Y. and Von Gunten, U. (2003), Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ. Sci. Technol*., 37, 1016-1024.

Huo, C.and Hickley, P. (2006), Anglian Water approach to the EDC demonstration programme as an early start company. Proceedings of the CIWEM conference on Endocrine disrupting chemicals in the water environment, 30th March, 2006, Biocity Nottingham, UK.

Hsueh, C. L., Huang, Y.H., Wang, C.C., Chen, Y. (2005), Degradation of azo dyes using low iron concentration of Fenton and Fenton-like System. *Chemosphere*, 58 (10), 1409-1414.

Ifelebuegu, A. O. Lester, J. N. Churchley J. and Cartmell, E. (2006), Removal of an endocrine disrupting chemical (17alpha-ethinyloestradiol) from wastewater effluent by activated carbon adsorption: effects of activated carbon type and competitive adsorption. *J. Environ. Technol.,* 27, 1343-1349.

Ifelebuegu, A. O., Theophilus, S. C. and Bateman, M.J. (2010), Mechanistic evaluation of the sorption properties of endocrine disrupting chemicals in sewage sludge biomass. *Int. J. Environ. Sci. Technol.,* 7 (4), 617-622

Ifelebuegu, A. O. (2011), The Fate and Behaviour of Selected Endocrine Disrupting Chemicals in Full Scale Wastewater and Sludge Treatment Unit Processes. *Int. J. Environ. Sci. Technol.,* 8 (2), 245-254.

Ifelebuegu A. O. and Ezenwa, C. P. (2011), Removal of endocrine disrupting chemicals in wastewater treatment by Fenton-like oxidation, Water Air Soil Poll. 217 (1-4), 213 – 220.

Ifelebuegu, A. O. (2012), Removal of Steriod Hormones by Activated Carbon Adsorption—Kinetic and Thermodynamic Studies. *J. Environ. Protection*, *3*(6), 469-475.

Ince, N. H., Tezcanli, G., Belen, R. K., and Apikyan, İ. G. (2001), Ultrasound as a catalyzer of aqueous reaction systems: the state of the art and environmental applications. *Appl. Catal. B- Environ., 29*(3), 167-176.

Irmak, S., Erbatur, O. and Akgerman, A. (2005), Degradation of 17 beta-estradiol and bisphenol A in aqueous medium by using ozone and ozone/UV techniques. *J. Hazard. Mater.,* 126, 54-62.

Ivashechkin, P., Corvini, P.F.X. and Dohmann, M. (2004), Behaviour of endocrine disrupting chemicals during the treatment of municipal sewage sludge. *Water Sci. Technol.,* 50(5), 133–140.

Jobling, S., Tyler, C.R., Nolan, M. and Sumpter, J.P. (1998a), The identification of estrogenic effect in wild fish. R & D Technical Report W119, Environment Agency, Bristol, UK.

Jobling, S., Nolan, M., Tyler, C.R., Brighty, G.C. and Sumpter, J.P. (1998b), Widespread sexual disruption in wild fish. *Environ. Sci Technol*. 32 (17), 2498 – 2506.

Johnson, A. C., Belfroid, A. and Di Corsa, A. (2000), Estimating steroid oestrogen inputs to activated sludge treatment works and observations on their removal from the effluent. *Sci. Total Environ*., 256(2-3), 163 – 173.

Johnson A.C. and Williams, R.J. (2004), A model to estimate influent and effluent concentrations of estradiol, estrone, and ethinylestradiol at sewage treatment works. *Environ. Sci. Technol*., 38, 3649–3658.

Jonkers, N., Knepper, T.P. and DeVoogt, P. (2001), Aerobic biodegradation of nonylphenol ethoxylates in river water using liquid chromatography-electrospray tandem mass spectrometry. Environ. Sci. Technol., 35, 335 – 340.

Joss, A., Andersen, H., Ternes, T., Richle, P.R. and Siegrist, H. (2004), Removal of estrogens in municipal wastewater treatment under aerobic and anaerobic conditions: Consequences for plant optimization. Environ. Sci. Technol. 38 (11), 3047-3055.

Jurgens, M. D., Holthaus, K. I. E., Johnson, A. C., Smith J. J.L., Hetheridge, M., Williams, R. (2002), The potential for estradiol and ethinylestradiol degradation in English Rivers. *Environ. Toxicol. Chem.,* 21 (3), 480-488.

