

## Research Article

# Pilot-Scale Removal of Trace Steroid Hormones and Pharmaceuticals and Personal Care Products from Municipal Wastewater Using a Heterogeneous Fenton's Catalytic Process

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The pollution of water sources by endocrine disrupting compounds (EDCs) and pharmaceutical and personal care products (PPCPs) is a growing concern, as conventional municipal wastewater treatment systems are not capable of completely removing these contaminants. A continuous stir tank reactor incorporating a modified polyacrylonitrile (PAN) catalyst and dosed with hydrogen peroxide in a heterogeneous Fenton's process was used at pilot scale to remove these compounds from wastewater that has undergone previous treatment via a conventional wastewater treatment system. The treatment system was effective at ambient temperature and at the natural pH of the wastewater. High levels of both natural and synthetic hormones (EDCs) and PPCPs were found in the effluent after biological treatment of the wastewater. The treatment system incorporating the modified PAN catalyst/H<sub>2</sub>O<sub>2</sub> decomposed >90% of the EDCs and >40% of PPCPs using 200 mgL<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 3 hr residence time. The estrogenic potency EE2-EQ was removed by 82.77%, 91.36%, and 96.13% from three different wastewater treatment plants. BOD was completely removed (below detection limits); 30%–40% mineralisation was achieved and turbidity reduced by more than 68%. There was a <4% loss in iron content on the catalyst over the study period, suggesting negligible leaching of the catalyst.

## 1. Introduction

Endocrine disrupting compounds (EDCs) which include natural sex hormones such as estrone—E1 and 17  $\beta$ -estradiol—E2 produced by humans and animals as well as some synthetic estrogens such as 17  $\alpha$ -ethinylestradiol (EE2) used for contraception purposes are able to produce endocrine disruption in living organisms at trace concentrations (nanogram per litre levels) [1, 2]. EDCs have been attributed as a cause of reproductive disturbance in humans and wildlife such as feminisation of fish, developmental abnormalities, and demasculinisation of alligators [3]. Pharmaceutical products such as antibiotics, blood lipid regulators, analgesics, nonsteroidal anti-inflammatory drugs, antidepressants, antiepileptics, impotence drugs, tranquilizers, and many personal care products such as fragrances, soaps,

preservatives, and disinfectants (generally called pharmaceutical and personal care products (PPCPs)) have different modes of action, toxicity, and effects on nontarget organisms [4].

EDCs and PPCPs are released into the environment by humans, animals, and industry, mainly through sewage treatment systems before reaching the receiving bodies (soil, surface water, sediment, and groundwater) [2]. Municipal wastewater treatment plants are therefore major sinks of several EDCs and PPCPs. These micropollutants go through most conventional wastewater treatment plants (activated sludge systems) partially removed or untreated. Several studies have shown that most conventional municipal treatment plants are capable of removing only 27% of micropollutants to below detection limits; up to 64% of micropollutants are removed by less than 50% and 9% are not removed at all

[1, 4]. ECDs and PPCPs have been detected in effluents of sewage treatment plants (STPs) in different countries at concentrations of up to  $70 \text{ ngL}^{-1}$  for E1,  $64 \text{ ngL}^{-1}$  for E2, and  $42 \text{ ngL}^{-1}$  for EE2 and  $6.3 \mu\text{gL}^{-1}$  for carbamazepine,  $2.7 \mu\text{gL}^{-1}$  for triclosan, and  $53 \mu\text{gL}^{-1}$  for aspirin [1, 5, 6], suggesting that conventional treatment methods are not efficient in removing low level EDCs and PPCPs.

Human exposure to these chemicals in the environment is of serious worry with unidentified long-term impacts. In the past few decades, research efforts to combat this problem have grown immensely. EDCs removal methods fall into three categories: physical removal (such as activated carbon, sorption/coagulation, nanofiltration, and reverse osmosis), biodegradation (membrane bioreactors, activated sludge, and weed beds), and advanced chemical oxidation processes (AOP) such as Fenton's oxidation, ozonation,  $\text{UV}/\text{H}_2\text{O}_2$ , photocatalysis on  $\text{TiO}_2$ , or a combination of these technologies and chemical treatment method such as chlorine dioxide.

Biological methods such as membrane bioreactor and activated sludge systems show inconsistency in removal efficiencies as it is highly dependent on the type of pollutant, temperature, membrane, matrix, loads, variability in loads, and quality of water to be treated. The use of membrane bioreactors (MBR) in wastewater treatment showed >80% removal of the target EDCs and PPCPs (ZeeWeed-1  $0.04 \mu\text{m}$  hollow fiber ultrafiltration,  $0.094 \text{ m}^2$  surface area, 24 hrs hydraulic retention time corresponding to average flux of  $4.3 \text{ Lm}^{-2} \text{ h}^{-1}$ , air flow rate of  $150 \text{ Lmin}^{-1}$ ) [7]. Biological systems require long solid and hydraulic retention times and have a high human resource requirement for operation. Adsorption of contaminant onto sludge is a significant removal mechanism hence requiring appropriate sludge treatment.

