REMOVAL OF EMERGING MICROPOLLUTANTS FROM WATER USING CYCLODEXTRIN

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INTRODUCTION

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 pharmaceuticals (ibuprofen, ketoprofen, naproxen, diclofenac), industrial additive (bisphenol-A), hormones (17β-estradiol, ethinylestradiol, estriol) and steroid compound (cholesterol) at 5 µg/L level. For comparison different filter systems combined with various sorbents (ß-cyclodextrin bead polymer, 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 pollutant removal efficiency and selectivity of the applied sorbents.

CHEMICALS AND MODEL SOLUTIONS

The spiked model solution contained ibuprofen (0.20 µg/L), naproxen (3.89 µg/L), ketoprofen (6.69 µg/L), diclofenac (4.66 µg/L), bisphenol-A (4.06 µg/L), 17β-estradiol (3.23 µg/L), ethinylestradiol (3.45 µg/L), estriol (2.32 µg/L) and cholesterol (2.44 µg/L).
We received the β-cyclodextrin bead polymer (BCDP, CYL-3417) from CycloLab Cyclodextrin R&D Laboratory Ltd. The β-cyclodextrin bead polymer was prepared by the collaborators of CycloLab Ltd with approx. 60% β-cyclodextrin content by crosslinking with epichlorohydrin.

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 (Figure 1) and 2) the post-purification of traditionally treated waste water with fluidization (Figure 2).
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.

MONITORING METHODS USED TO FOLLOW THE EXPERIMENTS

- *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. The analytical measurement was carried out by collaborators of Cooperative Research Center for Environmental Sciences.

- *Ecotoxicological tests used for effect-based monitoring of pollutants removal*
  - *Lemna minor* growth inhibition test (measuring the chlorophyll-content)
  - *Daphnia magna* immobilization test
  - *Daphnia magna* heartbeat rate test

Filtration experiment

Composition of the filter systems:

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) mixed
5) 25.0 g quartz sand + 25.0 g activated carbon (QS+AC)

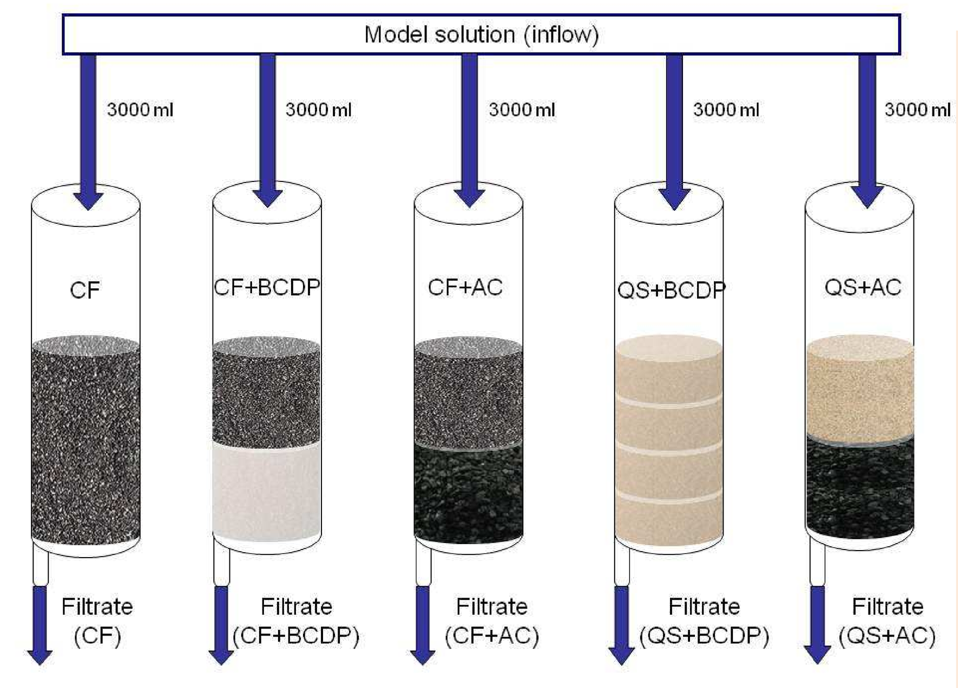


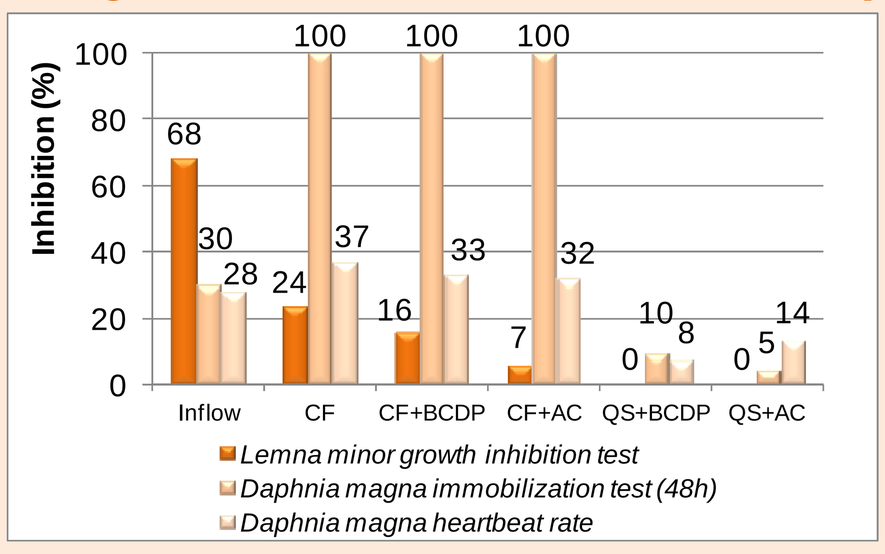
Figure 1: Schematic set up of the drinking water filtration