Kanda, R. and Churchley, J. (2008), Removal of endocrine disrupting chemicals during conventional wastewater treatment. *Environ. Technol.* 29, 315 – 323.

Katsumata, H., Kawabe, S., Kaneco, S., Suzuki, T. and Ohta, K. (2004), Degradation of bisphenol A in water by the photo-Fenton reaction. J. Photochem. Photobiol. A: Chem., 162(2-3), 297 – 305.

Kavitha, V., and Palanivelu, K. (2004), The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere*, 55(9), 1235–1243.

Keenan, H. E., Sakultantimetha, A. and Bengkedphol, S.(2008), Environmental fate and partition co-efficient of oestrogenic compounds in sewage treatment process. *Environ. Res*., 106 (3), 313-318.

Kim, J.K.; Huang, C.P.; Chiu, P. C., (2001), Sonochemical decomposition of dibenzothiophene in aqueous solution, *Water Res*., 35 (18), 4370 -4378.

Kiran Kumar, K. S. Mohan S. V. and Sarma, P. N. (2009), Sorptive removal of endocrine disruptive compound (estriol, E3) from aqueous phase by batch and column studies: kinetic and mechanistic Evaluation, *J. Hazard. Mater.,*164, 820-828.

Kiran Kumar, A. K. and Mohan, S. V. (2011), Endocrine disrupting synthetic estrogen (17α-ethinyloestradiol) removal from aqueous phase through batch and column sorption studies: mechanistic and kinetic Analysis. *Desalination*, 276, 66-74.

Kiran Kumar, A., & Venkata Mohan, S. (2012), Removal of natural and synthetic endocrine disrupting estrogens by multi-walled carbon nanotubes (MWCNT) as adsorbent: Kinetic and mechanistic evaluation. *Sep. Purif. Technol.*, *87*, 22-30.

Koda, S.K.T., Kondo, T. and Mitome, H. (2003), A standard method to calibrate sonochemical efficiency of an individual reaction system. *Ultrason. Sonochem*., 10 (3), 149-156.

Koh, Y.K.K., Chiu, T.Y., Boobis, A., Cartmell, E. and Lester, J.N. (2008),Treatment and removal strategies for estrogens from wastewater. *Environ. Technol.,* 29, 245–267.

Koh, Y.K.K., Chiu, T.Y., Boobis, A., Scrimshaw, M.D., Bagnall, J.P., Soares, A., Pollard, S., Cartmell, E. and Lester, J.N. (2009), Influence of operating parameters on the biodegradation of steroid estrogens and nonylphenolic compounds during biological wastewater treatment processes. *Environ. Sci. Technol*., 43 (17), 6646–6654.

Korner, W., Bolz, U., Sussmuth, W., Hiller, G., Schuller, W., Hanf, V. and Hagenmaier, H. (2000), Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany. *Chemosphere*, 40(9-11), 1131-1142.

Langford, K. and Lester, J. N. (2003), Fate and behavior of endocrine disrupters in wastewater treatment processes. In: Birkett, J. W. and Lester, J. N., (Eds.), Endocrine Disrupters in Wastewater and Sludge Treatment Processes, Lewis Publishers and IWA Publishing, London, UK.

Lai, K.M., Scrimshaw, M.D. and Lester, J.N. (2002a), Biotransformation and bioconcentration of steroid estrogens by Chlorella vulgaris. *App. Environ. Microbiol*., 68, 859-864.

Lai, K.M., Scrimshaw, M.D. and Lester, J.N. (2002b), Prediction of the bioaccumulation factors and body burden of natural and synthetic estrogens in aquatic organisms in river systems. *Sci. Total Environ*., 289, 159-168.

Lee, H-B. and Peart, T. E. (1998), Determination of 17β-estradiol and it metabolites in sewage effluent by solid phase extraction and gas chromatography/mass spectrometry. *J. AOAC Int*., 81, 1209 – 1216.

Lindsey, M. E. and Tarr, M. A. (2000a), Inhibition of hydroxide radical reaction with aromatics by dissolved natural organic matter. *Environ. Sci. Technol*., 34(3), 444–449.

Li, Q., Snoeyink, V.L., Mariñas, B.J., Campos C. (2003), Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. *Water Res*., 37, 4863–4872.

Lin, H., Peng, W., Zhang, M., Chen, J., Hong, H., & Zhang, Y. (2013), A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives. *Desalination*, *314*, 169-188.

