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Technical Note

Occurrence and removal of endocrine disrupting chemicals in wastewater

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ABSTRACT

This paper discusses the occurrence and removal of endocrine disrupting chemicals (EDCs) in Horsham sewage treatment plant (STP), West Sussex, UK. Photodegradation aided by a catalyst (TiO_2) was studied for its efficiency of removing EDCs from wastewater. The degradation of estrone and 17β-estradiol under natural sunlight followed a pseudo-first-order kinetics, with a rate constant of 0.01 h^{-1}. The degradation by sunlight is also independent of initial chemical concentration, suggesting some potential of using this environmentally friendly method for waste minimisation. In comparison, more efficient degradation was observed with UV irradiation (253 nm), with the rate constants being increased to 2.7 and 2.5 h^{-1} for the two compounds. Subsequent application of the photocatalysis method to real effluent treatment at Horsham STP was successful, as demonstrated by the non-detection of the target compounds following treatment.

1. Introduction

The fact that endocrine disrupting chemicals (EDCs) can disrupt the endocrine systems in animals and humans has received considerable attention worldwide. There have been various definitions of EDCs, but essentially they are either naturally occurring or synthetic substances that interfere with the functioning of endocrine systems resulting in unnatural responses. Exposure to EDCs can have an effect on the exposed organism, and the offspring of those organisms may also suffer drastic repercussions. For example, health effects on humans may include lower sperm counts (Carlsen et al., 1992), altered sex ratio (Mocarelli et al., 1996), increased incidence of female breast cancer (Wolff and Toniolo, 1995), and neurological effect (Brody and Rudel, 2003). In wildlife, the health impacts include reproductive abnormalities (Sumpter and Jobling, 1995), abnormal sex ratios (Matthiessen and Gibbs, 1998), intersex in wild roach and vitellogenin induction in rainbow trout (Rodger-Gray et al., 2001).

Estrogenic hormones have been detected in influents and effluents of sewage treatment plants (STP) in many countries (Desbrow et al., 1998; Belfroid et al., 1999; Ternes et al., 1999; Baronti, et al., 2000; Jeannot et al., 2002), surface water (Liu et al., 2004; Zhou et al., 2007), as well as drinking water (Kuch and Ballschmiter, 2001). Considering the widespread occurrence and potential impacts of EDCs, it is highly important to remove them before discharge. The current data suggest that wastewater treatment processes (e.g. activated sludge) have variable performance in removing EDCs. By comparing the influent and effluent estrogen concentrations, Baronti et al. (2000) concluded that the removal efficiency for estrone (E1) and 17β-estradiol (E2) were 87 and 61%, respectively. In a Brazilian STP, the observed removal efficiency for 17α-ethynylestradiol (EE2) ranged from 64% to 78% (Ternes et al., 1999). In a study of 20 STP in Sweden, the average removal efficiency was 81% by activated sludge treatment and only 28% by solid supported bacterial treatment (Svenson et al., 2003). It is therefore essential to install additional treatment processes after secondary treatment step, to ensure a more complete removal of such compounds.

Granular activated carbon (GAC) adsorption is a versatile technology and particularly suited for removing both synthetic organic pollutants and naturally occurring dissolved organic matter from water and wastewater. Recently, GAC has been shown to be effective in adsorbing both E1 and E2 (Zhang and Zhou, 2005). However, GAC only transports EDCs from one medium (water) to another (GAC). In addition, the relatively high cost of activated carbon has prevented it from wide application, particularly in developing countries. Consequently, alternative treatment technology has to be sought; among which photodegradation has been widely explored (Ohko et al., 2001; Ohko et al., 2002; Zhang, 2006; Belgiorno et al., 2007; Zhang et al., 2007). So far most photocatalysis studies focused on EDC removal in water, and further work is needed to assess feasibility of EDC removal in wastewater by photocatalysis.

The objectives of the study are to determine the levels of selected EDCs in the Horsham STP, West Sussex, UK; to assess the efficiency of the current treatment processes in removing EDCs; and finally to explore the potential of using photocatalytical technology to remove the most potent EDCs from wastewater.

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2. Methods and Materials

2.1. EDC standards and solvents

Seven EDC compounds were selected for tracing their levels in wastewater: 4-*tert*-octylphenol, bisphenol A (Aldrich, UK), 4-nonylphenol, E1, E2, EE2, and 16α-hydroxyestrone (HE1) (Sigma, UK). Two internal standards, E2-d_2 (Sigma, UK) and bisphenol A-d_{16} (Aldrich, UK), were used to quantify the target compounds.

All the other solvents used including methanol, ethyl acetate and dichloromethane, purchased from Rathburn Chemicals Ltd (Scotland), were of distilled-in-glass grade, and bis(trimethylsilyl)trifluroroacetamide (BSTFA) containing 1% of trimethylchlorosilane were supplied by Aldrich (Dorset, UK). Ultrapure water was obtained from a Maxima Unit from USF Elga, UK.

2.2. EDCs survey and analysis

Wastewater samples were collected from Horsham STP, West Sussex, UK, on the following dates: 08/09/04, 01/12/04, and 10/05/05. Samples were taken to cover the whole treatment processes including influent (site 1), post sedimentation (site 2), post biological filter (site 3), and the final effluent (site 4). Samples were collected in pre-cleaned amber glass bottles (2.5-l) and spiked with sodium azide (final conc. = 0.02 M) to minimise any biodegradation. In situ measurement of basic water quality was taken including pH, dissolved oxygen, and temperature (Table 1).

