ARTICLE IN PRESS

Journal of Hazardous Materials xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Electrodialytic 2-compartment cells for emerging organic contaminants removal from effluent

Ana Rita Ferreira[a], Nazaré Couto[a,*], Paula Guedes[a,b], Joana Pinto[a], Eduardo P. Mateus[a], Alexandra B. Ribeiro[a]

[a] CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal
[b] Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. da República, 2780-157, Oeiras, Portugal

ARTICLE INFO

Keywords:
Effluent
ED process
2-compartments cell
Cell design
Pharmaceuticals and personal care products
Phosphorus recovery

ABSTRACT

The present work discusses the efficiency of the electrodialytic (ED) process to remove emerging organic contaminants (EOCs) from effluent. The ED process was carried out in a cell of two-compartments (2 C-cell) with effluent in either the anode or cathode compartment, separated from the electrolyte compartment through an anion or a cation exchange membrane (AEM and CEM, respectively). As effluent destination might be soil irrigation, and having in mind the nutrient recycling, phosphorus was also monitored in the process.

The ED removals showed to be dependent of EOCs characteristics and cell design. Removals were higher when using an AEM (60–72%) than a CEM (8–63%), except for caffeine when the effluent was placed in the cathode, that did not show any removal. When using an AEM with the effluent placed in the anode compartment, all the EOCs (including caffeine) were removed between 57–72%, mainly through electrodegradation phenomena.

Regarding phosphorus, a polarity switch may be done to a 2 C-cell with a AEM, depending on the effluent final use. This technology is still in its first steps and, in both cases, further optimization of ED parameters is needed. Still, this technological innovation and cross-cutting research envisages the promotion of economic, social and environmental benefits.

1. Introduction

The emerging organic contaminants (EOCs) have been detected worldwide in the aquatic environment, being recognized as an environmental issue [1,2].

One of the prominent entry routes of EOCs is through wastewater treatment plants (WWTP) as they are not efficiently removed during the treatment steps. Due to the wide range categories of EOCs, their removal is also dependent on their properties [3]. The discharge of effluent to aquatic environment does not have specific legislation for most of the contaminants (Directive 2008/105/EC), and the continuous input of EOCs into surface water may cause adverse impacts in the environment even at low concentrations [1,4]. In addition, due to water scarcity, effluent has been extensively reused for various purposes in many regions of the world including landscape and agriculture irrigation [5]. Effluent reuse in agriculture also contributes to nutrients recycling, as phosphorus, alleviating pressure on over-exploited resources (e.g. phosphate rock, included in the EU list of 27 Critical Raw Materials). In this context, developing cost-effective technologies for EOCs removal from effluent is thus of great interest to public and the environmental health.

Among the various technologies that have been developed over the last decades, the so-called electrochemical advanced oxidation processes (EAOPs) have been under increased interest, as a promising class of advanced oxidation processes (AOPs) [6]. Literature reports the use of AOPs [7] such as ozonation [8], photocatalysis [9], UV [10], UV/H_2O_2 [11] and fenton [12] as effective on EOCs degradation in wastewater. The use oxidizing agents such as hydroxyl radicals ($\cdot OH$, redox potential of 2.80 V/SHE) can oxidize organic contaminants. Hydroxyl radicals initiate a series of oxidation reactions then leading to the ultimate mineralization products CO_2, H_2O and inorganic ions. Moreover, $\cdot OH$ have a short life-time, estimated as only a few nanoseconds in water [13], and so they can be self-eliminated from the treatment system. The electrokinetic process (EK) is based on the application of a low level direct current and due to water electrolysis, $\cdot OH$ are continuously being generated. Due to the formation of hydrogen cations at the anode and hydroxide anions at the cathode there will be a pH decrease and increase, respectively. The electrodialytic (ED) process

---

* Corresponding author.
E-mail address: md.couto@fct.unl.pt (N. Couto).

https://doi.org/10.1016/j.jhazmat.2018.04.066
Received 17 August 2017; Received in revised form 23 April 2018; Accepted 25 April 2018
0304-3894/

Please cite this article as: Ferreira, A.R., Journal of Hazardous Materials (2018), https://doi.org/10.1016/j.jhazmat.2018.04.066

accounts with the use of ion exchange membranes (anion exchange membrane, AEM and cation exchange membrane, CEM). The AEM only allows the passage of anions and the CEM the cations [14]. Few studies tested the applicability of the ED process in WWTP with contaminants removal (e.g. metals) from wastewater [15] and sewage sludge ash [16]. More recently, the removal of EOCs was carried out using EK and ED in soil [17,18] and in sewage sludge using ED [19,20]. It was reported that soil slurry and sewage sludge in the cathode compartment separated from anode by an AEM was effective in decreasing EOCs levels. Some studies also show that this same setup is useful to mobilize solubilized P from the cathode to the anode compartment [21].

Still, to the best of our knowledge, no works have been published regarding EOCs removal from effluent using ED process.

In this work, the ED process was applied to effluent testing the 2-compartments cell with different configurations. As the aim is to develop a cost-effective electro-technology to decrease EOCs concentrations from the effluent in WWTP, five compounds with different properties were selected after a literature survey. The chosen EOCs comprise a neural stimulant (caffeine, CAF), an industrial chemical (bisphenol A, BPA), two estrogenic steroid hormones (17β-oestradiol, E2; 17α-ethinyloestradiol, EE2) and a sunscreen compound (oxybenzone, MBPh). All EOCs have been detected in influent and effluent samples worldwide at relatively high concentrations (ng/L - ug/L) [22]. The properties of the studied contaminants can be found in Table 1. As the destination of the effluent might be for soil irrigation and having in mind the nutrient recycling, phosphorus was also monitored along the process.

