Session: C.1 – Assessment and monitoring: Fate, transport and risks

REMOVAL OF EMERGING MICROPOLLUTANTS FROM WATER USING CYCLODEXTRIN

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1. ABSTRACT

Small scale laboratory experiments were performed to study the suitability of a new cyclodextrin-based sorbent (ß-cyclodextrin bead polymer, BCDP) for removal of the bioactive micropollutants from drinking water and purified waste water using model solution spiked with emerging micropollutants such as ibuprofen, naproxen, ketoprofen, bisphenol-A, diclofenac, β-estradiol, ethinylestradiol, estriol, cholesterol at 5 μg/L level. For comparison different filter systems combined with various sorbents (commercial filter and activated carbon) were applied and evaluated.

The spiked model solution (inflow) and the treated outflows were characterized by integrated methodology including GC-MS-MS for chemical analysis and various environmental toxicity tests to determine the efficiency and selectivity of the applied sorbents.

Under the experimental conditions the CD-based filters used for purification of drinking water were able to absorb more than 90% of bisphenol-A and of estrogenic compounds. Both the chemical analytical and toxicity results showed efficient elimination of these pollutants. Especially high decrease in the toxicity of the filtrate was observed, because – contrary to commercial filters and activated carbon – no release of organic matter from BCDP could be detected.

Laboratory experiment modeling post-purification of waste water was also performed applying ß-cyclodextrin bead polymer. The BCDP removed efficiently most of the micropollutants, especially bisphenol-A (94%) and hormones (87–99%) from spiked model solution.

Keywords: cyclodextrin sorbent, drinking water purification, ecotoxicology, emerging contaminants, micropollutants, waste water treatment

2. 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. Their largely unknown long-term effects on aquatic systems and on human health are one of the key environmental problems facing humanity nowadays.

Research focuses worldwide on measurement of xenobiotics using sensitive sophisticated physical-chemical methods to detect and quantify them at the low concentrations at which they occur in the environment [1, 2, 3, 4]. The research of these chemical substances is even more difficult because they are present as complex mixtures in the environment. These pollutants possess high biological activity so they are able to affect the non-target organisms as well. 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 [5, 6]. These emerging pollutants are suspected and proved of having secondary adverse effects, such as endocrine disrupting, immune-disrupting, sensitizing, allergizing effects on non-target organisms. Therefore many scientists deal with acute or chronic adverse effects and environmental/human risks caused by these emerging substances [7, 8, 9, 10, 11, 12, 13].

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, etc. Most of these emerging contaminants are not currently covered by water-quality regulations in spite of the fact that they appeared in natural, untreated and treated waters at μg/L concentrations [14, 15, 16, 17, 18]. Another problem is that the currently applied conventional water treatment technologies and drinking water treatment technologies are not suitable for their efficient removal [19, 20, 21, 22], as a consequence, their introduction in the aquatic environment is continuous.

One of the solutions addressing this water-quality problem can be the development and implementation of cost-effective and appropriate technologies able to reduce risk. Cyclodextrins (CDs) which are traditionally used in pharmaceuticals and personal care products can form complexes with the majority of organic micropollutants. Based on our knowledge cyclodextrin sorbents can extract hazardous substances selectively from contaminated water [23].

Our main objectives were to develop innovative technologies that are able to remove these emerging pollutants from water. One of the developed technologies refers to drinking-water purification; the other one to the removal of emerging contaminants from the traditionally treated waste water.

3. MATERIALS AND METHODS

3.1. Experimental setup

Two different technological experiments had been implemented to model the pollutant removal efficiency of the applied sorbents. Our purposes were 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 spiked model solution containing ibuprofen, naproxen, ketoprofen, bisphenol-A, diclofenac, β-estradiol, ethinylestradiol, estriol, cholesterol at 5 μg/L level.

The aims of the following laboratory experiments were 1) to determine and to compare with other sorbent systems the removal efficiency of the β-cyclodextrin bead polymer and 2) to select ecotoxicological methods which are able to detect toxic effects of micropollutants.

