Elimination of Microcystin-LR and selected pharmaceutical residuals using biologically active filters

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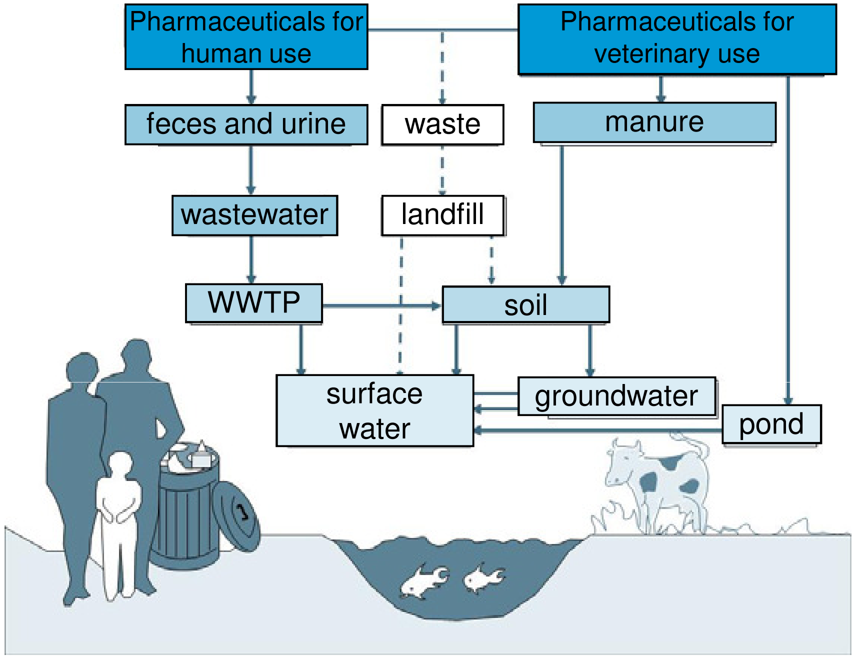
Significance of the thesis

- Discovery of „Emerging pollutants“ e.g. Microcystin-LR (MC-LR) and pharmaceutical residues (PCPPs) over the last decades due to the improvement of analytical methods
- Defined or potential health and environmental risks

- MC-LR:
  - The most toxic compound of the family cyanotoxine, a group of toxine produced by cyanobacteria, also known as blue-green algae.
  - MC-LR can cause severe liver damages by inhibiting the activities of protein phosphatase in the liver
  - Public health risks: obtaining drinking water from eutrophic surface water, a practice not unusual in developing countries
  - Guideline value of 1 µg/L in the drinking water by WHO


Significance of the thesis

- Pharmaceutical residues
  - Detection in the aquatic systems in the 90th
  - Discharged along with waste water and waste and distributed in all environmental matrices
  - Adverse effects e.g.
    - feminization of male fishes under the influence of endocrine disruptors
    - antibiotic resistance due to the increasing concentration of antibiotics in the environment
  - a growing effort to establish advanced treatment processes in Germany to remove pharmaceutical residues from the wastewater, minimizing the amount entering the surface water and ground water

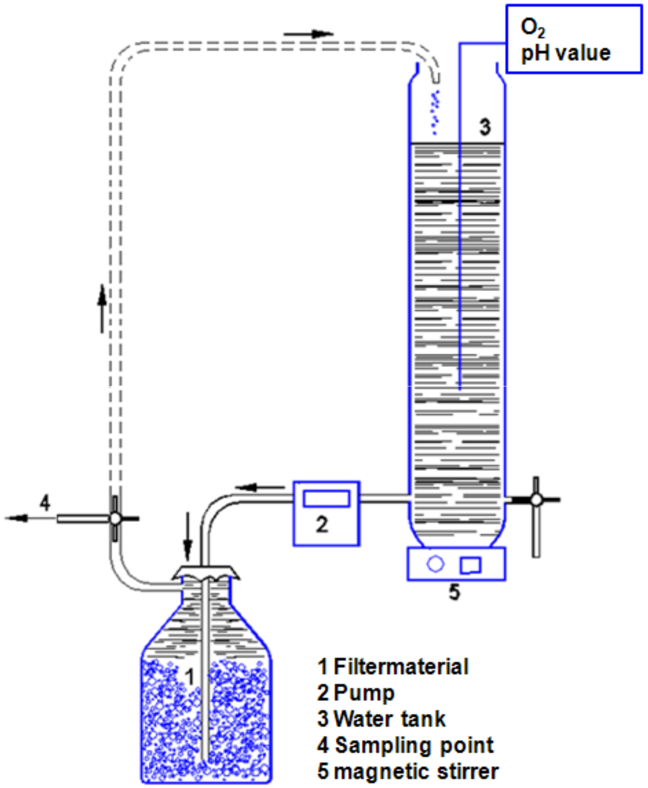


(Bayerisches Landesamt für Umwelt, 2008)