2. Materials and methods

2.1. Chemicals and standards

Solvents were from Panreac (Barcelona, Spain), Merck (Darmstadt, Germany) and Sigma–Aldrich (Steinheim, Germany). Acetonitrile (ACN), methanol (MeOH) and acetone were HPLC gradient grade and formic and acetic acid were LC/MS grade. Deionized water further purified with a Milli-Q plus system from Millipore (Bedford, MA, USA) was also used. Sodium hydroxide (NaOH) were purchased from Sigma–Aldrich and sodium nitrate ($NaNO_3$) was from Panreac. Caffeine (≥90%), BPA (≥99%), E2 (≥97%), EE2 (≥98%) and MBPh (≥98%) were purchased from Sigma-Aldrich (Steinheim, Germany). Individual stock solutions for calibration purposes were prepared at 4000 mg/L in MeOH and stored at −18 °C.

2.2. Effluent sampling procedure

Effluent samples were collected at a WWTP from Simarsul located in Quinta do Conde, Sesimbra, Portugal. The WWTP has infrastructures with capacity to treat urban wastewater corresponding to about 94,000 equivalent inhabitants and the level of installed treatment is tertiary (UV light).

Table 2
Characteristics of effluent samples.

Effluent sample Code (Eff#)	TSS mg/L	pH	Conductivity *µS/cm*	BOD_5 mg/L	COD mg/L	P mg/L
Eff1	17	7.31	947	6.1	47	11.5
Eff2	30	8.00	1880	30	150	5.8

The WWTP has an aerobic reactor of suspended biomass to allow the biological treatment of wastewater. The effluent from this reactor goes to the secondary settling tank for phase separation where liquid samples were collected. Once at the laboratory, and to remove colloidal particles from the secondary effluent, the samples were pretreated using a 0.45-mm MF filter, and the filtered effluent was used in all experiments. Effluent samples were collected in May and June and initial characterization is presented in Table 2. Initial screening was done and none of the studied contaminants were detected in the collected samples.

2.3. Electrodialytic set-up

The 2-compartment (2 C) ED cell design was tested in accordance to designs presented in Fig. 1a–d. The 2 C ED laboratorial cell was assembled with two compartments (cathode and anode both with an internal diameter of 8 cm) separated by an ion exchange membrane [either an anion exchange membrane, AEM: AR204 SZRA B02249 or cation exchange membrane, CEM: CR67 HUY N12116B) both from Ionics Inc., Massachusetts, USA]. The electrodes were platinized titanium bars (diameter 3 mm) obtained from Permascand® and a power supply (Hewlett Packard E3612A) was used to maintain a constant current. The fresh electrolyte was a 10^{-2} M $NaNO_3$ solution with pH 6.4 (± 0.4) and conductivity of 1215 (± 62) µS/cm. The electrolyte was circulated by means of a peristaltic pump (Watson-Marlow503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK) in a closed circulation system.

2.4. Experimental set-up

Effluent was spiked with a mixture of 3 mg/L of each compound (CAF, BPA, E2, EE2 and MBPH) in 1:1 MeOH:Acetone. The effluent (300 mL) was placed in one of the electrode compartments. Electrolyte (500 mL) was put in the other electrode compartment and recirculated at 4 mL min^{-1}. Fig. 1a–d shows the different 2 C-cell configurations tested in the present work in which the (i) effluent was placed either in the anode or cathode compartment, and (ii) either a cation or anion exchange membrane were used for separating the compartments. The experiments were carried out for 12 h with current intensity applied of 20 mA. To assess EOCs removal kinetics, samples were collected hourly

Table 1
Chemical structure and properties of the emerging organic contaminants.

Compound	Caffeine	Bisphenol A	Estradiol	Ethinyl Estradiol	Oxybenzone
IUPAC Name	1,3,7-trimethylxanthine	4,4’-Isopropylidenediphenol	17β-estradiol	17α-ethinylestradiol	2-hydroxy-4-methoxybenzophenone
Category	CSN stimulant	Plasticizer	Estrogen	Estrogen	UV filter
Formula	$C_8H_{10}N_4O_2$	$C_{15}H_{16}O_2$	$C_{18}H_{24}O_2$	$C_{20}H_{24}O_2$	$C_{14}H_{12}O_3$
Molecular weight (g mol^{-1})	194.19	228.29	272.38	296.40	228.24
Solubility (mg L^{-1}) at 25 °C	2.16×10^4	120	3.9	11.3 (27 °C)	69
pKa[1]	14	9.6-10.2	10.7	10.3	7.6
Log K_{ow}[2]	−0.07	3.32	4.01	3.67	3.79
H (Pa m^3 mol^{-1})[3]	3.58×10^{-11}	1.0×10^{-6}	3.64×10^{-11}	7.94×10^{-12}	1.5×10^{-8}

References: http://pubchem.ncbi.nlm.nih.gov/, www.chemicalbook.com, http://SigmaAldrich.com.

[1] Ionization constant.

[2] Logarithm of the octanol-water partition coefficient.

[3] Henry’s Law constant.