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Endocrine disrupting compounds: A comparison of removal between conventional activated sludge and membrane bioreactors

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ABSTRACT

The removal of endocrine disrupting compounds (EDCs) was investigated in a conventional activated sludge plant connected with a tertiary treatment (CAS-TT) and two membrane bioreactor pilot plants installed with flat sheet (MBR-FS) and hollow fibre (MBR-HF) modules.

Chemical compounds such as alkylphenols (4OP and 4tOP), nonylphenols (NP), bisphenol A (BPA), phthalates (DMP, DEP, DBP, BBP, BEHP, and DOP) and estrogens (E1 and EE2) were determined in dissolved wastewater by employing stir bar sorptive extraction and thermal desorption–gas chromatography–mass spectrometry. Samples were taken during three months from the outlet of the primary settling tank (PS), the tertiary treatment and the flat sheet and hollow fibre modules.

All the target compounds were detected in the effluent of the PS during the monitored period except DMP, 4OP, DOP and EE2.

The MBR modules were more efficient in the removal of DEP, DBP and BBP than CAS-TT, whereas CAS-TT was more efficient in the removal of BEHP. For 4tOP and BPA the removal efficiency found was very similar when CAS-TT or MBR treatments were applied.

Only slight differences were detected comparing both MBR modules. MBR-HF seemed to be adequate for DBP and NP removal, while MBR-FS was better for DEP and BBP removal.

1. Introduction

In recent years, a group of xenobiotic compounds denominated endocrine disrupting compounds (EDCs) have been investigated due to their adverse effects in animals and humans inhibiting the normal action of the endocrine system. The European Commission (1996) defined an EDC as an exogenous substance that causes adverse health effects in an intact organism, or its progeny, consequent to changes in endocrine functions [1]. Exposure to these compounds has been linked to a decrease in the sperm count, and an increment of episodes of prostate cancer and other reproductive disorders in humans [2].

The list of compounds that have estrogenic activity is extensive. In this study, the compounds studied were limited to the following families of chemicals:

- Alkylphenols are used in industrial, agricultural and household applications such as detergents, emulsifiers, wetting agents, dispersants or solubilizers [3].
- Nonylphenols (sub-product of degradation of nonylphenol ethoxilates) have been considered as priority hazardous compounds while octylphenols are subject for inclusion in this category [4].
- Phthalates have been used in the manufacture of PVC, plasticizers for building materials and insect repellents [5].
- Bisphenol A is used in tyre production, as a stabilizing agent in polycarbonate, epoxy resins and as the basic chemical in the production of certain flame retardants [6].
- Natural estrogens such as Estrone (E1) and synthetic estrogens like 17-α-Ethynilestradiol (EE2) show endocrine disrupting properties [7].

Wastewater treatment plants (WWTP) receive raw water containing EDCs from domestic and industrial discharges [8]. These contaminants are partially removed from treated wastewaters and are one of the major sources of pollution in the aquatic environment. In conventional activated sludge plants (CAS), the biological degradation and the secondary settling tank form one process unit to remove EDCs from wastewater and the biomass concentration in the mixed liquor depends on the settling tank capacity [9]. Membrane bioreactors (MBRs) are able to operate at higher biomass concentrations obtaining a better permeate quality, less than 5 mg/L of total suspended solids [10] and higher biochemical oxygen demand (BOD) removal due to membrane separation by micro or ultrafiltration processes. The quality of the effluents obtain in a CAS plant can improve in terms of chemical oxygen demand (COD) (less than 50 mg/L) and total suspended solids (less than 10 mg/L) by connecting the CAS plant

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in line with a conventional tertiary treatment (CAS-TT) [11]. The quality of the effluents obtained in these plants is similar to that obtained in MBRs.

The number of articles studying the elimination of these compounds in treatment plants has increased over the last few years. Thus, nonylphenols are usually detected in the influent of the treatment plants at concentrations up to 50 μg/L as a result of its formation in sewer system [12].

Between 10 and 100 μg of β-estradiol (E2), EE2, E1 and estriol (E3) are excreted daily by women in their normal cycle but pregnant women can excrete much more, up to 5 mg/day. In function of excretion, dilution levels and previous observations of other authors, we expect the level of concentration in ng/L [13].

The removal efficiency of EDCs in different treatment stages installed in WWTP has been studied by several authors. The elimination of some phthalates was evaluated in a WWTP located in France containing different units as the pre-treatment (grid removal and sand trap degreaser), the primary clarifier, the biological treatment (aeration basin and the secondary clarifier) and the nitrification tank [14]. They concluded that the major removal efficiency found for light compounds took place in the biological reactor whereas heavy substances with long chains were removed in the primary clarifier by sorption to the suspended matter.

There are several reports that have evaluated the removal of EDCs in CAS or MBRs and some authors have compared both technologies when the same raw wastewater entered each treatment. But there are not evidences of previous investigations comparing the removal efficiencies of a CAS connected to a conventional tertiary treatment and a MBR plant.

To understand the possible effects of these compounds on the environment it is necessary to carry out the study of their removal in wastewater treatment plants. This study concerns the identification and the removal of EDCs identified as industrial source and natural chemicals that present an endocrine activity dissolved in wastewater comparing two technologies of treatment: a CAS connected with a conventional tertiary treatment and two MBR pilot plants containing flat sheet and hollow fibre modules. We analyzed only the dissolved fraction of these compounds because the concentration of suspended solids in the effluent of both treatment plants with tertiary treatment and MBRs can be considered negligible.