Lindsey, M. E. and Tarr, M. A. (2000a), Quantitation of hydroxyl radical during Fenton oxidation following a single addition of iron and peroxide. *Chemosphere*, 41(3), 409–417.

Lindsey, M. E., & Tarr, M. A. (2000b), Inhibition of hydroxyl radical reaction with aromatics by dissolved natural organic matter. *Environ. Sci. Technol.*, *34*(3), 444-449.

Liu, B. and Liu, X.L. (2004), Direct photolysis of estrogens in aqueous solutions. *Sci. Total Environ.,* 320, 269-274.

Liu Z.H., Kanjo, Y. and Mizutani, S. (2009), Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment - physical means, biodegradation, and chemical advanced oxidation: a review. *Sci. Total Environ*., 407 (2), 731 -748.

Lucas, M. S., & Peres, J. A. (2009), Removal of COD from olive mill wastewater by Fenton's reagent: kinetic study. *J. Hazard. Mater*., 168(2–3), 1258–1259.

Madhavan, J., Grieser, F. and Ashokkumar, M. (2010), Combined advanced oxidation processes for the synergistic degradation of ibuprofen in aqueous environments. *J. Hazard. Mater*. 178 (1-3), 202 – 208.

Maguire, R. J. (1999), Review of the persistence of nonyphenol and nonyphenol ethoxylates in aquactic environment. Water Qual. Res. J. Can., 34, 37 – 78.

Mason, T. J. (1999), Sonochemistry. New York, Oxford University Press.

Mason, T. J., and Petrier, C. (2004), Ultrasound processes. *Advanced Oxidation Processes for Water and Wastewater Treatment, IWA Publishing, London*, 185-208.

Mastrup, M., Jensen, R.L., Schafer, A.I. and Khan, S. (2001), Fate modeling – an important tool for water recycling. In Recent Advances in Water Recycling Technologies, Edited by: Schafer, A.I., Sherman, P. and Waite, T.D. 103–112. Australia: University of New South Wales, Sydney and Environmental Protection Agency (EPA). Centre for Water and Waste Technology, Civil and Environmental Engineering

Méndez-Arriaga, F., Torres-Palma, R. A., Petrier, C., Esplugas, S., Gimenez, J., & Pulgarin, C. (2008), Ultrasonic treatment of water contaminated with ibuprofen. *Water Res.*, *42*(16), 4243-4248.

Mendez-Arriaga, F., Esplugas, S., and Gimenez, J. (2010), Degradation of the emerging contaminant ibruprofen in water by photo-Fenton. *Water Res*., 44(2), 589–595.

Metcalf and Eddy, Inc., Tchobanoglous, G., Burton, F.L. and Stensel, H.D. (2003), *Wastewater Engineering : Treatment and Reuse*. McGraw-Hill, Boston, London.

Miege, C., Choubert, ., J.M., Ribeiro, L., Eusebe M. and Coquery, M. (2009), Fate of pharmaceuticals and personal care products in wastewater treatment plants — conception of a database and first results, Environ. Poll., 157 (5), 1721–1726.

Mohan, S. V., Shailaja, S., Rama Krishna, M. and Sarma, P. N. (2007), Adsorptive removal of phthalate ester (di-ethyl phthalate) from aqueous phase by activated carbon: A kinetic study *J. Hazard. Mater.,* 146 (1-2), 278-282.

Moharikar, A., Purohit, H.J. and Kumar, R. (2005), Microbial population dynamics at effluent treatment plants. *J. Environ. Monitor*., 7, 552–558.

Naddeo, V., Landi, M., Belgiorno, V. and Napoli, R. (2009), Wastewater disinfection by combination of ultrasound and ultraviolet irradiation. *J. Hazard. Mater*. 168 (2-3), 925-929.

Nakada, N., Tanishima, T., Shinokara, H., Kiri, K. and Takada, H. (2006), Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. *Water Res*. 40 (17), 3297 – 3303.

Nakagawa, S., Kenmochi, Y., Tutumi, K., Tanaka, T. and Hirasawa, I.(2002), A study on the degradation of endocrine disruptors and dioxins by ozonation and Advanced Oxidation Processes. *J. Chem. Eng. Jpn*., 35, 840-847 (2002).

