Chemosphere 117 (2014) 124–131

Contents lists available at ScienceDirect

Chemosphere

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

Electrokinetic remediation of six emerging organic contaminants from soil

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HIGHLIGHTS

- Electrokinetic remediation is a viable method for organic contaminants removal.
- Between 50% and 80% of the contaminants were remediated after four days.
- Electroosmosis was the main mechanism responsible for contaminants mobilization.
- Electrodegradation should also be taken into account in this remediation process.

ARTICLE INFO

Article history:
Received 19 February 2014
Received in revised form 5 June 2014
Accepted 6 June 2014

Handling Editor: E. Brillas

Keywords:
Electrokinetic remediation
Organic contaminants
Electroosmotic flow
Electrodegradation
Soil

ABSTRACT

Some organic contaminants can accumulate in organisms and cause irreversible damages in biological systems through direct or indirect toxic effects. In this study the feasibility of the electrokinetic (EK) process for the remediation of 17β-oestradiol (E2), 17α-ethinyloestradiol (EE2), bisphenol A (BPA), nonylphenol (NP), octylphenol (OP) and triclosan (TCS) in soils was studied in a stationary laboratory cell. The experiments were conducted using a silty loam soil (S2) at 0, 10 and 20 mA and a sandy soil (S3) at 0 and 10 mA. A pH control in the anolyte reservoir (pH > 13) at 10 mA was carried out using S2, too. Photo and electrodegradation experiments were also fulfilled. Results showed that EK is a viable method for the remediation of these contaminants, both through mobilization by electroosmotic flow (EOF) and electrodegradation. As EOF is very sensible to soil pH, the control in the anolyte increased EOF rate, consequently enhancing contaminants mobilization towards the cathode end. The extent of the mobilization towards the electrode end was mainly dependent on compounds solubility and octanol-water partition coefficient. In the last 24 h of experiments, BPA presented the highest mobilization rate (ca. 4 μg min^{-1}) with NP not being detected in the catholyte. At the end of all experiments the percentage of contaminants that remained in the soil ranged between 17 and 50 for S2, and between 27 and 48 for S3, with no statistical differences between treatments. The mass balance performed showed that the amount of contaminant not detected in the cell is similar to the quantity that potentially may suffer photo and electrodegradation.

1. Introduction

Over the past years, adverse effects including endocrine disruption and antibiotic resistance of some compounds, defined as 'emerging' have been observed in humans, animals and other organisms (Lapworth et al., 2012) and some can display a biological response even at very low concentrations. These, emerging organic contaminants comprise a wide array of different compounds (as well as metabolites and transformation products) including: pharmaceuticals and personal care products, pesticides, veterinary products, industrial compounds/by-products, food additives, as well as engineered nanomaterials (Clarke and Smith, 2011).

The main transfer pathway for organic contaminants (OCs) to enter the environment is via wastewater treatment plants (Kuster et al., 2005; Boleda et al., 2009; Madureira et al., 2010). Several OCs have been detected in effluents of urban wastewater treatment plants (Golet et al., 2002), ground and river water (Golet et al., 2001), sewage sludge (Göbel et al., 2005), as well as soil and manure (due to veterinary use) (Golet et al., 2003).

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http://dx.doi.org/10.1016/j.chemosphere.2014.06.017
0045-6535/

The land application of municipal biosolids (typically to agricultural fields) is one potential route of soil exposure to OCs. The long-term risks associated with land application of biosolids are poorly characterized and, in some cases, difficult to accurately quantify (NRC, 2002). The OCs, once in soils, can be translocated to crop plants, and thus potentially enter in the food chain (Wu et al., 2012). In fact, the consumption of these plants might increase both human and livestock exposure to OCs (Zohair et al., 2006). For example, triclocarban (3,4,4′-trichlorocarbanilide) and triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol), that are toxic, lipophilic and persistent, were found in vegetables tissues of pumpkin and zucchini (Aryal and Reinhold, 2011). In a laboratory study, carbamazepine, diphenhydramine, and triclocarban were also detected in plants (pepper, tomato, collard, lettuce and radish) that were grown in biosolids-treated soils (Wu et al., 2012).

