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Evaluation of emerging contaminants in a drinking water treatment plant using electrodialysis reversal technology

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HIGHLIGHTS

- 49 of 90 monitored emerging contaminants (ECs) were found in the raw water of a DWTP.
- ECs were monitored through oxidation (ClO_2), adsorption (GAC), and desalination (EDR).
- The DWTP reduced EC concentrations well, mostly by >90%, and by at least 65%.
- Oxidation (ClO_2) and adsorption (GAC) were the most efficient steps in the DWTP.
- For the first time, EDR was shown as an effective barrier for ionized ECs.

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ABSTRACT

Emerging contaminants (EC) have gained much attention with globally increasing consumption and detection in aquatic ecosystems during the last two decades from ng/L to lower ug/L. The aim of this study was to evaluate the occurrence and removal of pharmaceutically active compounds (PhACs), endocrine disrupting chemicals (EDCs) and related compounds in a Drinking Water Treatment Plant (DWTP) treating raw water from the Mediterranean Llobregat River. The DWTP combined conventional treatment steps with the world's largest electrodialysis reversal (EDR) facility. 49 different PhACs, EDCs and related compounds were found above their limit of quantification in the influent of the DWTP, summing up to a total concentration of ECs between 1600–4200 ng/L. As expected, oxidation using chlorine dioxide and granular activated carbon filters were the most efficient technologies for EC removal. However, despite the low concentration detected in the influent of the EDR process, it was also possible to demonstrate that this process partially removed ionized compounds, thereby constituting an additional barrier against EC pollution in the product. In the product of the EDR system, only 18 out of 49 compounds were quantifiable in at least one of the four experimental campaigns, showing in all cases removals higher than 65% and often beyond 90% for the overall DWTP process.

1. Introduction

Emerging contaminants (EC) have gained much attention in recent years with the worldwide increasing consumption of these substances. EC include pharmaceutically active compounds (PhACs), which are a group of chemical substances that have medicinal properties produced worldwide on a 100 000 t scale [1]. Most modern drugs are small organic compounds with a molecular weight (MW) below 500 Da, which are moderately water soluble as well as lipophilic, in order to be bioavailable and biologically active [2]. In the European Union (EU) around 3000 different pharmaceuticals are used in human medicine (i.e., analgesics and

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anti-inflammatory drugs, ß-blockers, lipid regulators, antibiotics, etc) [3]. Moreover, there is another broad spectrum of anthropogenic and naturally occurring chemicals that can alter the normal endocrine function and physiological status of wildlife species. Among the chemicals that act as endocrine disrupting chemicals (EDCs) are natural and synthetic hormones (estrogens and progestogens) and some common industrial and household products such as plasticizers, antioxidants, pesticides and non-ionic surfactants and their degradation products [4]. Some of the main sources of EDCs include urban wastewaters, tannery effluents, paper and pulp mill effluents[4].

Consequently, these compounds have been detected in aquatic environment in concentrations typically ranging from ng/L to lower μg/L [5]. Specifically, pharmaceutical data sets collected from river systems around the world have recently been critically evaluated [5]. Results from Spain [6] showed that the national mean for some compounds is much higher than the global mean of the ten most studied countries, being the ten most frequently identified compounds in Spanish rivers: ibuprofen, diclofenac, naproxen, clofibric acid, carbamazepine, sulfamethoxazole, trimethoprim, bezafibrate, atenolol and gemfibrozil.

Since the presence of EC has been demonstrated in surface waters, it is evident that the removal efficiencies achieved in the facilities using this water for drinking water production should be evaluated. Specifically, while studies have shown that conventional water treatment processes are relatively ineffective in removing PhAcs, EDCs and related compounds, advanced treatment technologies such as activated carbon, reverse osmosis and advanced oxidation may be viable for the removal of many trace pharmaceuticals [7].

Focusing on the Llobregat River basin (Catalonia, NE Spain), both priority and ECs have been shown to pollute the water of the river to significant extent as a result of the intense human activities (agriculture, industry, urban) taking place in the Barcelona area and upstream [8]. The organic contaminants found in the Llobregat River include PhACs and EDCs, among them natural and synthetic hormones and alkylphenolic compounds [9].

