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Characterization of cyclodextrin containing nanofilters for removal of pharmaceutical residues

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ABSTRACT

Due to the increasing amount of persistent organic pollutants (POPs) in general and pharmaceutical residues in particular in municipal wastewater, the efficiency of water treatment technologies should be improved. Following the biological treatment of wastewater nanofiltration offers a possible way for the removal of POPs. In this study β-cyclodextrin containing nanofilters having different chemical composition and thickness (1.5–3.5 mm) were investigated. For their characterization, their adsorption capacity was determined applying ibuprofen containing model solution and total organic carbon (TOC) analyzer.

It could be established that the regeneration of nanofilters with ethanol and the application of inorganic additives (NaCl, $NaHCO_3$, NH_4HCO_3) increased the adsorption capacity of nanofilters. The best results were achieved with chemical composition of 30 m/m% β-cyclodextrin polymer beads and 70 m/m% ultra-high molecular weight polyethylene in the presence of 12 mmol ammonium hydrogen carbonate/nanofilter.

1. Introduction

Over the last decades increasing amount of micro-pollutants have been released into the aquatic environment. Among these substances numerous harmful chemicals can be found such as pharmaceuticals, personal care products (PPCPs), endocrine disruptor chemicals (EDCs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, etc., which are hailed from different sources like industrial, agricultural and municipal wastewaters [1–5].

For removal of organic micro-pollutants numerous studies have been carried out during the past few years applying membrane technologies [6–8] and large variety of adsorbents. In the field of wastewater treatment the main adsorbents are ion-exchange resins [9], zeolites [10] and activated carbons [11]. However, activated carbon is a widely used and cheap adsorbent, the regeneration of it is complicated and this regeneration process decreases the adsorption capacity.

Nowadays the application of cyclodextrins (CDs) in wastewater treatment is in the focus of research and development. CDs are cyclic oligosaccharides containing a cylindrical, hydrophobic inner cavity and having hydrophilic outer surface. According to these structural properties CDs are water-soluble and they are able to form host–guest complexes with numerous types of substances without creating chemical bonds so they are called nowadays as "molecular capsules". They have three major types – α-, β- and γ-cyclodextrins – consisting of 6, 7 and 8 glucopyranose units, respectively. These compounds are produced from starch during microbiological enzymatic degradation by cyclodextrin glycosyltransferase [12–14].

It is well known that the otherwise water-soluble CDs can be immobilized either by polymerization or by grafting onto various surfaces (polymer beads, membranes, carbon nanotubes, nanofibers) to be applied for the removal of harmful substances from the aquatic phase [15–19]. The CDs-based sorbents are able to remove polycyclic aromatic hydrocarbons [20], pesticides [21], heavy metals [22], dyes [23], phenol compounds [24,25], phthalates [26], pharmaceutically active compounds e.g. naproxen, carbamazepine and bisphenol-A [27,28] from water via complex formation as the main mechanism of sorption. While the CDs immobilized keep their ability to form inclusion complexes, some of the cavities are less accessible for the guest compounds because of steric reasons. The immobilization generally leads to reduced number of the active CD units. It means the technology of immobilization can influence the adsorption capacity of such CD-containing adsorbents. Therefore, the optimization of

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immobilization technology and the quality assurance of the CD-containing filter production need reliable test methods. According to the literature data methyl-orange, phenolphthalein [29,30] as well as a special blue dye [31] were applied as model compounds to determine the adsorption capacity of CD-containing materials and their accessible CD content. In the case of methyl-orange and phenolphthalein measurements, the CDs were embedded into special fabrics (cotton and polyethylene terephthalate) or in polyurethane copolymers, while the blue dye was applied for capacity measurements of β-CD crosslinked with epichlorohydrin in the presence of carboxymethylcellulose. In these experiments, spectrophotometric methods were used to determine the model compounds remained in the liquid phase in order to calculate the adsorption capacity of the modified carriers. Gas chromatography was used to measure the adsorbed amount of toluene [29]. The results vary with the model compounds therefore we decided to use a micro-contaminant, ibuprofen abundant in surface waters. Ibuprofen is an often studied non-steroidal anti-inflammatory drug, which was previously investigated also in our research group [32,33].

In this work β-cyclodextrin polymer beads (BCPB) and BCPB-containing nanofilters developed for removal of pharmaceutical residues from water matrix were tested with ibuprofen model solutions in order to optimize the nanofilter production by measuring the adsorption capacity. During our experiments total organic carbon (TOC) concentration was measured to follow the adsorption process of ibuprofen. Using this novel test method the chemical composition and the thickness of nanofilters were optimized and the most efficient additive material was selected.

2. Materials and methods

2.1. Chemicals

Ibuprofen (Sigma–Aldrich Co., USA) and ethanol (Merck KGaA, Germany) were analytical grade compounds. For the sample preparation ultrapure water was used produced by Milli Q Plus equipment.