Many researchers have demonstrated the effectiveness of physical methods such as activated carbon (granulated or powder) and membranes towards the removal of a broad range of EDCs and PPCPs from artificial and real wastewater in the laboratory, pilot- and full-scale plants. A removal of >90% of several PPCPs and EDCs from a drinking water source (spiked with  $100 \text{ ngL}^{-1}$  each of targeted contaminants) by powdered (PAC) activated carbon at pilot scale, with dynamic dosing of  $35 \text{ mgL}^{-1}$  PAC at  $20\text{--}25^\circ\text{C}$ , has been reported [8]. Similarly, an evaluation of full-scale drinking water and wastewater treatment facilities utilizing granulated activated carbon technology showed that regularly regenerated facilities were very effective in the removal of trace contaminants whereas irregular regeneration was very poor due to fouling [6, 8]. Membrane filtration processes using a combination of reverse osmosis (RO) and nanofiltration (NF) have been reported with excellent removal (>95%) of target compounds whereas microfiltration and ultrafiltration are not very effective [6, 9]. Notwithstanding this high removal efficiency, physical methods only transfer the contamination from one medium to another. Additionally, membrane and sorption technologies require frequent costly regeneration and/or backwashing due to organic fouling and biofouling, as several compounds are often detectable in membrane permeates and carbon effluent hence limiting the adoption of these technologies in the industry [6, 8, 9]. Additionally,

physical and biological processes generally generate sludge or reject which is more contaminated than the original wastewater and so require further treatment.

AOPs involving the generation of radicals have gained significant interest because of their excellent removal capabilities and their ability to decompose the micropollutants rather than simply transferring from one medium to another [4, 10–12]. While ozonation [11, 13, 14], Fenton's, photo-Fenton's [14, 15], and solar photocatalysis [16] have shown excellent performances, operational costs of ozonation systems remain high, and the generation of sludge in homogeneous Fenton's system due to the formation of insoluble iron species, coupled with restricted operational pH range (2–4), remains a problem. Heterogeneous Fenton's systems therefore exhibit greater potential with regard to costs and no sludge generation. However, there is limited information on heterogeneous Fenton's processes in the literature.

The heterogeneous polyacrylonitrile (PAN) catalyst/ $\text{H}_2\text{O}_2$  has shown potential at lab scale in the treatment of synthetic organic contaminants [17–19]. This study aims to examine the effectiveness of the heterogeneous PAN catalyst/ $\text{H}_2\text{O}_2$  at a pilot scale, towards the removal of selected EDCs and PPCPs from pretreated (activated sludge treated) municipal wastewater. The pretreated wastewater was obtained from three of Severn Trent Water's sewage works in the Midlands, UK. Lump parameters such as chemical oxygen demand (COD) and total organic carbon (TOC) were determined. The effectiveness of the system towards the removal of natural hormones estrone (E1) and 17  $\beta$ -estradiol (E2), synthetic hormone 17  $\alpha$ -ethinylestradiol (EE2) and PPCPs such as carbamazepine, triclosan, and aspirin detected in effluents discharges from the sewage treatment plants, was investigated. In this work, the use of the heterogeneous PAN catalyst in a continuous flow process and at pilot scale is being reported for the first time. Environmental legislation on the discharge of emerging contaminants and micropollutants is likely to become tighter in the near future, rendering the search for new effective treatment technologies relevant.

## 2. Materials and Methods

**2.1. Wastewater Source.** Severn Trent Water (STW) is a municipal water company—serving over 8 million customers across the heart of the UK, stretching from the Bristol Channel to the Humber and from mid-Wales to the East Midlands. The company treats around 2.7 billion litres of wastewater and sewage each day, from communities and businesses across the region and the treated water is discharged into neighbouring streams and rivers. This is performed in about 1018 sewage treatment works, 20 surface water treatment works, and about 43 sludge treatment facilities across the region. The pilot system was tested on sewage from three different STW treatment works in the Midlands, namely, Site A, Site B, and Site C. The true names of the different sites have not been included in this paper for security reasons and data protection. Wastewater used in this study had been through physical treatment (screens and grit removal and primary sedimentation tanks), activated sludge tanks, and secondary clarifiers (see Figure 1). The wastewater at this

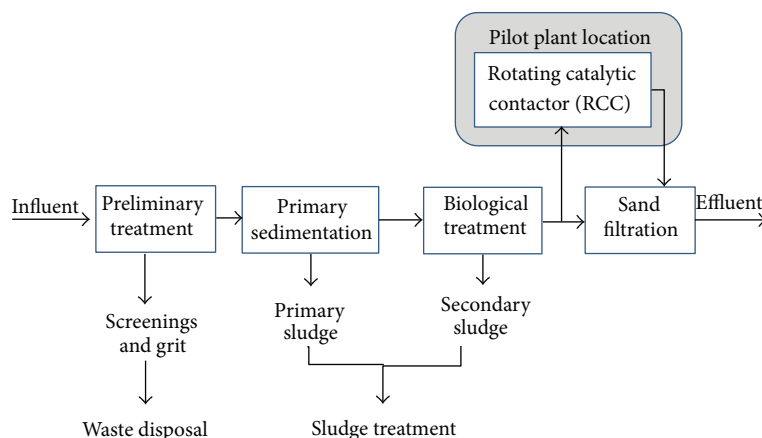


FIGURE 1: Conventional sewage treatment plant showing the location of the pilot plant for this study.

stage is normally treated on sand filters and subsequently discharged into receiving waters. The sand filter does not remove these recalcitrant EDCs and PPCPs; hence using presand filter effluent in this work was for convenience only.

## 2.2. Physicochemical Properties of EDCs and PPCPs Studied.

Tables 1(a) and 1(b) show the physical and chemical properties of EDCs and PPCPs studied. Amongst the compounds studied, aspirin is the most soluble (lowest  $\log K_{ow}$ ) and triclosan is the least soluble, suggesting that triclosan is the most likely to adsorb onto sludge during biological or physical treatment.