3.1.1. Laboratory modeling of drinking water purification – Drinking Water Filtration

We compared to each other the contaminant removal efficiencies of different filter systems (Figure 1) combined from various sorbents. These filters consisted 1) randomly chosen commercial filter (CF, mixture of activated carbon and ion exchangers), 2) β-cyclodextrin bead polymer (BCDP, CYL-3417), 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), 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), as an universal, widely used adsorbent. The filter systems were composed of the below materials:

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

The values are dry mass values, because the BCDP bloats tenfold after getting in touch with water.

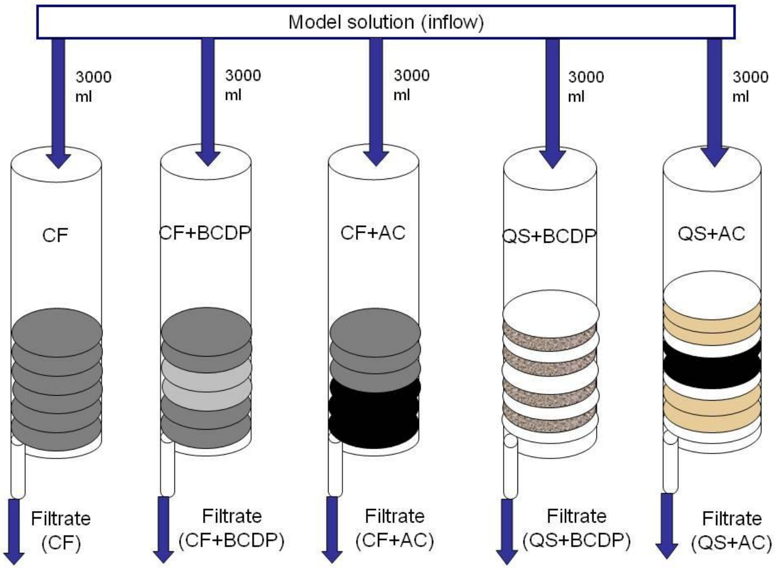

Figure 1: Schematic set up of the drinking water filtration experiment

3.1.2. Laboratory modeling of post-purification of treated waste water – Fluidization

Fluidized flow-through system was designed to model and study the removal of emerging pollutants from water with the use of β-cyclodextrin bead polymer as a final operational step of a waste water treatment technology. The flow-through system consists of 1) a container filled with the spiked model solution, 2) a fluidized column-reactor (absolute volume: 840 cm^3, useable volume: 790 cm^3, inside diameter: 53 mm, grossness of the wall/ skin: 3.5 mm) filled with 20 g of dry β-cyclodextrin bead polymer and 790 ml of spiked model solution, 3) a magnetic stirrer (Stuart SB 162 type, rev: 50 rpm) under the fluidized column-reactor and 4) a receptacle for the outflow solution (Figure 2). The driving force of the flow is the pressure difference between the fluids found in the model solution container and in the column-reactor.

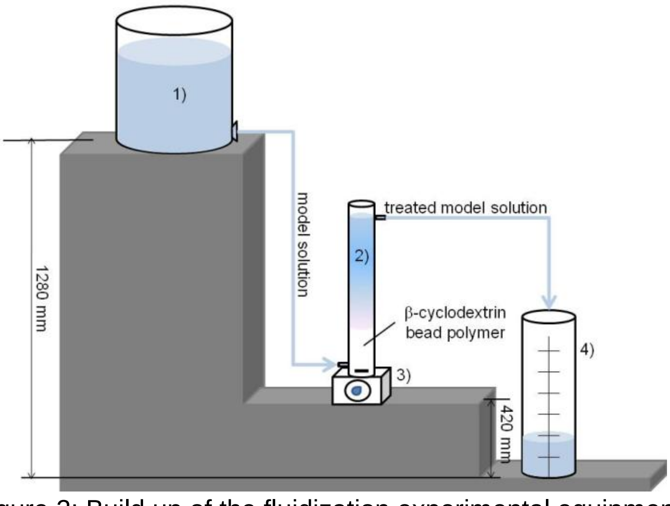

Figure 2: Build up of the fluidization experimental equipment

3.2. Chemicals and model solutions

The spiked model solution contained pharmaceuticals (ibuprofen, ketoprofen, naproxen, diclofenac), industrial additive (bisphenol-A), hormones (17β-estradiol, ethinylestradiol, estriol) and steroid compound (cholesterol). Table 1 shows the concentration of each compound in the model solution. All the compounds used in the following experiment were purchased from Sigma-Aldrich and they were of analytical grade.