2. Materials and methods

2.1. Chemicals and reagents

The chemicals used in the study were dimethyl phthalate (DMP), diethyl phthalate (DEP), 4-tert-octylphenol (4tOP), nonylphenol (NP), 4-octylphenol (4OP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bisphenol A (BPA), bis (2-ethylhexyl) phthalate (BEHP), di-n-octyl phthalate (DOP), Estrone (E1), 17-α-Ethynilestradiol (EE2) and acetic anhydride. All chemicals were purchased from Sigma Aldrich (Steinheim, Germany).

Solvents such as methanol and acetone (HPLC grade) and sodium carbonate were purchased from Merck (Darmstadt, Germany).

Water used was from a Milli-Q Synthesis A10 System (Millipore, Bedford, MA, USA).

Individually stock solutions of EDCs were prepared at concentration of 1000 mg/L and a mix stock solution of 10 mg/L was prepared in methanol and stored at −18 °C. Working solutions were obtained by a serial dilution of stock solution with Milli-Q water.

2.2. Sewage treatment plants

This study was carried out at a municipal wastewater treatment plant (WWTP) located in Alicante (Spain) that operates with a conventional activated sludge (CAS) treatment. The capacity of this plant is around 75,000 m^3/d and treats wastewater of 420,000 inhabitants approximately. The processes carried out in CAS (Fig. 1) start with a pre-treatment (grid removal, sand trap and degreaser), after that wastewater enters the primary settling (PS) tank and flows through a biological reactor and a settlement of suspended matter. Next, a tertiary treatment consisting of flocculation–coagulation and sand filtration treatments is installed in the CAS plant.

Two membrane bioreactors (MBR) were installed in a pilot plant (Fig. 1); a MBR containing four modules of hollow fibre (MBR-HF) from Porous Fibre, total area of 20 m^2 and a flow rate of 400 L/h and a second MBR with 20 flat sheet (MBR-FS) modules from Kubota, total area of 16 m^2 and flow rate of 400 L/h. These MBRs are feed with water from the outlet of the primary settling tank and worked in parallel with the secondary and tertiary treatment of the CAS-TT.

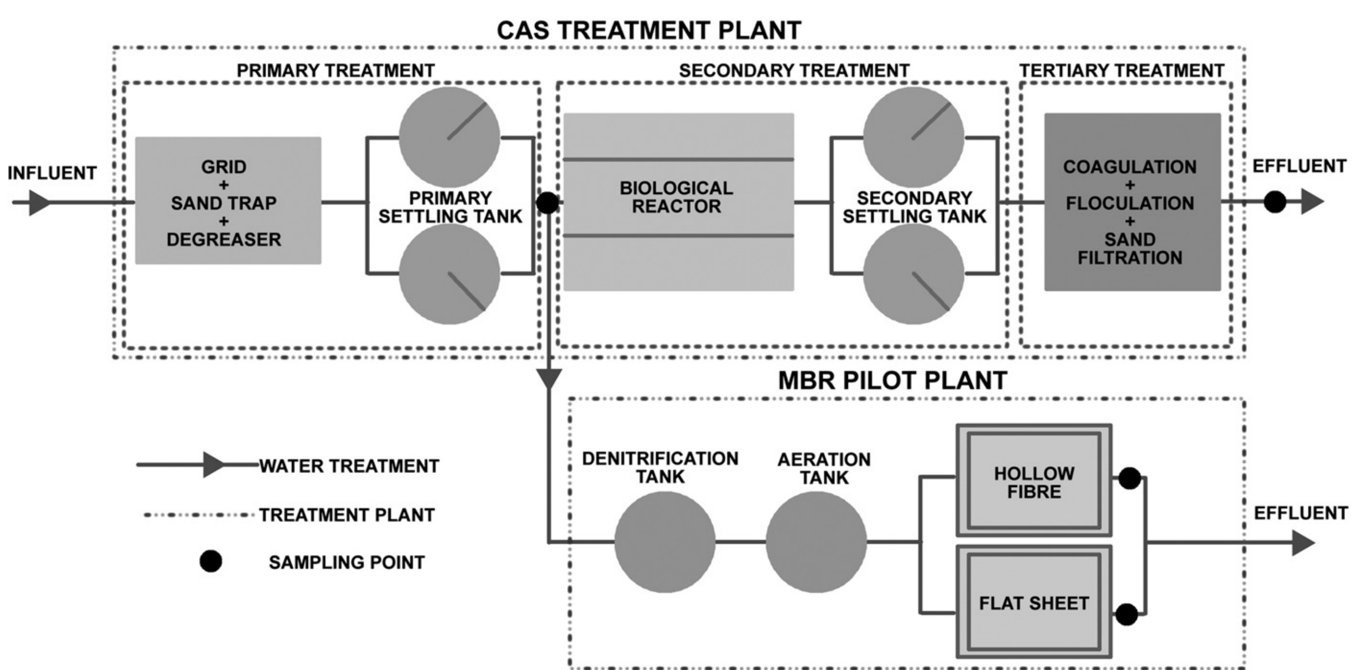

Fig. 1. Wastewater treatment in CAS and MBR pilot plant.