**2.3. Reagents.** All EDC, PPCPs, and metal standards were of analytical grade (>95% purity) and were purchased from Sigma-Aldrich (Gillingham, Dorset, UK). Solvents used for extraction and as HPLC mobile phase (dichloromethane, diethyl ether, methanol, hexane, and acetone) were all HPLC grade and were purchased from Rathburn Chemicals (Walkerburn, Scotland, UK) and Fisher Scientific (Loughborough, UK). Solid phase extraction cartridges and hydroxylated polystyrene divinylbenzene (ENV+) were obtained from International Sorbent Technologies (Hengoed, Mid Glamorgan, UK) and Oasis HLB was obtained from Waters Ltd (Elstree, Hertfordshire, UK). Ultrapure water was obtained with a Milli-Q water purification system.

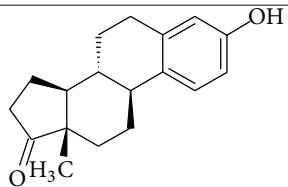
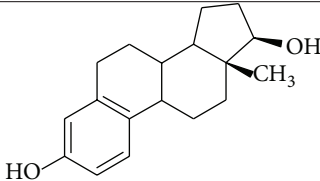
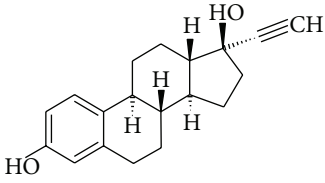
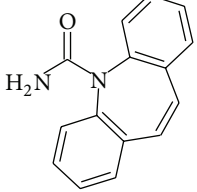
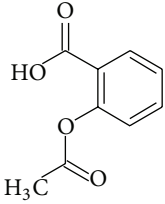
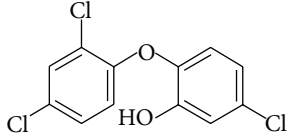
**2.4. Sampling.** Inlet and outlet samples from the pilot plant were collected as a single grab sample and transferred to sampling containers containing preservative as follows: 2.5 L amber glass bottles containing copper nitrate (0.5 g) and hydrochloric acid (6 mL) (for measuring EDCs and PPCPs), 2.5 L amber glass bottle containing hydrochloric acid (6 mL) (for metals), and 1.0 L PET bottle for standard sanitary analysis (no preservative added). Samples were transported to the laboratory in ice-packed coolers (4–6°C). The samples were stored in a refrigerator below 6°C prior to extraction of analytes, performed within 48 hours of sampling. Influent and effluent samples were filtered through 0.45  $\mu\text{m}$  methanol washed glass fiber filters (Fisher Scientific, Milford, MA).

Processed samples were then stored at  $-5^\circ\text{C}$ . Samples were collected twice a day.

**2.5. Modified PAN Catalyst Production.** Wet spun PAN yarn was supplied by PERA Innovation, Melton Mowbray, UK. An open mesh structure comprising PAN yarn enhances the hydrodynamic properties and physical strength of the finished product. The PAN mesh was chemically modified by reacting 27.9 g of PAN mesh in 1 L solution of 49.6  $\text{g L}^{-1}$  hydroxylamine sulphate (99%) and 23.17  $\text{g L}^{-1}$  dihydrazine sulphate (98%) at pH 9.5,  $100 \pm 2^\circ\text{C}$ , under reflux for 2 h, and with constant stirring. It was thoroughly washed to remove residual chemicals. The modified PAN was impregnated at room temperature using a solution of 7.5  $\text{g L}^{-1}$   $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (99%) and 2.249%w/v  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  for 2 h with continuous stirring. The catalyst was then washed thoroughly and spin dried at room temperature. The catalyst production process is described in detail elsewhere [18].

**2.6. Analytics.** Samples were analysed for EDCs (E1, E2, and EE2) using the LC-MS/MS method as described elsewhere [20, 21]. Briefly, the samples were first filtered to remove particulate matter (Whatman GFD/GFF of 1  $\mu\text{m}$  nominal pore size). After addition of a mixed deuterated internal standard (2, 4, 16, 16- $\text{d}_4$ -estrone, 2, 4, 16, 16- $\text{d}_4$ -17  $\alpha$ -estradiol; and 2, 4, 16, 16- $\text{d}_4$ -17  $\beta$ -ethynyl estradiol), 500 mL of the sample was extracted onto a conditioned styrene divinylbenzene cartridge (ENV+). The cartridge was dried under vacuum and then eluted with dichloromethane which was then concentrated to 100  $\mu\text{L}$  prior to an initial clean-up using gel permeation chromatography (GPC). The GPC extract was then concentrated to 200  $\mu\text{L}$  using a TurboVap concentrator and nitrogen blowdown apparatus. The extract was further cleaned using an Isolute aminopropyl SPE cartridge, which was loaded and was washed with ethyl acetate in hexane prior to elution with ethyl acetate in acetone. The extract was then reduced to incipient dryness using nitrogen and the residue was taken up in methanol and quantified by liquid chromatography with tandem mass spectrometry (LC-MS/MS).

TABLE 1: EDCs and PPCPs investigated in the effluents.

(a)				
Chemical name	Classification	Molecular weight ( $\text{g mol}^{-1}$ )	Water solubility ( $\text{mg L}^{-1}$ at $25^\circ\text{C}$ )	$\log K_{ow}$
Estrone (E1)	Steroid	270.4	30	3.43
17 $\beta$ -Estradiol (E2)	Steroid	272.4	25	3.94
17 $\alpha$ -Ethinylestradiol (EE2)	Steroid	296.4	4.8	4.15
Carbamazepine	Analgesic	236.3	17.7	2.45
Aspirin	NSAID	180.2	5295	1.13
Triclosan	Antiseptic	289.5	4.6	4.76
(b)				
Names	Structure	Uses and effects		
Estrone (E1)		Estrogenic hormone secreted by the ovary.		
17 $\beta$ -Estradiol (E2)		Sex hormone—Oestrogen. Estradiol has a critical impact on reproductive and sexual functioning, as well as organs including bone structure.		
17 $\alpha$ -Ethinylestradiol (EE2)		Synthetic form of Estradiol used for contraception.		
Carbamazepine		Anticonvulsant and mood stabilizing drug, used primarily in the treatment of epilepsy and bipolar disorder.		
Aspirin		Used to treat fever, pain, rheumatic fever, and inflammatory diseases, such as rheumatoid pericarditis and arthritis.		
Triclosan		Triclosan is found in soaps (0.15–0.30%), deodorants, toothpastes, mouth washes, and cleaning supplies, acting as antifungal and antibacterial. It is an endocrine disruptor. It can combine with chlorine in water to form chloroform which is a carcinogen.		

