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Removal of emerging micropollutants from water using cyclodextrin

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HIGHLIGHTS

- Removal of micropollutants from water was evaluated in lab-scale studies.
- Experiments were performed to assess the efficiency of cyclodextrin-based sorbents.
- Efficiency of the treatments was characterized and evaluated by complex methodology.
- The cyclodextrin-based sorbent removed the micropollutants from water.
- The removal of bisphenol-A and hormones was the most efficient (more than 85%).

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ABSTRACT

Small scale laboratory experiment series were performed to study the suitability of a cyclodextrin-based sorbent (ß-cyclodextrin bead polymer, BCDP) for modelling the removal of micropollutants from drinking water and purified waste water using simulated inflow test solutions containing target analytes (ibuprofen, naproxen, ketoprofen, bisphenol-A, diclofenac, β-estradiol, ethinylestradiol, estriol, cholesterol at 2–6 μg/L level). This work was focused on the preliminary evaluation of BCDP as a sorbent in two different model systems (filtration and fluidization) applied for risk reduction of emerging micropollutants.
For comparison different filter systems combined with various sorbents (commercial filter and activated carbon) were applied and evaluated in the filtration experiment series.
The spiked test solution (inflow) and the treated outflows were characterized by an integrated methodology including chemical analytical methods gas chromatography–tandem mass spectrometry (GC–MS/MS) and various environmental toxicity tests to determine the efficiency and selectivity of the applied sorbents.
Under experimental conditions the cyclodextrin-based filters used for purification of drinking water in most cases were able to absorb more than 90% of the bisphenol-A and of the estrogenic compounds. Both the analytical chemistry and toxicity results showed efficient elimination of these pollutants. Especially the toxicity of the filtrate decreased considerably.
Laboratory experiment modelling post-purification of waste water was also performed applying fluidization technology by ß-cyclodextrin bead polymer. The BCDP removed efficiently from the spiked test solution most of the micropollutants, especially the bisphenol-A (94%) and the hormones (87–99%)
The results confirmed that the BCDP-containing sorbents provide a good solution to water quality problems and they are able to decrease the load and risk posed by micropollutants to the water systems.

1. Introduction

Due to anthropogenic activities, freshwater systems are worldwide confronted and impacted with thousands of synthetic organic compounds (xenobiotics) produced for industrial, domestic or agricultural use. Although most of these chemicals are present at very low concentrations, lots of them raise significant toxicological concerns (Schriks et al., 2010; Schwarzenbach et al., 2006). Their largely unknown long-term effects on aquatic systems and on human health are one of the key environmental problems facing humanity nowadays (Crane et al., 2006; Daughton and Ternes, 1999; Fent et al., 2006; Schwarzenbach et al., 2006).

Research focuses worldwide on measurement of micropollutants using sensitive sophisticated chemical analytical methods to detect

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and quantify them at low concentrations at which they occur in the environment (Boles and Wells, 2010; Boyd et al., 2003; Kasprzyk-Hordern et al., 2007; Kosjek et al., 2005; Sebők et al., 2009). The effect-assessment of these chemical substances is even more difficult because they are present as complex mixtures in the environment (Daughton and Ternes, 1999; Cleuvers, 2004). Some of these pollutants, mainly the pharmaceuticals and the active ingredients in personal care products, possess high biological activity so they are able to affect also the non-target organisms (Castiglioni et al., 2006; Bendz et al., 2005; Daughton and Ternes, 1999; Enick and Moore, 2007). The presence of emerging contaminants in the environment is not necessarily new but raises concern due to their suspected and proved dangerous effects on the ecosystem and on human health. In the last few decades several harmful effects have been observed on aquatic organisms caused by these pollutants (Jobling et al., 2006; Oaks et al., 2004). Therefore many scientists deal with acute or chronic adverse effects and environmental/human risks caused by these emerging substances (Carlsson et al., 2006; Crane et al., 2006; Enick and Moore, 2007; Fent et al., 2006; Halling-Sorensen et al., 1998; Kümmerer, 2009).

This newly defined group includes many different types of compounds, such as pharmaceuticals, personal care products, industrial additives and agents, hormones, nanomaterials, pesticides and surfactants. Most of these emerging contaminants are not covered currently by water-quality regulations in spite of the fact that they appear in natural, untreated and treated waters at μg/L concentrations (ICPDR; Kasprzyk-Hordern et al., 2008; Miege et al., 2009; Sebők et al., 2009; Yoon et al., 2010). Another problem is that the currently applied conventional water treatment technologies and drinking water treatment technologies are not suitable for their efficient removal (Carballa et al., 2004; Dlugolecka et al., 2006; Tauxe-Wuersch et al., 2005; Ternes, 1998); as a consequence, their introduction into the aquatic environment is continuous. In addition, the use of more efficient, advanced processes in waste water treatment such as nanofiltration (NF) and reverse osmosis (RO) is still limited due to their high cost (Dlugolecka et al., 2006; Kimura et al., 2003; Xu et al., 2005).