On return to the laboratory, samples were immediately filtered using pre-combusted Whatman GF/F filter paper (0.7 μm) to remove particulate matter, and spiked with 100 ng each of bisphenol A-d_{16} and E2-d_2. These were then ready for solid-phase extraction (SPE) following established procedures (Liu et al., 2004; Zhang et al., 2006). First the SPE cartridges (Oasis HLB, Waters, USA) were conditioned with 5 ml of ethyl acetate to remove residual bonding agents, followed by 5 ml of methanol and ultra-pure water (3 * 5 ml). Then water samples were extracted at a flow rate less than 5 ml min^{-1}, which were subsequently eluted with 15 ml of ethyl acetate solvent. The extracts then were concentrated to 1–2 ml under a gentle flow of nitrogen at 45 °C. The extracts were then derivatised by the addition of 50 μl pyridine and 50 μl BSTFA, which were heated at 65 ± 5 °C for 30 min.

GC–MS analysis was performed using a gas chromatograph (Trace GC 2000, Themoquest CE Instruments, TX, USA) coupled with an ion trap mass spectrometer (Polaris Q, Themoquest CE Instruments, Texas, USA) and an autosampler (AS 2000, Thermoquest). A ZB5 (5% diphenyl–95% dimethylpolysiloxane) capillary column of 30 m × 0.25 mm i.d. (0.25 μm film thickness) was used. Helium carrier gas was maintained at a constant flow rate of 1.5 ml min^{-1}. The GC column temperature was programmed from 100 °C (initial equilibrium time 1 min) to 200 °C via a ramp of 10 °C min^{-1}, 200–260 °C via a ramp of 15 °C min^{-1}, 260–300 °C via a ramp of 3 °C min^{-1} and maintained at 300 °C for 2 min. The MS was by electron impact ionisation and operated in full-scan mode from 50 *m/z* to 600 for qualitative analysis or selected ion monitoring mode for quantitative analysis. The inlet and MS transfer line temperatures were maintained at 280 °C, and the ion source temperature was 250 °C. Sample injection (1 μl) was in splitless mode. The limits of detection (LOD) for EDCs have been reported by Liu et al. (2004).

Table 1
Water quality data in Horsham sewage treatment plant

Sampling site	Measurement	08/09/04	01/12/04	10/05/05
Influent	pH	6.48	7.56	7.26
	Temperature (°C)	19.7	12.1	14.8
	Dissolved O_2 (mg l^{-1})	8.53	0.29	4.18
Post-sedimentation	pH	6.56	7.56	7.33
	Temperature (°C)	19.7	10.9	14.1
	Dissolved O_2 (mg l^{-1})	8.50	0.32	5.22
Post-biological filter	pH	6.57	7.56	7.26
	Temperature (°C)	19.6	12.1	14.7
	Dissolved O_2 (mg l^{-1})	8.51	0.29	6.67
Effluent	pH	6.79	7.59	7.31
	Temperature (°C)	19.7	13.0	15.0
	Dissolved O_2 (mg l^{-1})	8.49	0.46	7.53

2.3. Photodegradation experiments

Separate stock solutions of individual compounds were made up at 1000 mg l^{-1} by dissolving an appropriate amount of each chemical in methanol. From these standards, a working solution containing each compound at 10 mg l^{-1} was prepared by diluting the individual stock solution in methanol. The working solution was then spiked into water and stirred with a magnetic stirrer to obtain an initial concentration of 500 ng l^{-1} for the reactions irradiated by artificial UV light (15-W) and 0.5–100 μg l^{-1} for the reactions irradiated by sunlight. Following 30 min of mixing, TiO_2 was added at a concentration of 1 g l^{-1}, with stirring continued.

UV degradation experiments were conducted by transferring the prepared solution into a 15-W UV reactor irradiating at 253 nm (Heracus Noblelight, Germany), which was carried out in the dark to shield from sunlight. At different time intervals, samples were taken from the reactor vessel, spiked with internal standards, extracted by SPE, derivatised and analysed by GC–MS (Liu et al., 2004). Control experiments were also carried out in the absence of TiO_2, with the other conditions being the same. The results showed that, in the absence of TiO_2, the changes in the concentrations of both E1 and E2 were negligible.

The photodegradation induced by sunlight was carried out in a Pyrex conical flask (5-l) in a green house on university campus during June–September 2004. Duplicate samples of 100 ml were collected at every time interval and analysed by the procedure described above. To investigate the role of sunlight and catalyst, experiments were carried out in three other forms: no light and catalyst, light without catalyst and catalyst without light.

Further photodegradation experiments were performed with wastewater from Horsham STP. The wastewater samples were analysed for basic properties such as temperature (10–18 °C), pH (6.4–7.8) and dissolved O_2 (3.5–7.7 mg l^{-1}). Other parameters such as nitrate, phosphate, ammonia and dissolved organic carbon were not measured.

3. Results and discussion

3.1. EDCs in Horsham STP

The concentrations of EDCs found at different treatment stages during the three sampling periods are shown in Fig. 1. Both phenolic compounds and estrogenic compounds were detected. It can be seen that the most abundant EDC was bisphenol A, of which the concentration ranged from 298 to 1010 ng l^{-1} in the influent. This is expected due to the wide use of bisphenol A as a monomer for the production of polycarbonate and epoxy resins, unsaturated polyester-styrene resins and flame retardants (Staples et al., 1998, 2000). The concentrations of other compounds in the influent varied from 14 to 78 ng l^{-1} for 4-*tert*-octylphenol, 87–321 ng l^{-1} for 4-nonylphenol, 20–60 ng l^{-1} for E1, 26–51 ng l^{-1} for E2, < LOD (0.8 ng l^{-1}) – 10 ng l^{-1} for EE2, and 24–33 ng l^{-1} for HE1, respectively. Such levels are consistent with those reported in other STP influent samples (Belfroid et al., 1999; Ternes et al., 1999; Baronti et al., 2000).