Table 1: Concentration of each compounds found in the model solution

Compound	Concentration (μg/L)
Ibuprofen	0.20
Ketoprofen	6.69
Naproxen	3.89
Diclofenac	4.66
Bisphenol-A	4.06
17β-estradiol	3.23
Ethinylestradiol	3.45
Estriol	2.32
Cholesterol	2.44

We received the β-cyclodextrin bead polymer (BCDP, CYL-3417) from CycloLab Cyclodextrin R&D Laboratory Ltd. The β-cyclodextrin polymer beads were prepared by the collaborators of CycloLab Ltd with approx. 60% β-cyclodextrin content by crosslinking with epichlorohydrin.

3.3. Monitoring methods used to follow the experiments

3.3.1. Chemical method:

The micropollutant concentrations of the inflow model solution and the changes of compound contents in the treated outflow solutions were measured as their trimethylsilyl (TMS) (oxime) ester/ether derivatives by gas chromatography–mass spectrometry [12]. The results of the parallel preparation of the derivatives were the same within the margins of error (mean RSD%<<5). The analytical measurement was carried out by collaborators of Cooperative Research Center for Environmental Sciences.

3.3.2. Ecotoxicological tests used for effect-based monitoring of pollutants removal

All tests, used in this experiment (*Lemna minor* growth inhibition test, *Daphnia magna* immobilization test and *Daphnia magna* heartbeat rate test) are sensitive and cost effective tests. Duckweed is an ideal test organism for assessing phytotoxicity of many aquatic pollutants, while water flea is representative of a class of animals that serve as food for many aquatic creatures that are on higher trophic level. Both can be used as special indicator organisms in the early warning monitoring systems. These test organisms were used to follow the toxicity changes of the outflow solutions compared to the inflow solution after the removal of the micropollutants from the spiked model solution with the technologies applied in the laboratory experiments.

Lemna minor growth inhibition test (measuring the chlorophyll-content)

The *Lemna minor* plants (duckweed) were collected in Hungary in 2009. Plants were disinfected by immersing the fronds in NaOCl (0.01 M) for 20 seconds and rinsing with distilled water. The stock cultures were maintained in glass dishes containing Hoagland growth medium [24]. Duckweeds were cultured at 21.5±1°C with a 16 h photoperiod (Juwel Aquarium, Day-Lite, 15W, 438 mm lamp, 560 Lumen, 6500 K).

Duckweed bioassay was performed in three replicates of each sample. 10–10 double fronded, undamaged duckweeds were gently placed in 150 ml beakers (8 cm high, 6 cm I.D.) containing 25–25 ml of water sample. The beakers were incubated for 7 days in a thermostat. The total chlorophyll content was determined by extracting the fronds from each beaker in dark with 5–5 ml of 96% ethanol for 24 hours. Absorbance was measured in a SANYO SP55 UV-Vis spectrophotometer at 649 and 664 nm. The pigment contents were calculated according to Lichtenthaler [25]. The means and standard deviation were calculated for each sample and then the inhibition as compared to the control was calculated. The test validity requirements met the International Organization for Standardization (OECD) requirements [26], as the doubling time of frond number in the controls was less than 2.5 h.

Daphnia magna immobilization test

Daphnia magna water fleas were cultured at 21.5±1°C with a 16 h photoperiod (Juwel Aquarium, Day-Lite, 15W, 438 mm lamp, 560 Lumen, 6500 K) in boiled and cooled aerated tap water, the electric conductivity value of which should be always less than 500 mS cm^{-1} [27]. They were fed every other day with *Scenedesmus subspicatus* suspension.

Water flea immobilization bioassay was performed in triplicate for each water sample. 10–10 neonates (<24h old) were gently placed in 150 ml beakers (8 cm high, 6 cm I.D.) containing 50–50 ml of water sample. The test organisms were not fed during the test. The test vessels were maintained for 72 h in a thermostat. The examined endpoint was 24, 48 and 72 h immobilization, where an individual was considered to be immobile if it did not move after 15 sec of gentle agitation. The means and the standard deviation were calculated for each sample and then the inhibition percent was calculated. The test validity requirements met those set by the International Organization for Standardization [28], as the mortality in the control beakers did not exceed 20% at the end of the test.