Electrokinetic (EK) process is a remediation method for contaminated matrices (Virkutyte et al., 2002). This method aims to remove contaminants from low permeability contaminated soils under the influence of an applied low level direct current (DC), via electroosmosis, electromigration and electrophoresis (Acar et al., 1993). EK was already tested for some OCs namely for the soil removal of herbicides (Ribeiro et al., 2005; Ribeiro et al., 2011), hydrocarbons (Alcántara et al., 2012; Méndez et al., 2012) and simultaneous removal of OCs and heavy metals (Maturi and Reddy, 2006; Li et al., 2010; Alcántara et al., 2012; Cang et al., 2013).

The aim of this work is to assess the potential of EK for the remediation of soils contaminated with organic compounds and how they are mobilized. Six OCs, classified emerging, were selected to the study: two estrogenic steroid hormones, three industrial reagents and one antimicrobial agent. The target compounds were 17β-oestradiol (E2), 17α-ethinyloestradiol (EE2), bisphenol A (BPA), nonylphenol (NP), octylphenol (OP) and triclosan (TCS). All these compounds are known to be endocrine disrupting agents and their chemical properties can be found in Table 1. To the best of our knowledge, EK removal of these emerging organic contaminants has never been reported, and the understanding of their behavior during the treatment can be valuable for the design of further tests.

2. Materials and methods

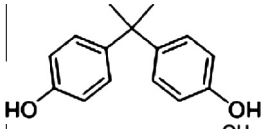
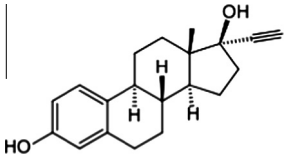
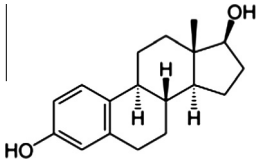
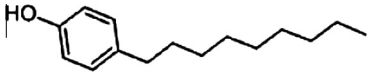
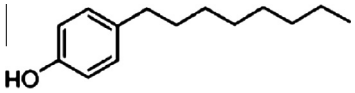
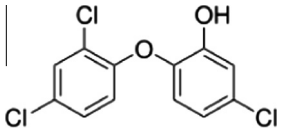
2.1. Chemicals and solvents

Bisphenol A (⩾99%), E2 (⩾97%), EE2 (⩾98%), OP (⩾99%), were purchased from Aldrich (Steinheim, Germany), TCS (Irgasan, ⩾97%) from Sigma–Aldrich (Steinheim, Germany) and NP (⩾90%) from Riedel Haën. All used solvents were from Sigma–Aldrich (Steinheim, Germany), Panreac (Barcelona, Spain) and Merck (Darmstadt, Germany). Acetonitrile, methanol and acetone were Gradient Grade. The water (type I) used for analyte extractions and their analytical determinations was deionized and purified with a Milli-Q plus system from Millipore (Bedford, MA, USA).

2.2. Organic contaminants analysis

The determination of the residual OCs was performed by high performance liquid chromatography with diode array detection (HPLC–DAD) in the range 200–800 nm.

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

Compound	Chemical structure	Formula	logK_{ow}[a]	pKa[b]	Solubility in water (mg L^{-1})	CAS-No
Bisphenol A (BPA)		$C_{15}H_{16}O_2$	3.32	9.6-11.3	120 (25 °C)	80-05-7
17α-ethinyloestradiol (EE2)		$C_{20}H_{24}O_2$	3.67	10.3	11.3 (27 °C)	57-63-6
17β-oestradiol (E2)		$C_{18}H_{24}O_2$	4.01	10.7	3.90 (27 °C)	50-28-2
p-Nonylphenol (NP)		$C_{15}H_{24}O$	5.76	10.7	7 (25 °C)	104-40-5
p-Octylphenol (OP)		$C_{14}H_{22}O$	5.30	10.4	19 (22 °C)	1806-26-4
Triclosan (TCS)		$C_{12}H_7Cl_3O_2$	4.76	7.9	10 (20 °C)	3380-34-5

References: http://pubchem.ncbi.nlm.nih.gov/, www.chemicalbook.com, www.SigmaAldrich.com.
Notes:
[a] Logarithm of the octanol-water partition coefficient.
[b] Logarithm of acid dissociation constant.