Nanofiltration has been demonstrated to be a promising option for eliminating pharmaceuticals, as it is able to achieve removal rates greater than 90% (Bolong et al., 2009; Yoon et al., 2006). It is also important to consider RO/NF brine disposal. In general, brine is much more toxic than the influent water, so its disposal into natural water is not sustainable (Watkinson et al., 2007).

One of the solutions addressing this water-quality problem is the development and implementation of cost-effective and appropriate technologies able to remove the micropollutants.

Cyclodextrins (CDs) which are traditionally used in pharmaceuticals and personal care products can form complexes with many organic micropollutants. Innovative use of cyclodextrin and cyclodextrin derivatives in environmental protection was reported during the last decade (Del Valle, 2004; Fenyvesi and Balogh, 2009; Liu et al., 2011; Szejtli, 2004). Different techniques (sorbents, filters, membranes etc.) using various cyclodextrins have been recently published for the elimination of hazardous materials from contaminated water (Allabashi et al., 2007; Baruch-Teblum et al., 2010; Chen et al., 2007; Crini, 2005; Mahlambi et al., 2010; Sancey et al., 2011). Our previous studies have shown that various cyclodextrin derivatives can extract hazardous substances selectively from contaminated environmental matrices (Gruiz et al., 2011).

Our main objective in this preliminary study was to develop innovative technologies that are able to remove emerging pollutants such as pharmaceuticals, hormones and industrial additives from water. One of the developed technologies presented in this paper refers to drinking-water purification; the other one to the removal of emerging contaminants from the traditionally treated waste water. Ibuprofen, naproxen, ketoprofen, bisphenol-A, diclofenac, β-estradiol, ethinylestradiol, estriol, and cholesterol were selected as model target compounds. These chemicals are among the most consumed non-steroidal anti-inflammatory drugs (NSAID), contraceptives/steroidal hormones, one of the widely used industrial additives frequently found in aquatic systems and cholesterol, a food constituent always present in municipal waste water. Because the presence of pharmaceuticals and hormones in drinking water is still not regulated, it is of great importance to know if the newly developed drinking water treatment can eliminate these compounds. It was not the purpose of this study to provide details of adsorption kinetics, but rather to give a general view of the feasibility of these techniques to remove micropollutants from drinking water or treated waste water.

2. Materials and methods

2.1. Experimental setup

Two different experiments based on two different technologies (filtration and fluidized bed) were implemented to model the pollutant removal efficiency of various sorbents. Our purpose was to model in laboratory 1) the purification of drinking water with filtration technology and 2) the post-purification of traditionally treated waste water with fluidization. As a new sorbent, we examined the micropollutant removal efficiency of β-cyclodextrin bead polymer from a spiked test solution containing ibuprofen, naproxen, ketoprofen, bisphenol-A, diclofenac, β-estradiol, ethinylestradiol, estriol, and cholesterol at 5 μg/L level.

The main objective of the laboratory experiments was to determine and to compare the removal efficiency of the newly developed β-cyclodextrin bead polymer with other sorbent systems applying a complex methodology for monitoring.

2.1.1. Laboratory simulation of drinking water purification—Drinking Water Filtration (DWF)

We compared the contaminant removal efficiencies of different filter systems (Fig. 1) simulating DWF combined with various sorbents. These filters consisted of 1) a commercial filter (CF, with activated carbon and ion-exchange resin, trade-name intentionally not given, the exact composition of the filter is not known, encrypted by the manufacturer), 2) β-cyclodextrin bead polymer (BCDP, CYL-3417, CycloLab, grain size: 0.1–0.3 mm, swelling volume: 5 mL/g, β-cyclodextrin content 60%), as a special, target-compound binding material, 3) quartz sand (QS, puriss., grain size (90%): 0.2–0.8 mm, CAS-No: 14808-60-7, Spektrum 3D), as an inert material to obtain the expected volume and/or 4) granulated activated carbon (AC, type: GAC 830 M, grain size: 0.5–2.4 mm, BET: 1050 m^3/g, Norit), as a universal, widely used adsorbent. The filter systems were set up as follows:

1) 50.0 g commercial sorbent/filter (CF)
2) 25.0 g commercial sorbent/filter + 2.5 g β-cyclodextrin bead polymer (CF + BCDP)
3) 25.0 g commercial sorbent/filter + 25.0 g activated carbon (CF + AC)
4) 2.5 g β-cyclodextrin bead polymer + 25.0 g quartz sand (BCDP + QS)
5) 25.0 g activated carbon + 25.0 g quartz sand (AC + QS)
6) 25.0 g activated carbon + 2.5 g β-cyclodextrin bead polymer (AC + BCDP)

The values are dry mass values. Because the BCDP swells tenfold in volume after getting in touch with water it was used in an amount to have an equal volume of sorbents. We filtered through 3–3 L of the test solution A on different filter systems. The average volumetric flow rate was 2.4 ± 0.5 L/h.

2.1.2. Laboratory simulation of tertiary waste water treatment (TWWT)—fluidization

The fluidized flow-through system was designed to model and study the removal of emerging pollutants from treated waste water using β-cyclodextrin bead polymer as tertiary treatment. The flow-through system consisted of 1) a container filled with the test solution B, 2) a fluidized column-reactor (absolute volume: 840 cm^3, useable volume:

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