Daphnia magna heartbeat rate test

Daphnia magna water fleas were cultured at 21.5±1°C with a 16 h photoperiod (Juwel Aquarium, Day-Lite, 15W, 438 mm lamp, 560 Lumen, 6500 K) in boiled and cooled aerated tap water, of which electric conductivity value should be always less than 500 mS cm^{-1} [27]. They were fed every other day with *Scenedesmus subspicatus* suspension.

This test method has been developed on the basis of two articles written by Villegas-Navarro et al. [29] and Dzialowski et al. [30]. Water flea bioassay using heartbeat rate as endpoint was performed in three replicates for each sample. 10 adult daphnids (about 10 days old) were placed individually on single cavity slides into 40–40 µl drop of the maintaining water to count the control (prior exposure) heartbeat of the individuals. The heartbeats of the daphnids were counted three times for 10 sec under Nikon SMZ800 stereomicroscope. After that 200–200 µl of the water samples were pipetted on the single cavity slides. After 10 minutes contact time, the heartbeats of the daphnids were counted three times in the same way as previously described. The means and standard deviation were calculated for each of the samples and then inhibition percent was calculated.

4. RESULTS

Integrated methodology (ecotoxicological and analytical methods) was applied to follow the technological experiments and to evaluate and characterize the removal efficiency of the sorbents. In the present article we introduce the results of three ecotoxicological tests of our integrated methodology and the chemical analytical results. We determined the toxicity of the inflow model solution and the outflow filtrates with ecotoxicological methods such as *Lemna minor* growth inhibition test (measuring chlorophyll-content), *Daphnia magna* immobilization test and *Daphnia magna* heartbeat rate test. Chemical analysis was carried out by ELTE Cooperative Research Center for Environmental Sciences.

4.1. Chemical results of drinking water filtration experiment

Table 2 shows the removal efficiency data determined from the chemical results of the filtration experiment. These results reflect that the quartz sand and β-cyclodextrin bead polymer (QS+BCDP), the commercial sorbent and β-cyclodextrin bead polymer (CF+BCDP), and the commercial sorbent and activated carbon (CF+AC) containing filter systems were able to remove the major part of bisphenol-A and estrogenic compounds, such as 17β-estradiol, ethinylestradiol, estriol. Quartz sand and activated carbon (QS+AC) filter proved to be less effective in the removal of micropollutants. The commercial filter (CF) seems to have the same removal efficiency as the quartz sand and β-cyclodextrin bead polymer (QS+BCDP) filter but when comparing them we need to take into account that the filters contained more commercial sorbent (50 or 25 g) than β-cyclodextrin bead polymer (2.5 g).

Table 2: Analytical results of the drinking water filtration experiment

Compounds	Contaminant removal efficiency of the sorbents (%)				
	CF	CF+BCDP	CF+AC	QS+BCDP	QS+AC
Ibuprofen	43	-	-	**>99.9**	-
Naproxen	80	86	83	19	62
Ketoprofen	78	84	80	-	67
Diclofenac	75	84	79	-	51
Bisphenol-A	**91**	**92**	**94**	**91**	64
17β-estradiol	**94**	**>99.9**	**95**	**95**	71
Ethinylestradiol	**94**	**97**	**95**	**97**	69
Estriol	87	**93**	**94**	**94**	54
Cholesterol	32	74	14	50	16

- There was no measurable concentration difference which would refer to the removal of the micropollutant