LC-MS/MS analysis was performed using a Hewlett Packard 1100 LC. Optimised HPLC conditions were Supelcosil LC-18 (4.6 mm  $\times$  250 mm, 5  $\mu\text{m}$ ) column supplied by Supelco, mobile phase 43% acetonitrile, 57% water, flow

rate 1 mL  $\text{min}^{-1}$ , and column temperature  $25^\circ\text{C}$ . An Applied Biosystems API5000 mass spectrometer using negative ion electrospray in multiple reaction monitoring (MRM) mode was used. Positive identification of EDCs was carried out by



comparison of retention time and ion abundance ratios of the quantitation and confirmation mass transitions to those of a reference standard compound.

The PPCPs were analysed by GC-MS without derivatisation as it is the best technique for such compounds [22]. In summary, 500 mL of the acidified and filtered samples was percolated through a Waters Oasis HLB 12 cm<sup>3</sup>, 500 mg cartridge preconditioned with 6 mL dichloromethane, 6 mL acetonitrile, and 6 mL of milliQ water at 5 mL min<sup>-1</sup>. The cartridge was rinsed with 2 mL milliQ water and dried by vacuum for 10 min. The elution was carried out with 5 mL of acetonitrile-dichloromethane (1:1) and 3.2 mL dichloromethane. The eluate was transferred to vials and excess solvent evaporated to dryness as described previously. The extract was subsequently taken up into isooctane and injected in the GC-MS system.

The GC-MS analyses were performed using a Fisons MD 800 mass spectrometer operated in EI mode at 70 eV. A sample volume of 1 µL was injected in splitless mode at an inlet temperature of 230°C. The carrier gas was helium and maintained at a constant flow rate of 0.9 mL min<sup>-1</sup>. The gas chromatograph was equipped with a capillary column DB-5MS (30 m long × 0.25 mm ID) with 0.25 µm film thickness (from Agilent Technologies). The temperature was programmed from 90°C for 1 min, ramped from 90°C to 120°C at 10°C min<sup>-1</sup>, and from 120°C to 200°C at 5°C min<sup>-1</sup> and then to 280°C at 10°C min<sup>-1</sup> and finally held for 5 min. The MS transfer line temperature was maintained at 280°C, whereas the ion source temperature was 180°C. Quantitative analysis was carried out using selected ion monitoring (SIM) mode. For each compound, the most abundant ions were selected from its spectrum. The chosen ions for SIM were 120, 43, 138, 92, and 180 for aspirin, 193, 236, and 192 for carbamazepine, and 288, 218, and 146 for triclosan.

The TOC content of the oxidised solution was analysed using the Thermalox TC/TIC analyser. The TOC content was determined indirectly by calculating the difference between total carbon (TC) and total inorganic carbon (TIC). Each sample was analysed in triplicates. Metals were analysed by ICP-AES after filtration and acidification of the sample. BOD, phosphates, and turbidity were analysed following well-documented standard methods [23]. Site measurements (temperature and pH) were performed using pH and temperature probes linked to data loggers.

**2.7. Experimental Conditions.** The continuous stir tank reactor contained the modified PAN catalyst, corresponding to 1.31 moles of iron catalyst. The treatment of effluent was performed at ambient temperatures and at natural pH. The residence time of treatment process was 3 hours with a corresponding flow rate of 10.6 Lhr<sup>-1</sup>. The total volume of the reactor was 31.34 dm<sup>-3</sup>.

Hydrogen peroxide was continuously dosed at the inlet and halfway along the length of the reactor with the help of peristaltic pumps. The amount of hydrogen peroxide dosing was calculated based on the theoretical amount of oxygen required for the complete mineralisation of the organic pollutants (in terms of COD), by considering the oxygen

requirement (COD) of the wastewater according to the following equation:

$$\begin{aligned} \text{Required H}_2\text{O}_2 \text{ (mgL}^{-1}\text{)} \\ = \text{COD (mgL}^{-1}\text{)} * 2 \left( \frac{\text{molar mass of H}_2\text{O}_2}{\text{molar mass of O}_2} \right). \end{aligned} \quad (1)$$

From (1), 1 g of COD = 1 g O<sub>2</sub> = 0.03125 mol O<sub>2</sub>.

Hence, required amount of H<sub>2</sub>O<sub>2</sub> (mgL<sup>-1</sup>) = COD (mg/L) \* 2.125.

The corresponding required concentration of H<sub>2</sub>O<sub>2</sub> was calculated to be 199.5 mgL<sup>-1</sup> for a COD of 93.9 mgL<sup>-1</sup>. The mass flow of hydrogen peroxide  $F$  (mg min<sup>-1</sup>) required to be mixed with the effluent flowing through the prototype was calculated using

$$F = \left( \frac{V * [\text{H}_2\text{O}_2]}{\tau} \right), \quad (2)$$

where  $V$ —main trough volume (L),  $[\text{H}_2\text{O}_2]$ —required H<sub>2</sub>O<sub>2</sub> concentration (mgL<sup>-1</sup>) and  $\tau$  residence time (min).