Nasu, M., Oshima, Y. and Tanaka, H. (2001), Study on endocrine disrupting chemicals in wastewater treatment plants, *Water Sci. Technol*. 43(2), 101-108.

Neyens, E., and Baeyens, J. A. (2003), Review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazard. Mater*., 98(1–3), 33–55.

Ohko, Y., Iuchi, K.I., Niwa, C., Tatsuma, T., Nakashima, T., Iguchi, T., Kubota, Y. and Fujishima, A. (2002), 17 beta-estrodial degradation by TiO_2 photocatalysis as means of reducing estrogenic activity. *Environ. Sci. Technol.,* 36, 4175-4181.

Pan, B., Lin, D., Mashayekhi, H. and Xing, B. (2008), Adsorption and hysteresis of bisphenol A and 17α-ethinyl Estradiol on carbon nanomaterials. *Environ. Sci. Technol.*, 2008, *42* (15), 5480–5485.

Panter, G. H., Thompson, R. S., Beresford, N. and Sumpter, J. P. (1999), Transformation of a non-oestrogenic steroid metabolite to an oestrogenically active substance by minimal bacterial activity. *Chemosphere,* 38, 3579-3596.

Patrolecco, L., Capri S., De Angelis S., Polesello S. and Valsecchi S. (2004), Determination of endocrine disrupting chemicals in environmental solid matrices by extraction with a non-ionic surfactant (Tween 80). J.Chromatogr. A, 1022 (1-2), 17.

Paul Raj, S., Kuriechem,S.K. and Murugesan, S. (2013), Mineralization of Azo Dye Using Combined Photo-Fenton and Photocatalytic Processes under Visible Light. *J. Catalysts*, *2013*.

Pétrier, C., Combet, E. and Mason, T. (2007), Oxygen-induced concurrent ultrasonic degradation of volatile and non-volatile aromatic compounds, *Ultrason. Sonochem*. 14 (2), 117–121.

Petrie, B., McAdam, E. J., Whelan, M. J., Lester, J. N., & Cartmell, E. (2013), The determination of nonylphenol and its precursors in a trickling filter wastewater treatment process. *Anal. Bioanal. Chem.,* 405(10, 3243-3253.

Petrovic, M. *and* Barcelo, D. *(*2006)*,* Liquid Chromotography-Mass Spectrometry in the Analysis of Emerging Environmental Contaminants*. Anal. Bioanal.Chem.,* 385*(*3*):*422-424*.*

Plósz, B. G., Leknes, H., Liltved, H. and Thomas, K. V. (2010), Diurnal variations in the occurrence and the fate of hormones and antibiotics in activated sludge wastewater treatment in Oslo, Norway. *Sci. Total Environ*., 408 (8), 1915 -1924

Purdom, C.E., Hardiman, P. A, Bye, V.J., Eno, N. C., Tyler, C. R. and Sumpter, J.P. (1994), Estrogenic effects of effluents from sewage treatment works. Chem. Ecol., 8 (4), pp. 456 – 457

Quinn-Hosey, K. M., Roche, J. J., Fogarty, A. M., & Brougham, C. A. (2012), A Toxicological Assessment of Endocrine Disrupting Chemicals Found in the BMW (Border, Midland and Western) Region of Ireland. *J. Environ. Protection*, *3*(4), 304-315.

Reddy, S., Iden, C. R. and Brownnawell, B. J. (2005), Analysis of steroid conjugates in sewage influent and effluent by liquid chromatography-tandem mass spectrometry *Anal. Chem*., 77 (21), 7032 -7038.

Ren, H.Y., Ji, S.L., Ahmad, N.U.D., Dao W., Cui, C.W. (2007). Degradation characteristics and metabolic pathway of 17 alpha-ethynylestradiol by Sphingobacterium sp JCR5. *Chemosphere* 66 (2), 340–346.

Rogers, H.R., Watts, C.D. and Palfrey, L. (2000), Fate and behaviour of steroid endocrines in sewage treatment. UKWIR Report.

Rosal, R., Rodríguez, A., Perdigón-Melón, J. A., Petre, A., García-Calvo, E., Gómez, M. J., Agüera, A. and Fernández-Alba, A. R. (2010), Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. *Water Res*., 44 (2), 578-588.

Rosenfeldt, E.J. and Linden K.G. (2004), Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. *Environ. Sci. Technol*., 38, 5476–5483.