4.2. Ecotoxicological results of drinking water filtration experiment

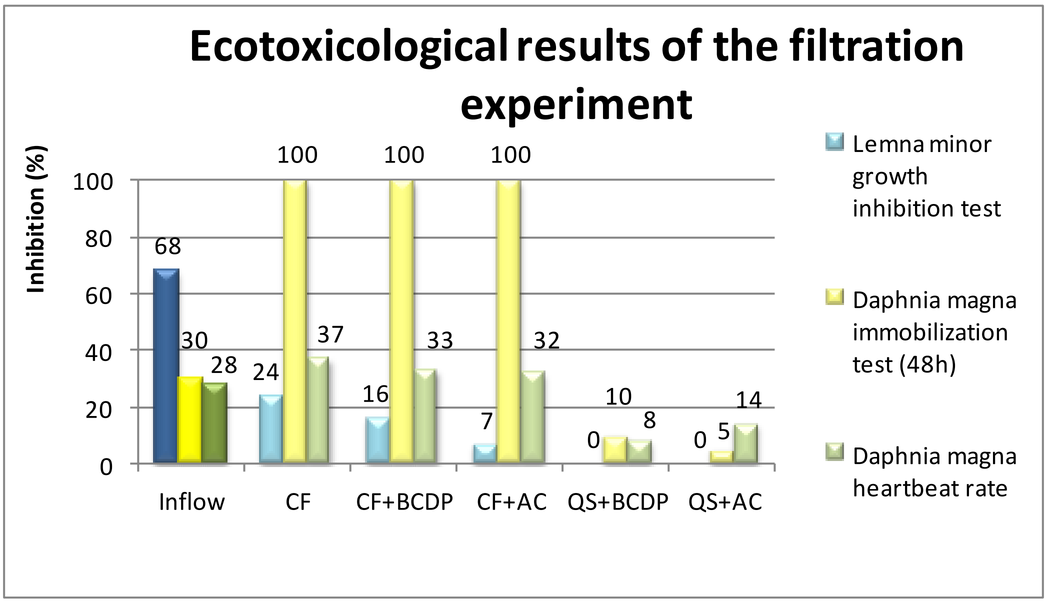

Figure 3: Ecotoxicological results of the drinking water filtration experiment;
CF: commercial sorbent, CF+BCDP: commercial sorbent + β-cyclodextrin bead polymer, CF+AC: commercial sorbent + activated carbon; QS+BCDP: quartz sand + β-cyclodextrin bead polymer, QS+AC: quartz sand + activated carbon

Columns of the diagram (Figure 3) that show the ecotoxicological results of the filtration experiment are marked with different colors. Different colors belong to different ecotoxicological methods, so the results of the *Lemna minor* growth inhibition test are indicated with blue, the *Daphnia magna* immobilization test is marked with yellow and the *Daphnia magna* heartbeat rate test is presented with green. The 68% toxic effect of the inflow model solution on the chlorophyll-content of the duckweeds ceased after filtered through the quartz sand and β-cyclodextrin bead polymer (QS+BCDP) filter system. The inflow model solution caused 30% and 28% inhibition of the water fleas, function of the examined endpoints (immobilization or heartbeat rate). This inhibition decreased to 10% and 8% in the case of the outflow, which was filtrated through the quartz sand+ β-cyclodextrin bead polymer (QS+BCDP) filter system. It's noticeable on the basis of the ecotoxicological results that the quartz sand+ activated carbon (QS+AC) filter system also removed the micropollutants from the model solution with a good efficiency. On the whole, it seems that the QS+BCDP outflow was the least toxic to the test organisms.

It is immediately visible that the samples which had been filtrated through the randomly chosen commercial sorbent containing filters (CF; CF+BCDP; CF+AC) were toxic 100% to the daphnids. We experienced the same outstanding toxic effect with the samples of the control experiment, which was carried out with the commercial sorbent and distilled water. Some kind of inhibition on the test organisms was noticeable in all cases of the commercial sorbent based filter systems. Until this time, we could not figure out the reason of this inhibition, but the most probable reason of this inhibition is the release of the micropollutants from the commercial sorbent.

4.3. Chemical results of fluidization experiment

Table 3 shows the chemical results of the fluidization experiment. These results reflect that the applied technology was able to remove major part of bisphenol-A (93%) and estrogenic compounds, such as 17β-estradiol (99%) and ethinylestradiol (95%).

Table 3: Analytical results of the fluidization experiment

Compounds	Contaminant removal efficiency of the model system (%)
Ibuprofen	35
Naproxen	67
Ketoprofen	13
Diclofenac	15
Bisphenol-A	**93**
17β-estradiol	**99**
Ethinylestradiol	**95**
Estriol	87
Cholesterol	43