The mass flow rate of H<sub>2</sub>O<sub>2</sub> was calculated according to (2) to be 34.7 mg min<sup>-1</sup>, dosed using peristaltic pumps.

### 3. Results

**3.1. Quality of Wastewater to Be Treated.** The characteristics of the wastewater used for the pilot treatment are shown in Table 2. The wastewater from Site A used as influent for this field trial (designated partially treated wastewater) had the smallest amounts of total suspended solids (about 6 mgL<sup>-1</sup>) and hence turbidity (0.65 Formazin Nephelometric Unit FTU) whereas wastewater from Site C had the largest amount of suspended solids (about 11 mgL<sup>-1</sup>). Meanwhile the minimum requirements for discharge of total suspended solids from urban wastewater treatment plants in the European Union are 35 mgL<sup>-1</sup> TSS [24].

The concentration of phosphates ranged from 0.2 mgL<sup>-1</sup> in Site A to 6.5 mgL<sup>-1</sup> in Site C. Site C was thought to be very high in phosphates because of the underlying ground properties of the area. The levels of metals found in the effluent from all the three sites were below UK discharge standards. The UK standards for the concentration of lead, aluminium, and copper in drinking water are 25 µgL<sup>-1</sup>, 200 µgL<sup>-1</sup>, and 2 mgL<sup>-1</sup>, respectively [20]. EDCs and PPCPs in the biologically treated wastewater ranged from below detection limits to 46 ngL<sup>-1</sup>, confirming that conventional sewage treatment plants are not capable of completely removing these compounds. The potency of steroid estrogens was expressed in terms of estradiol equivalents (E2-EQ) according to the following equation [25]:

$$\begin{aligned} \text{Estradiol equivalent (E2-EQ)} \\ = 0.33 * \text{E1} + \text{E2} + 10 * \text{EE2 (ngL}^{-1}\text{)}. \end{aligned} \quad (3)$$

Mean values of E1, E2, and EE2 were used to calculate the E2-EQ. The E2-EQ for Sites A, B, and C

TABLE 2: Characteristics of biologically treated wastewater used in the pilot tertiary treatment process.

	Units	LOQ	Site A: concentration		Site B: concentration		Site C: concentration	
			Range	Mean	Range	Mean	Range	Mean
BOD (ATU)	[mg L <sup>-1</sup> ]	1	1–3	2.5	1–5	3.5	6–13	8.3
TOC	[mg L <sup>-1</sup> ]	0.1	6.0–7.5	6.24	7.9–9.2	8.10	10.7–14.8	11.08
TSS	[mg L <sup>-1</sup> ]	0.1	4.0–8.1	8.5	6.4–12.9	9.5	10.0–12.0	10.7
Turbidity	[mg L <sup>-1</sup> ]	0.05	0.6–0.69	0.66	4.0–4.6	4.7	3.4–8.8	7.8
PO <sub>4</sub> <sup>3-</sup>	[mg L <sup>-1</sup> ]	0.004	0.12–38	0.26	0.49–0.99	0.69	3.30–6.64	5.38
Total								
Al	[μg L <sup>-1</sup> ]	11	24–38	31.5	25–39	29	35–124	89.7
Pb	[μg L <sup>-1</sup> ]	0.5	0.6–2.5	2.25	0.6–1.6	0.95	1.3–1.8	1.4
Cu	[μg L <sup>-1</sup> ]	2.7	2.7–3.9	3.4	<2.7	2.7	4.7–8	6.9
Fe	[μg L <sup>-1</sup> ]	1.5	538–618	574.5	163–219	209	67–91	84
Mn	[μg L <sup>-1</sup> ]	1.5	<1.5	<1.5	<1.5	<1.5	16–21	20
Estrone (E1)	[ng L <sup>-1</sup> ]	0.05	1.67–2.87	2.12	0.05–1.31	0.7	30.2–46.3	35.5
17 β-Estradiol (E2)	[ng L <sup>-1</sup> ]	0.05	0.33–0.42	0.39	<0.05	<0.05	4.22–6.52	5.12
17 α-Ethinylestradiol (EE2)	[ng L <sup>-1</sup> ]	0.05	0.23–0.26	0.255	0.51–0.68	0.575	1.53–1.72	1.565
Carbamazepine	[ng L <sup>-1</sup> ]	10	668–877	757.5	553–842	589	945–1160	1002.5
Aspirin	[ng L <sup>-1</sup> ]	10	10–23	17	10–29	16	<10	<10
Triclosan	[ng L <sup>-1</sup> ]	10	149–152	151	55–89	73.5	383–473	438

were 3.65 ngL<sup>-1</sup>, 5.98 ngL<sup>-1</sup>, and 32.60 ngL<sup>-1</sup>. According to Williams et al. [26] treated water discharged from the conventional STP at Sites A and B could be classed as low risk ( $1 < \text{E2-EQ} \leq 10 \text{ ngL}^{-1}$ ) whereas that from Site C could be classed as high risk ( $\text{E2-EQ} > 10 \text{ ngL}^{-1}$ ).

**3.2. pH and Temperature Change during the Treatment.** The pH of the effluent was monitored during the treatment process. The initial pH of Site A, Site B, and Site C wastewater were about  $6.53 \pm 3$ ,  $6.99 \pm 2$ , and  $7.99 \pm 2$ , respectively. After treatment using the modified PAN catalyst system, there was no significant change in pH. The performance of the heterogeneous Fenton's process at the natural pH of the wastewater is a major advantage of the modified PAN catalyst over traditional homogeneous Fenton's which is limited to pH 2–4 [27]. The effectiveness of the system at the natural pH of the effluent could be attributed to the fact that the ligands holding the metals prevent the iron from precipitating, as it is the case in homogeneous Fenton's at pH >4. A similar observation has been reported where Fenton's oxidation of organic pollutants was successfully performed at near neutral pH in the presence of dissolved organic matter in the form of humic as ligands for the homogeneous iron. Similarly, ethylenediamine-N-N'-disuccinic acid (EDD) complexes in another study were used for stabilisation and solubilisation of iron at natural pH [10, 27]. The pilot-scale modified PAN catalyst treatment was performed at ambient temperature, varying between 12°C and 20°C.