Rowsell, V. F., Pang, D. S. C., Tsafou, F., & Voulvoulis, N. (2009), Removal of steroid estrogens from wastewater using granular activated carbon: comparison between virgin and reactivated carbon. *Water Environment Research*, *81*(4), 394-400.

Singh, S. (2012), Ozone Treatment of Municipal Wastewater Effluent for Oxidation of Emerging Contaminants and Disinfection.

Standing Committee of Analyst (SCA), 2005, The determination of steroid estrogens in environmental and wastewater using chromatography and mass spectrometery, Environment Agency, Bristol, UK.

Soltanali, S. and Shams Hagani, Z. (2008), Modeling of air stripping from volatile organic compounds in biological treatment processes. *Int. J. Environ. Sci*. *Tech*nol., 5 (3), 353-360.

Sumpter, J.P. and Jobling, S. (1995), Vitellogenesis as a biomarker for estrogenic contamination of the aquatic environment. *Environ. Health Perspect*., 103 (Suppl. 7), 173-178.

Surujlal-Naicker, S., & Bux, F. (2013), Application of radio-immunoassays to assess the fate of estrogen EDCs in full scale wastewater treatment plants. *Environ, Sci. Heal. A*, *48*(1), 37-47.

Snyder, S. A., Keith, T. L., Verbrugge, D. A., Snyder, E. M., Gross, T. S., Kannan, K., & Giesy, J. P. (1999), Analytical methods for detection of selected estrogenic compounds in aqueous mixtures. *Environ. Sci. Technol.*, *33*(16), 2814-2820.

Snyder, S. A., Villeneuve, D. L., Snyder, E. M., & Giesy, J. P. (2001), Identification and quantification of estrogen receptor agonists in wastewater effluents. *Environ. Sci. Technol., 35*(18), 3620-3625.

Snyder, S.A., Westerhoff, P., Yoon, Y. and Sedlak, D.L. (2003), Pharmaceuticals, personal care products and endocrine disrupters in water: implication for water treatment. *Environ. Eng. Sci*., 20, 449-469.

Suri, R.P.S. Nayak, M. Devaiah, U. Helmig E. (2007), Ultrasound assisted destruction of estrogen hormones in aqueous solution: effect of power density, power intensity and reactor configuration. *J. Hazard. Mater*., 146, 472–478.

Svenson, A., Allard, A.S. and Ek, M. (2003), Removal of estrogenicity in Swedish municipal sewage treatment plants. *Water Res*., 37, 4433–4443.

Ternes, T. A., Kreckel, P and Muller, J. (1999a), Behavior and occurrence of estrogens in municipal sewage treatment plants ll. Aerobic batch experiments with activated sludge. *Sci. Total Environ.,* 225(1-2), 91-99.

Ternes, T A., Stumpf, M., Mueller, J., Haberer, K., Wilken R-D., Servos, M. (1999b), Behaviour and occurrence of estrogens in municipal sewage treatment plants -1 investigation in German, Canada and Brazil. *Sci. Total Environ*., 225(1-2), 81-90.

Ternes, T.A., Andersen, H., Gilberg, D. and Bonerz, M. (2002), Determination of estrogens in sludge and sediments by liquid extraction and GC/MS/MS. *Anal. Chem.,* 74, (14), 3498-3504.

Ternes, T.A., Stuber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M. and Teiser, B. (2003), Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Res*., 37, 1976-1982.

Ternes, T. A., Herrmann, N., Bonerz, M.; Knacker, T., Siegrist,H. and Joss, A. (2004), A rapid method to measure the solid water distribution coefficient (Kd) for pharmaceuticals and musk fragrances in sewage sludge. *Water Res*., 38 (19), 4075-4084

Torres, R. A., Abdelmalek, F., Combet, E., Pétrier, C., & Pulgarin, C. (2007), A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in deionised and natural waters. *J. Hazard. Mater.*, *146*(3), 546-551.

Torres, R., Petrier, C., Combet, E., Carrier, M. and Pulgarin, C. (2008), Ultrasonic cavitation applied to the treatment of bisphenol A. effect of sonochemical parameters and analysis of BPA by-products. *Ultrason. Sonochem*. 15 (4), 605-611.

Turan, A. (1995), Excretion of natural and synthetic estrogens and their metabolites: Occurrence and behaviour in water. In Endocrinally Active Chemicals in the Environment, 15–50. Berlin: German Federal Environment Agency.