Analytical results of the filtration experiment

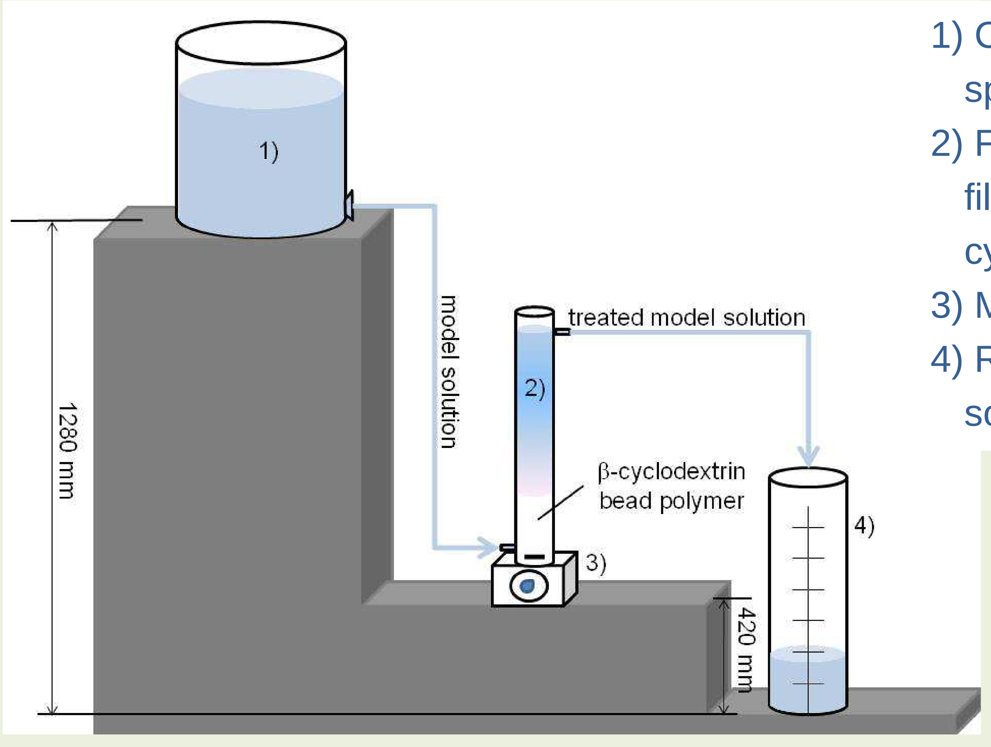
Compounds	Contaminant removal efficiency of the sorbents (%)				
	CF	CF+BCDP	CF+AC	QS+BCDP	QS+AC
Ibuprofen	43	-	-	>99.9	-
Naproxen	80	86	83	19	62
Ketoprofen	78	84	80	-	67
Diclofenac	75	84	79	-	51
Bisphenol-A	91	92	94	91	64
17β-estradiol	94	>99.9	95	95	71
Ethinylestradiol	94	97	95	97	69
Estriol	87	93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

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

Ecotoxicological results of the filtration experiment



Fluidization experiment



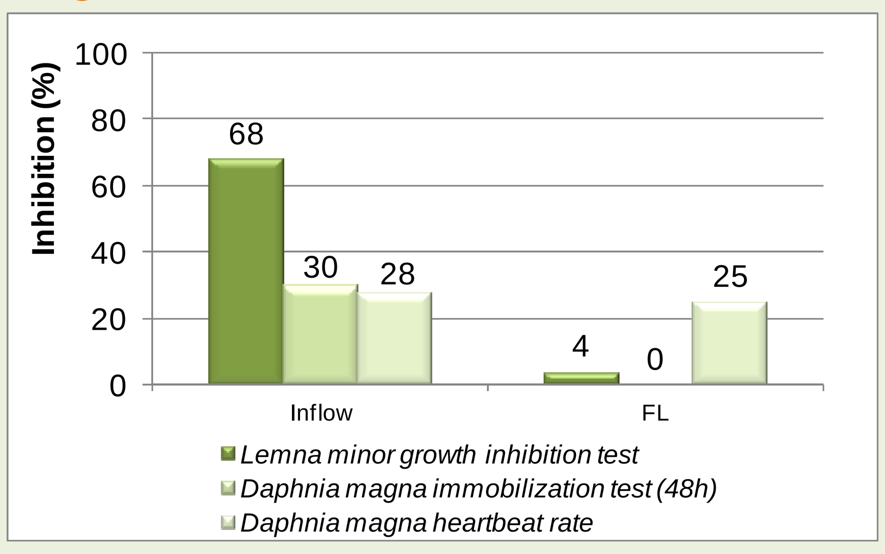
1) Container filled with the spiked model solution
2) Fluidized column-reactor filled with 20 g of dry β-cyclodextrin bead polymer
3) Magnetic stirrer
4) Receptacle for the outflow solution (FL)

Figure 2: Build up of the fluidization experiment

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

Ecotoxicological results of the fluidization experiment



CONCLUSION

Both lab-scale applications of the ß-cyclodextrin bead polymer have demonstrated its outstanding capabilities to remove emerging contaminants. The results of the technological experiments proved unambiguously that the β-cyclodextrin bead polymer containing filter systems are suited to bind and remove effectively 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. Aiming to reduce environmental risk these sorbents can be effective for source and emission control in water treatment technologies, especially in the case of bisphenol-A and hormones.

ACKNOWLEDGEMENT

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