**3.3. Removal of EDCs and PPCPs.** As shown in Table 2, the concentration of estrogens in the effluents ranged from

<0.05 to 46.3 ngL<sup>-1</sup>, with highest concentrations at Site C. Estrone was the most abundant estrogen in the effluent from all three sites. The presence of steroid hormones in the conventionally treated wastewater is consistent with several studies which have shown that sewage treatment plants are a significant point source of endocrine disrupting compounds, particularly for surface water and underground water [14, 16]. Natural estrogens, for example, estrone (E1), 17 β-estradiol (E2), and estriol (E3), and synthetic estrogens such as 17 α-ethinylestradiol (EE2) and nonylphenols have been found to be the major contributors to the estrogenic activity observed in sewage effluents in the United Kingdom [28]. Concentrations as low as 0.1 ngL<sup>-1</sup> of an estrogen can cause significant estrogenic effects [29].

More than 80% of the estrogens were decomposed by the modified PAN catalyst/H<sub>2</sub>O<sub>2</sub> treatment system. Removal was generally higher for Site C even though the concentrations of the EDCs in Site C were significantly higher than those in Sites A and B (Figure 2). The estrogenic potency EE2-EQ was removed by 82.77%, 91.36%, and 96.13% from Sites A, B, and C, respectively. The treated effluent from Sites A and B could be classed as no risk as E2-EQ was <1 ngL<sup>-1</sup>, whereas E2-EQ after treatment in Site C was 1.26 ngL<sup>-1</sup> and could be classed as low risk as it is less than 10 ngL<sup>-1</sup> [26].

The concentration of triclosan in the untreated effluents ranged from 55 to 493 ngL<sup>-1</sup>. More than 84% of triclosan was constantly removed at each of the three treatment sites. High levels of carbamazepine were found in the effluent from all three sites ranging from 553 ngL<sup>-1</sup> to 1060 ngL<sup>-1</sup>. After treatment, 84.48%, 46.01%, and 47.88% of carbamazepine were removed from the wastewater from Sites A, B, and C,

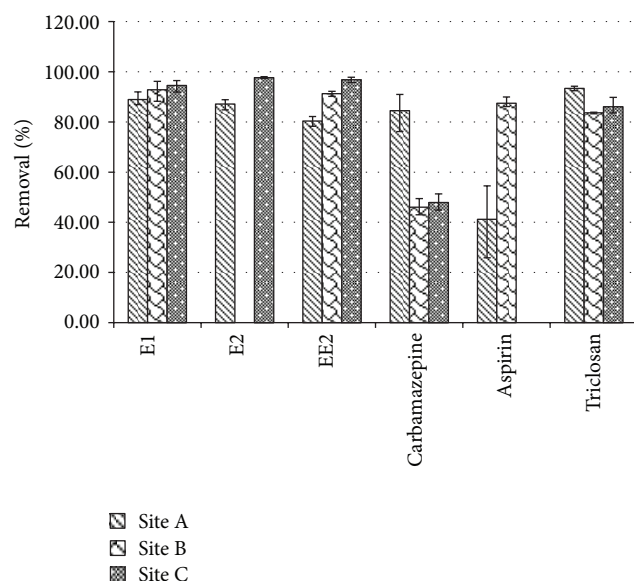


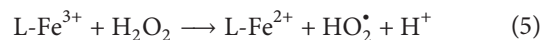
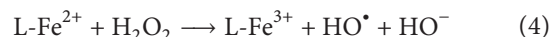
FIGURE 2: Removal of EDCs and PPCPs (E1—estrone, E2—17  $\beta$ -estradiol, and EE2—17  $\alpha$ -ethinyl estradiol).

respectively (Figure 2). The removal of carbamazepine was low for Sites B and C and the reason for the deviation in performance from Site A is not well understood. Meanwhile, the removal of this compound could be enhanced by increasing the initial concentration of hydrogen peroxide and/or extending the residence time.

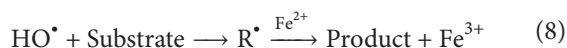
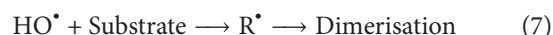
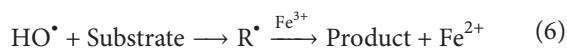
In comparison to other AOPs, a 65.8%, 8.25%, and  $91 \pm 8\%$  removal of estrone, carbamazepine, and triclosan from initial concentrations of  $23.3 \text{ ngL}^{-1}$ ,  $36 \text{ ngL}^{-1}$ , and  $118 \text{ ngL}^{-1}$ , respectively, has been reported in the pilot-scale ozonation treatment of municipal wastewater that has been pretreated biologically and sand filtered, using  $3 \text{ mg/L}^{-1} \text{ O}_3$  with a 27 min residence time [14]. Poor removal times (85% after 475 mins) of micropollutants including carbamazepine ( $50\text{--}114 \text{ ngL}^{-1}$  initial concentration) have been reported in the tertiary treatment of municipal wastewater using heterogeneous solar photocatalysis at pilot plant scale (treatment conditions:  $20 \text{ mgL}^{-1} \text{ TiO}_2$ , pH 6, 35 L batch treatment of biologically treated municipal wastewater followed by carbonate elimination) [16]. However, the same group reported a  $>90\%$  removal of the micropollutants within 20 minutes using homogeneous solar photo-Fenton's ( $60 \text{ mgL}^{-1} \text{ H}_2\text{O}_2$ ,  $5 \text{ mgL}^{-1} \text{ Fe(II)}$ , pH 2.8) and within 60 mins using ozone ( $9 \text{ mg/L}^{-1} \text{ O}_3$ , pH 8). This technology is therefore very competitive with other advanced oxidation technologies in terms of reaction times and performance, with the added advantage of natural pH operating conditions and the simplicity of a heterogeneous mode. In comparison, acidic conditions and continuous iron dosage require pH readjustment and metal removal after treatment using homogeneous Fenton's and photo-Fenton's systems.