Tyler, C. R., & Filby, A. L. (2011), Feminized Fish, Environmental Estrogens, and Wastewater Effluents in English Rivers. In *Wildlife Ecotoxicology* (pp. 383-412). Springer New York.

Vader, J.S., van Ginkel, C.G., Sperling, F.M.G.M., de Jong, J., de Boer, W., de Graaf, J.S., van der Most, M. and Stokman, P.G.W. (2000), Degradation of ethinyl estradiol by nitrifying activated sludge. *Chemosphere,* 41, 1239-1243.

Van Emmerik, T., Angove, M. J., Johnson, B. B., Wells, J. D., and Fernandes, M. B. (2003), Sorption of 17β-estradiol onto selected soil minerals. J. Colloid Interface Sci., 266(1), 33–39.

von Gunten, U. (2003), Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res*., 37, 1443-1467.

Wang, Q. and Lemley, A. T. (2002), Oxidation of diazinon by anodic Fenton's treatment. *Water Res*. 36 (13), 3237–3244.

Wang, H. X., Zhou, Y., & Jiang, Q. W. (2012), Simultaneous screening of estrogens, progestogens, and phenols and their metabolites in potable water and river water by ultra-performance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry. *Microchem. J., 100*, 83-94.

Wegener, G., Roisch, U., Karrenbrock, F. and Hubner, I. (2001), Endocrine disrupters – no hazard to drinking water. Presented at conference in Berlin, April 2001.

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005), Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ. Sci. Technol*., 3 (17), 6649–6663.

Williams, R.J, Johnson, A.C., Smith, J.J.L. and Kanda, R. (2003), Steriod estrogens profiles along river streches arising from sewage treatment discharges. Environ. Sci. Technol. 37, 1744-1750.

Xin, T., Wang, X., Jin, H., Liang, S., Lin, J. and Li, Z. (2009), Development of magnetic particle-based chemiluminescence enzyme immunoassay for the detection of 17 beta-estradiol in environmental water", *Appl. Biochem. Biotechnol.,* 158 (3), 582-594.

Xu, X. R., Wang, W. H., Li, H. B., and Gu, J. D. (2004), Degradation of dyes in aqueous solutions by the Fenton process. *Chemosphere*, 57(7), 595–600.

Xu, J., Wu, L.S., Chen, W.P., Chang, A.C., (2008), Simultaneous determination of pharmaceuticals, endocrine disrupting compounds and hormone in soils by gas chromatography–mass spectrometry. *J. Chromatogr*. A 1202, 189–195.

Xu, N., Zhang, Y., Tao, H., Zhou, S. and Zeng, Y. (2013), Bio-Electro-Fenton System for Enhanced Estrogens Degradation. *Bioresource technol., 138, 136-140*.

Yang, G.C.C. and Long Y.W. (1999), Removal of degradation of phenol in a saturated flow by in-situ electrokinetic remediation and Fenton-like process. *J. Hazard. Mater*., 69, 259–271.

Yoochatchaval, W., Ohashi, A., Harada, H., Yamaguchi, T. and Syutsubo, K. (2008), Characteristics of granular sludge in an EGSB reactor for treating low strength wastewater. *Int. J. Environ. Res*., 2 (4), 319-328.

Yoon, Y., Westerhoff, P., Snyder, S. A., and Esparza, M. (2003), HPLC-fluorescence detection and adsorption of Bisphenol A, 17β-estradiol, and 17α-ethynyl estradiol on powdered activated carbon. *Water Res*., 37(14), 3530–3537.

Zhang, Y. and Zhou, J.L. (2008), Occurrence and removal of endocrine disrupting chemicals in wastewater. *Chemosphere*, 73 (5), 848-853.

Zhang, Z. H., Feng, Y. J., Gao, P., Liu, J. F., & Ren, N. Q. (2012), Comparing the adsorption and desorption characteristics of 17α-ethinylestradiol on sludge derived from different treatment units. *Inter. J. Environ. Sci. Technol., 9*(2), 247-256.

Zhou, H., Huang, X., Wang, X., Zhi, X., Yang, C., Wen, X., Wang, Q., Tsuno, H. and Tanaka, H. (2010), Behaviour of selected endocrine disrupting chemicals in three sewage treatment plants of Beijing, China. *Environ. Monit. Assess*., 161, 107-121.