4.4. Ecotoxicological results of fluidization experiment

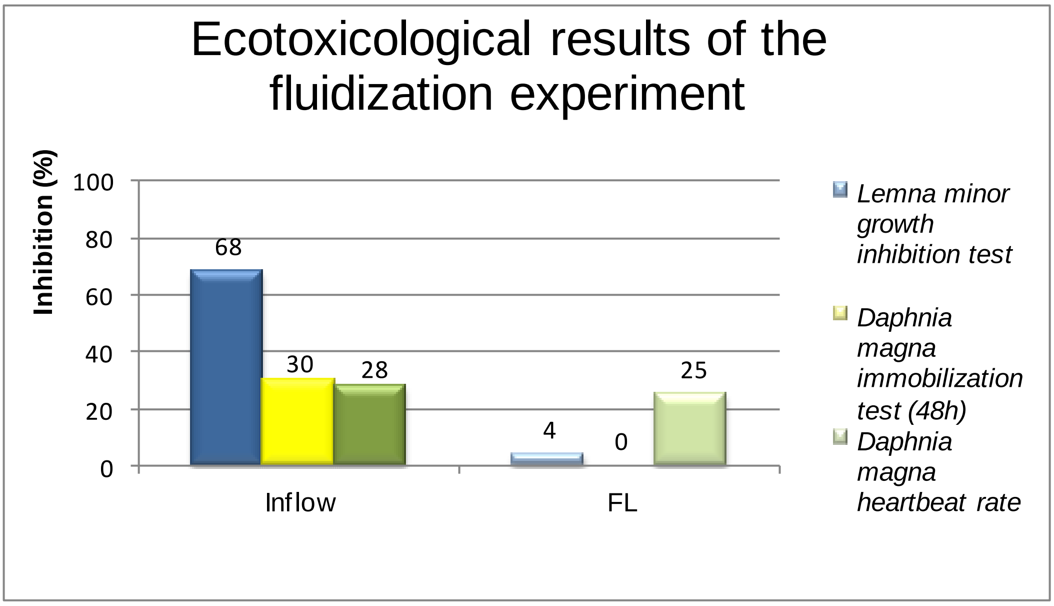

Figure 4: Ecotoxicological results of the fluidization experiment, FL: fluidized sample

Columns of the diagram (Figure 4) that show the ecotoxicological results of the fluidization experiment are marked with different colors. Different colors belong to different ecotoxicological methods, so the results of the *Lemna minor* growth inhibition test are indicated with blue, the *Daphnia magna* immobilization test is marked with yellow and the *Daphnia magna* heartbeat rate test is presented with green. The incipient toxic effects of the inflow model solution (68% at *Lemna minor* test and 30% at *Daphnia magna* immobilization test) decreased to almost zero after the treatment in both tests. Due to the chemical results, the fluidized sample contained relatively high concentration of non-steroidal anti-inflammatory drugs (ibuprofen, ketoprofen and diclofenac), so their removal efficiency was inadequate (35%, 14%, and 16%) as opposed to the BPA (94%) and estrogenic compounds (99%, 95%, and 87%). Therefore the *Daphnia magna* heartbeat rate test seems to be very sensitive to the non-steroidal anti-inflammatory drugs. Probably the pharmaceuticals in the outflow caused 25% toxic effect in the case of *Daphnia magna* heartbeat rate test while the untreated inflow solution had almost the same toxic effect (28%).

5. CONCLUSION

Both lab-scale applications of the ß-cyclodextrin bead polymer have demonstrated the outstanding removal capabilities of emerging contaminants. A BCDP-containing unit after mechanical, biological treatment and ultrafiltration of waste water can be effective tool in risk reduction of emerging contaminants considering especially the treatment of waste water at the sources (e.g. the effluents of hospitals) to avoid dilution due to mixing with the communal sewage.

The results of the technological experiments proved unambiguously that the β-cyclodextrin bead polymer containing filter systems are suited to bind and remove effectively and selectively the bisphenol-A which compound possesses high environmental and human health risk.

The special, β-cyclodextrin bead polymer containing filter systems removed also with high efficiency the estrogenic compounds (17β-estradiol, ethinylestradiol, estriol) from the inflow model solution.

The bisphenol-A and estrogenic compounds can be bounded selectively to cyclodextrin sorbents. These sorbents can be effective as source and emission control technology for water treatment, especially in the case of BPA and hormones in order to reduce environmental risk.

The ecotoxicological results of the experiments proved that *Daphnia magna* heartbeat rate test is very sensitive to detect toxic effects of the non-steroidal anti-inflammatory drugs (as micropollutants) in an aqueous medium.

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