2.2. β-Cyclodextrin polymer beads (BCPB) and BCPB-containing nanofilters

The BCBP-s were the product of Cyclolab Ltd. (Budapest, Hungary) produced by crosslinking β-cyclodextrin with epichlorohydrin. The grain size was in the range of 0.1–0.3 mm and the swelling volume in water was amounted to 4.5 cm^3/g. The cyclodextrin content of the BCBP beads was 60–65% according to the results of the iodometry after acidic hydrolysis. The BCPB-containing nanofilters were made in the Bay Zoltán Applied Research Nonprofit Ltd. (Budapest, Hungary) by sintering the BCPB-s with ultrahigh molecular weight polyethylene (UHMWPE) (Aetna Plastics Corporation, USA) at 190 °C for 25 min. Both the BCPB-containing nanofilters and the blank filter (without BCPB) had round shape with diameter of 5.9 cm. The thickness of the filters was set to 1.5, 2.5 and 3.5 mm. The BCPB content of the nanofilters was 20, 30 and 40 m/m%, namely 100 mg dry matter of nanofilters (before sintering) contained 20, 30 and 40 mg of dry BCDP, respectively. In order to make the filter structure looser various inorganic additives (sodium chloride, sodium hydrogen carbonate, ammonium hydrogen carbonate) were added to the UHMWPE and homogenized. The additive concentrations amounted to 12 mmol/nanofilter. The BCPB was applied in dry state except the filter with lab code of F-30-D-3.5, where the BCPB was swelled in water before sintering. For specification of nanofilters the following code system was used (Table 1).

Table 1
Code system for specifying the produced nanofilters.

Code of nanofilter	Thickness of nanofilter (mm)	BCPB content (m/m%)	Additive material
F-0-N-3.5	3.5	0	–
F-20-N-3.5	3.5	20	–
F-30-N-3.5	3.5	30	–
F-30-N-2.5	2.5	30	–
F-30-N-1.5	1.5	30	–
F-40-N-3.5	3.5	40	–
F-40-N-2.5	2.5	40	–
F-40-N-1.5	1.5	40	–
F-30-A-3.5	3.5	30	NaCl
F-30-B-3.5	3.5	30	$NaHCO_3$
F-30-C-3.5	3.5	30	NH_4HCO_3
F-30-D-3.5	3.5	30	H_2O

2.3. Pretreatment and regeneration of BCPB-s and nanofilters

Before the adsorption capacity measurements, both the BCPB-s and the nanofilters were treated in the following manner: 3–7 g of polymer beads or nanofilters were washed in 200–500 ml ultrapure water under intensive stirring in five steps (each step took 5 min). After decantation, the BCPB-s and the nanofilters were steeped in 100 ml ultrapure water for 24 h, then the TOC concentration of the unified washing water fractions was measured applying a Multi N/C 2100S TC-TN analyzer (Analytik Jena, Germany) according to the EN 5667-3:1995 standard. In the case of nanofilters containing inorganic additives the specific electric conductivity was also measured in the washing water fractions using a conductometer (Radelkis OK-102/1, Radelkis, Hungary). Following the washing steps the BCPB-s and the nanofilters were dried at room temperature and stored in closed quartz containers.

After the first adsorption experiments the BCPB-s and the nanofilters were regenerated with 200–500 ml ethanol (50 m/m%) in five steps (for 5 × 5 min) in order to remove the adsorbed pharmaceutical compounds. During the experiments the nanofilters were used in three adsorption–regeneration cycles.

2.4. Adsorption measurements

BCBP-s (0.5 g) were weighed into 50 ml aqueous solution of ibuprofen with concentration of 0.2 mmol/L for 48 h. Following the adsorption step the BCPB-s were separated from the solutions by centrifugation at 2000 rpm for 5 min (Hermle Table Top Centrifuge Z300). The TOC content of this solution was measured by the TC/TN analyzer. The adsorbed amount of ibuprofen was calculated on basis of the TOC content of the solution before and after the adsorption step considering the carbon content of the ibuprofen molecule. In order to verify the TOC measurements the ibuprofen concentration of five solutions was also determined by GC–MS/MS method developed in our laboratory [33]. The deviations among the analytical data obtained by these two analytical methods amounted to maximum 7% at ibuprofen concentration of 50 μmol/L. Based on the results of our preliminary adsorption experiments the nanofilters were contacted with the ibuprofen solution for 8 days to reach the equilibrium. Depending on the BCPB content of nanofilters the volume of ibuprofen solution with concentration of 0.2 mmol/L was adjusted for keeping the ibuprofen/BCPB ratio at the level of 20 μmol/g.

3. Results and discussion

3.1. Adsorption capacity of polymer beads

Prior to the adsorption capacity measurements, the release of organic contaminants from polymer beads into the washing water