Appendix 1 Contribution by Others

The author has been the lead researcher and corresponding author for all the Outputs contained in this portfolio. The Table below estimates the contributions made by other collaborators to the entire process of research, data collection and write-up.

Outputs 1	**Contributors**				**Remarks**
	Ifelebuegu, A.O.	Churchley, J.	Lester, J.	Cartmell, E.	Project was initiated by Churchley. The author was responsible for carrying out the laboratory experiments and the write up of the paper under the supervision of Cartmell and Lester.
	80%	10%	5%	5%	
Output 2	Ifelebuegu, A.O.	Theophilus, S. C.	Bateman, M.J.		The research was initiated by the author. Laboratory experiments were carried out by the author and Theophilus. Paper was written 100% by the author
	80%	17%	3%		
Output 3	Ifelebuegu, A.O.	-	-	-	-
	100%				
Output 4	Ifelebuegu, A.O.	Ezenwa, P.C.	-	-	Research was initiated by the author and experiments carried out in collaboration with Ezenwa. Paper was written 100% by the author.
	90%	10%			
Output 5	Ifelebuegu, A.O.				-
	100%				
Output 6	Ifelebuegu, A.O.	Onubogu, J.	Joyce, E.	Mason, T.	Research was initiated by the author. Laboratory experiments were carried out by Onubogu with the direction of the author. Paper was written 100% by the author.
	80%	10%	5%	5%	

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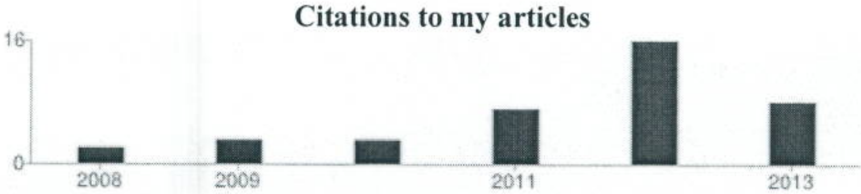

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Title / Author	Cited by	Year
Removal of an endocrine disrupting chemical (17α-ethinyloestradiol) from wastewater effluent by activated carbon adsorption: effects of activated carbon type and competitive adsorption AO felebuegu, JN Lester, J Churchley, E Cartmell Environmental technology 27 (12), 1343-1349	16	2006
The fate and behavior of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes AO Ifelebuegu Int J Environ Sci Tech 8 (2), 245-254	13	2011
Mechanistic evaluation of the sorption properties of endocrine disrupting chemicals in sewage sludge biomass	7	2010

	AO Ifelebuegu, SC Theophilus, MJ Bateman International Journal of Environmental Science and Technology 7 (4), 617-622		
☐	Removal of Endocrine Disrupting Chemicals in Wastewater Treatment by Fenton-Like Oxidation AO Ifelebuegu, CP Ezenwa Water, Air, & Soil Pollution 217 (1-4), 213-220	4	2011
☐	Removal of Steriod Hormones by Activated Carbon Adsorption—Kinetic and Thermodynamic Studies AO Ifelebuegu Journal of Environmental Protection 3 (6), 469-475		2012
☐	Coventry University Repository for the Virtual Environment (CURVE) AO Ifelebuegu, MJ Bateman, SC Theophilus Int. J. Environ. Sci. Tech 7 (4), 617-622		2010
☐	The fate and behavior of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes Article 3: Volume 8, Number 2, Pages 245-254 (10), Spring 2011 XML PDF (985 K) AO Ifelebuegu		

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Environmental Technology - Petroleum Engineering & Management - QHSE
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Title
Removal of an endocrine disrupting chemical (17α-ethinyloestradiol) from wastewater effluent by activated carbon adsorption: effects of activated carbon type and competitive adsorption
Authors
AO felebuegu, JN Lester, J Churchley, E Cartmell
Publication date
2006/12/1
Journal name
Environmental technology
Volume
27
Issue
12
Pages
1343-1349
Publisher
Taylor & Francis Group
Description
Granular activated carbon has been extensively used for the adsorption of organic micropollutants for potable water production. In this study the removal of an endocrine disrupting chemical from wastewater final effluent by three types of granular activated carbon (wood, coconut and coal based) has been investigated in batch adsorption experiments and correlated with the removal of chemical oxygen demand (COD), total organic carbon (TOC) and ultraviolet absorbance (UV). The results obtained ...
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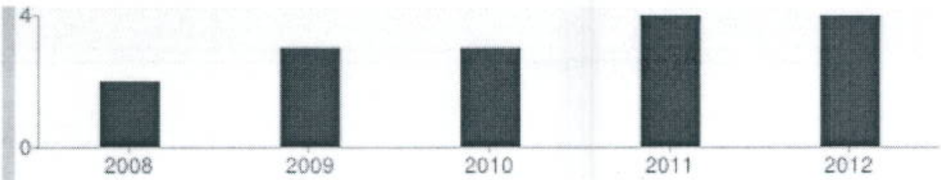