The removal of the EDCs is through the decomposition of the compounds by hydroxyl radicals and other oxidative species generated from the reaction between peroxide in

solution and iron on the catalyst according to the Fenton-like process as illustrated in (4)–(8) and Scheme 1 [11, 12]:



The free or bound radicals produced then react with the organic pollutant (substrate) as shown in (6)–(8):



The very good removal of the steroid hormones (E1, E2, and EE2) could be attributed to the attack of the phenolic moieties present in these compounds. Phenolic compounds generally have high removal efficiencies by hydroxyl radicals as a result of the activating ability of the benzene ring by the hydroxyl group [11, 12]. The removal of carbamazepine was not very good and could be attributed to the deactivation of the azepine ring by the electron withdrawing amide group. This poor removal is consistent with a removal of 37% from postbiologically treated municipal wastewater containing  $263 \text{ ngL}^{-1}$  carbamazepine by homogeneous Fenton's ( $5 \text{ mgL}^{-1} \text{ Fe(II)}$  and  $50 \text{ mg/L}^{-1} \text{ H}_2\text{O}_2$ , 30 min treatment time at  $17^\circ\text{C}$ ) [10]. The effective removal of triclosan is consistent with the presence of the phenolic moiety which is dominant over the weakly deactivating chlorine substitutes. The oxidation of aspirin was not consistent probably due to the very low levels that are close to the limit of quantification.

Negligible hydrogen peroxide was measured in the effluent that had been treated, suggesting that all the peroxide was used up; hence negligible discharge of  $\text{H}_2\text{O}_2$  to receiving waters. Additionally, only small amounts of iron ( $0.067\text{--}0.67 \text{ mgL}^{-1}$ ) were present in the feed. At such small concentrations, neutral pH, low temperature, and  $200 \text{ mgL}^{-1} \text{ H}_2\text{O}_2$ , the contribution of homogeneous Fenton's reactions towards the degradation of the organic compounds is insignificant [30].

**3.4. Removal of BOD, TOC, TSS, and Turbidity.** The sanitary (BOD, TOC, TSS, and turbidity) and inorganic characteristics of the samples before and after treatment were analysed. The Biological Oxygen Demand (BOD) was reduced to less than  $1 \text{ mgL}^{-1}$  for all the effluents treated using the RCC/modified PAN catalyst treatment system. The reduction in BOD could be attributed to the oxidation of organic pollutants into forms that are no longer able to be oxidised by the bacteria used in BOD measurement. According to BOD classification for water quality, Site C was the worst of the three sites in terms of pollution by organics ( $6\text{--}13 \text{ mgL}^{-1}$  BOD—Poor: somewhat polluted). However, the requirements for BOD discharge from urban wastewater treatment plants in the European Union are  $25 \text{ mgL}^{-1}$  oxygen [24].

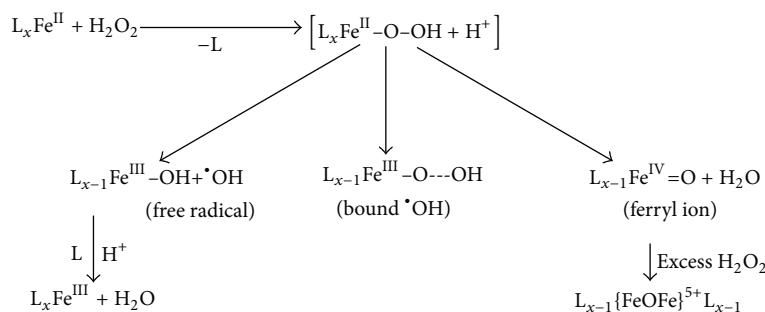
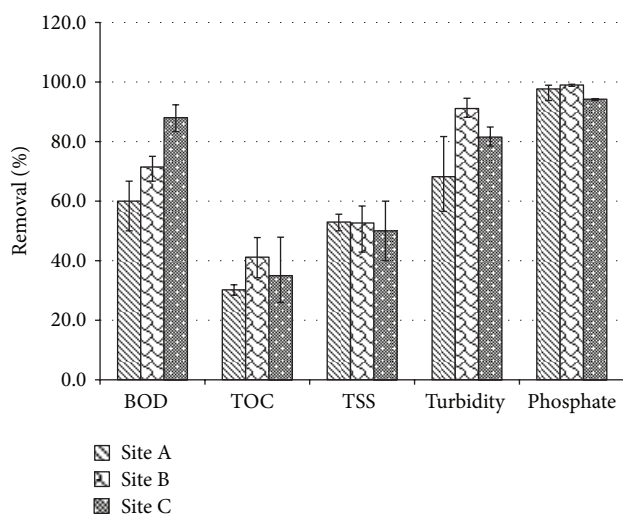
SCHEME 1: Possible reactions of  $H_2O_2$  with ligated ferrous iron.

FIGURE 3: Sanitary and inorganic parameters monitored during the pilot-scale tertiary treatment of municipal wastewater using the rotating catalytic contactor.