The presence of unusually high bromide concentrations in the Llobregat river can pose a risk of generating bromide containing disinfection by-products during potable water treatment since DBPs are generated when naturally occurring organic matter, anthropogenic contaminants, bromide and iodide react with disinfectants such as chlorine, ozone, chlorine dioxide or chloramines [10]. To mitigate this risk treatment technology reducing total organic carbon and bromide is necessary [11]. Moreover, Mediterranean rivers characteristics, represented by the low and irregular flow together with a high water demand due to the large population served, causes the need for a high recovery technology in the facilities treating water from this river. In this context, electrodialysis reversal (EDR) shows recoveries higher than other membrane technologies applied for brackish water desalination, such as nanofiltration (NF) or reverse osmosis (RO), with average results higher than 90% [11]. EDR is also considered to be a robust and energy efficient technology for brackish water desalination and hence, this technology was chosen for treating the surface water at the studied DWTP. At present it is the largest EDR facility in the world to the knowledge of the authors.

The electrodialysis process uses a driving force of direct current power to transfer ionic species from the source water through cation and anion exchange membranes to a concentrate waste stream, creating a more diluted product water stream. EDR is a variation on the electrodialysis process, which uses periodic electrode polarity reversal to automatically clean membrane surfaces [11,12]. Despite the number of advantages associated with this technology, its efficiency to remove EC is largely unknown, since few studies on water quality in the context of the EDR process have been conducted as the process is mostly applied to reduce salinity.

Therefore, the aim of this study is to evaluate the occurrence and removal of PhACs and EDCs (including some suspected EDCs and related compounds) in a DWTP treating raw water from the Mediterranean Llobregat River. The DWTP is a very modern plant and combines a series of conventional treatment steps including pre-oxidation by chlorine dioxide and filtration through granular activated carbon (GAC) with the EDR technology. The present study evaluated the removal efficiencies of each process in the DWTP, whereby the study of the removal of a group of emerging contaminants in a full-scale EDR process is the first of its kind.

2. Experimental methods

2.1. DWTP description

The Llobregat DWTP can process up to 3 m^3/s with the conventional treatment including [11,12]: pre-oxidation with potassium permanganate, coagulation, flocculation, oxidation with chlorine dioxide, sand filtration, granular activated carbon filtration (GAC), and final chlorination using NaClO (Fig. 1). After GAC, it is possible to process up to 2.3 m^3/s by means of an EDR brackish water desalination plant, with the aim of reducing bromide and also salinity (approximately 75% reduction of electric conductivity) to controltrihalomethanes (THMs) formation in the distribution system. The EDR process includes nine modules with two hydraulic EDR stages with a total of 576 stacks of 600 cell pairs in each stack. The EDR effluent is remineralized and disinfected by using NaClO and can be distributed directly to the network or optionally mixed with the water produced in the conventional units.

2.2. Sampling protocol

Water samples were collected at seven different locations pointed in Fig. 1: (s1) the raw water station, (s2) after pre-oxidation ($KMnO_4$), coagulation/flocculation, sedimentation and oxidation (ClO_2), (s3) effluent of sand filters, (s4) effluent of GAC filters, (s5) effluent of the first EDR stage, (s6) effluent of the second EDR stage, and (s7) concentrate of the EDR system. Four sampling campaigns (M1, M2, M3 and M4) were conducted between June and July of 2014.

In order to assess the efficiency of the different steps of the treatment, grab samples were collected before and after each treatment unit, taking into account the hydraulic retention times (HRTs) of the processes. Samples were collected using polyethylene terephthalate (PET) bottles for the analysis of micropollutants and plastic bottles for the water physicochemical properties and inorganic parameters.

2.3. EC analysis

For the EC analysis, samples were collected, filtered (size) and stored in PET bottles at 4 °C until extraction within 24 h. Ascorbic acid (up to 25 mg/L) was added to samples S2 and S3 in order to prevent further reaction with chlorine dioxide. Off-line solid phase extraction (SPE) followed by ultra high performance liquid chromatography tandem mass spectrometry (UHPLC–MS/MS) method was applied for PhACs analysis [13], while EDCs and related compounds were analyzed by on-line chromatography coupled to a LC–MS/MS system [14]. The entire system was controlled via Xcalibur 2.2 software and data were processed using TraceFinder 3.1.