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Title
The fate and behavior of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes
Authors
AO Ifelebuegu
Publication date
2011
Journal name
Int J Environ Sci Tech
Volume
8
Issue
2
Pages
245-254
Description
ABSTRACT: Endocrine disrupting chemicals are discharged into the environment mainly through wastewater treatment processes. There is a need for better understanding of the fate of these compounds in the unit processes of treatment plant to optimise their removal. The fate of oestrone, 17âestradiol, 17áethinyestradiol and nonylphenol in the unit processes of full scale wastewater treatment plants in the UK, including activated sludge plant, oxidation ditch, biofilter and rotating biological contactor were investigated. The overall removal ...
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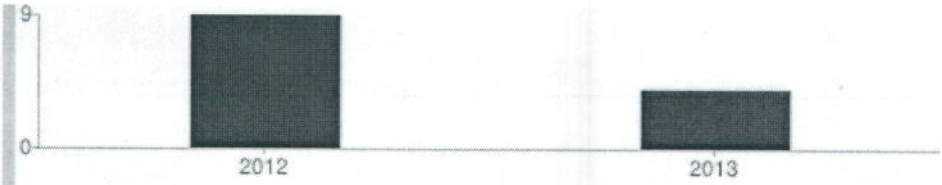

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Augustine Ifelebuegu
Senior Lecturer, Coventry University
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Title
Mechanistic evaluation of the sorption properties of endocrine disrupting chemicals in sewage sludge biomass

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Authors
AO Ifelebuegu, SC Theophilus, MJ Bateman
Publication date
2010/9
Journal name
International Journal of Environmental Science and Technology
Volume
7
Issue
4
Pages
617-622
Description
ABSTRACT: This study investigated the sorption behaviour of two endocrine disrupting chemicals; 17β-estradiol (E2) and 17β-ethinylestradiol and their thermodynamic properties in an activated sludge biomass. The partition coefficient values measured for E2 and EE2 at varying temperatures range from 245-604 L/kg (log K d 2.39-2.78) and 267-631 L/kg (Log K d 2.43 2.80), respectively. The K d values were inversely related to temperature. The average percentages of E2 and EE2 adsorbed to the solid phase at 4.3% dry solid were ...
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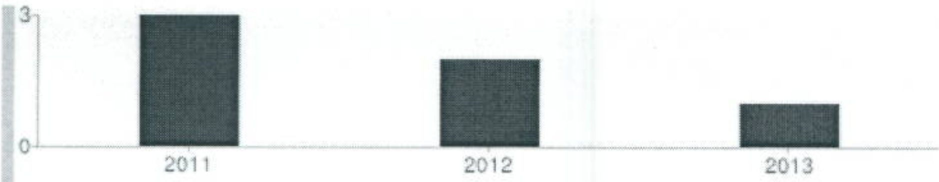

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Mechanistic evaluation of the sorption properties of endocrine disrupting chemicals in sewage sludge biomass
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Title
Removal of Endocrine Disrupting Chemicals in Wastewater Treatment by Fenton-Like Oxidation
Authors
Augustine O Ifelebuegu, Chinyere P Ezenwa
Publication date
2011/5/1
Journal name
Water, Air, & Soil Pollution
Volume
217
Issue
1-4
Pages
213-220
Publisher
Springer Netherlands
Description
Abstract The presence of endocrine-disrupting chemicals (EDCs) in wastewater effluent is a major concern to the scientific community. This research effort was aimed at investigating Fenton-like degradation of two EDCs 17β-estradiol (E2) and 17α-ethinylestradiol (EE2). The results of the study showed that E2 and EE2 were effectively removed by the Fenton-like oxidation process. Removal efficiencies of 95% and 98% at ferric concentration of 1× 10− 3 M (58.6 mg l− 1) were achieved for E2 and EE2, respectively. The kinetics of Fenton-like ...

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