Moreover, there was about 30%–40% reduction in the total organic carbon (TOC) content of wastewaters treated (Figure 3). This suggests that 30%–40% of organic compounds present in the wastewater were mineralised to produce  $CO_2$  and water. Although TOC removal is somewhat low, the oxidation of these organic pollutants generally results in the formation of low molecular weight organic acids that are readily biodegradable [18] but which results in no change in TOC. It has been widely reported that the oxidation of PPCP and steroid hormones by hydroxyl radicals results in loss of estrogenicity [14]. TOC removal can be enhanced by increasing hydrogen peroxide dosing.

In comparison, TOC removal of 18.9% and 53.9% has been reported for homogeneous dark Fenton's and photo-Fenton's using zero valent iron ( $Fe^0$ ) (conditions:  $9.9 \text{ mgL}^{-1} H_2O_2$ ,  $5 \text{ mgL}^{-1} Fe^0$ ,  $H_2O_2 : COD \text{ } 2 : 1$ ,  $2730 \text{ mgL}^{-1}$  initial TOC in real wastewater, pH 3, 120 min reaction time, bench scale, batch mode) [31]. Hence the heterogeneous modified PAN system is better in that it uses less  $H_2O_2$  with  $H_2O_2 : COD$  of 1:1, neutral pH though with a residence time of 180 min.  $H_2O_2$  is the single most expensive cost item in Fenton's

processes; hence lower peroxide usage renders the technology more competitive.

Moreover, a 50% reduction in total suspended solids was achieved. This could be attributed to the breakdown of humic substances and the filtration properties of the modified PAN catalyst. The net-like structure (mesh) of the modified PAN catalyst makes it very suitable for filtering out Coarse particles. This was evident as the catalyst upstream of the reactor looked physically fouled by solids in comparison to those downstream.

After treatment, the turbidity reduced by 68% up to 91% for the three sites. Turbidity values of  $<2 \text{ FTU}$  were achieved, thereby rendering the water more suitable for discharge into streams. The removal mechanism for turbidity is thought to be a consequence of suspended solids removal.

Phosphates were found in significant amounts especially at Site C. The consequences of eutrophication, resulting from high nutrient levels in waters (lakes, streams, and rivers), are of great concern. Phosphate levels were reduced by more than 90% (Figure 3). The ability of the modified PAN catalyst to remove phosphate serves as an added advantage though its effect on the performance of the catalyst is still under investigation.

**3.5. Catalyst Leaching.** The amount of iron on modified PAN catalyst used in this field trial was determined from three different positions on pieces of mesh at increasing distances from the inlet. Iron content at each position was measured in triplicates. From Figure 4, there was no significant change in the iron content on the modified PAN catalyst after the study period, suggesting that there is negligible leaching of catalyst. However, there was a slight decrease in iron content towards the outlet of the treatment unit. There was high uniformity in iron content on the catalytic mesh.

After 2 months of continuous use, the catalytic media were chemically regenerated in situ by backwashing with a solution of  $1 \text{ gL}^{-1}$  peroxide at pH 3.5. The washing process effectively removed the suspended solids from the catalytic media and also desorbed some of the weakly adsorbed metals. This was evident by the presence of metals in the wash solution. However, the amounts of metals in the wash solution were very small, and so nutrient recovery was not considered in this work.



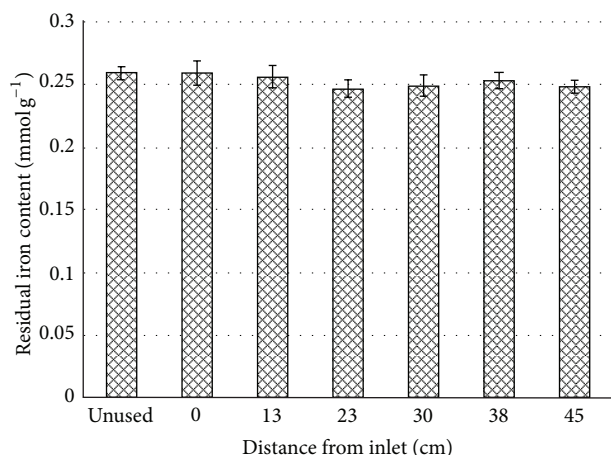


FIGURE 4: Iron content on fresh and used modified PAN catalyst.

#### 4. Conclusion

The modified PAN catalyst system was effective in the treatment of the wastewater owing to its ease of use, potential for automation, and rigidity of the catalytic mesh. The treatment system was effective at ambient temperature and at the natural pH of the effluent; hence no pH adjustment was required. High levels of both natural and synthetic hormones (EDCs) and PPCPs were found in the effluent after biological treatment (but before sand filtration) at the municipal wastewater sites of STW. The treatment system incorporating the modified PAN catalyst/H<sub>2</sub>O<sub>2</sub> decomposed >90% of the EDCs and >40% of PPCPs using 200 mgL<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 3 hr residence time. The estrogenic potency EE2-EQ was removed by 82.77%, 91.36%, and 96.13% from Sites A, B, and C, respectively. There was a <4% loss in iron content from the catalyst over the study period, suggesting negligible leaching of the catalyst. BOD was completely removed (below detection limits); 30%–40% mineralisation was achieved and turbidity reduced by more than 68%. The modified PAN catalyst system shows great potential in the removal of low levels of PPCPs and EDCs when compared to homogeneous Fenton's, photo-Fenton's, electro-Fenton's, and photocatalysis on TiO<sub>2</sub>, owing to the low energy requirement, ease of operation, ambient temperature, and natural pH performance. However, the cost and life time of the catalyst will need to be assessed so as to be compared with other AOPs. The effect of operational parameters on the performance of the system is a subject for further work.

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