Objectives

- Determining the efficiencies of the biofilter using different filter materials for the removal of MC-LR and pharmaceutical residues
- Investigating the influences of the influent concentration and the empty bed contact time (EBCT) on the removal of MC-LR
- Developing mathematical descriptions of the removal process in the biofilter

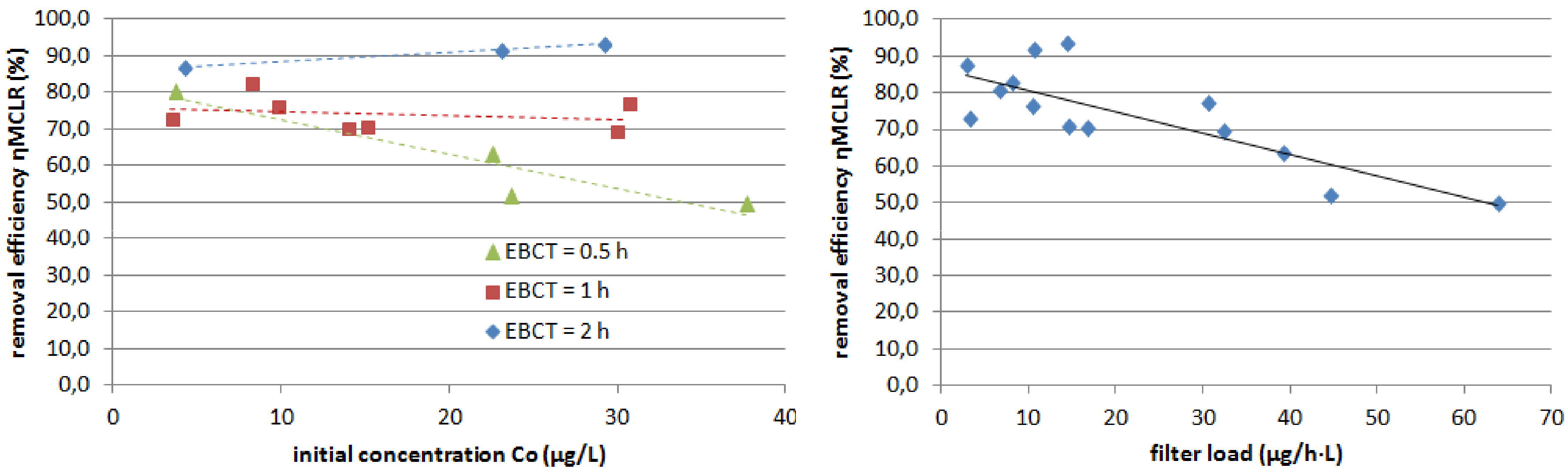
Experimental set-up



Experimental Parameters	
room temperature	20°C ± 1
Filter materials	granular activated carbon, lignite, basalt
Filter bed volume	ca. 1 Liter (H = 12 cm, D = 10 cm)
medium	Effluent of the WWTP Braunschweig / Artificial freshwater
Operation modes	Continuous-flow mode / Circulation mode
Pre-Treatment	All three filter columns adapted for over 12 months, depleting Adsoption capacity and developing biological activities

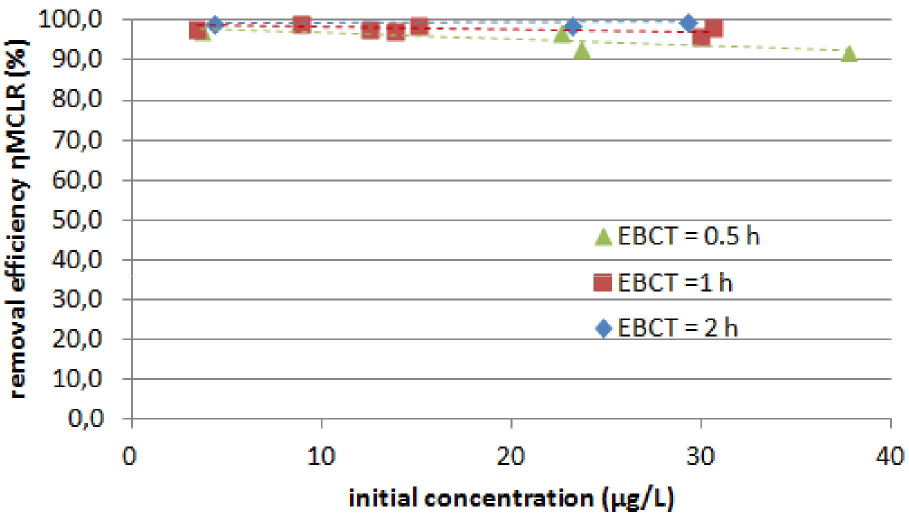
Removal efficiencies of MC-LR

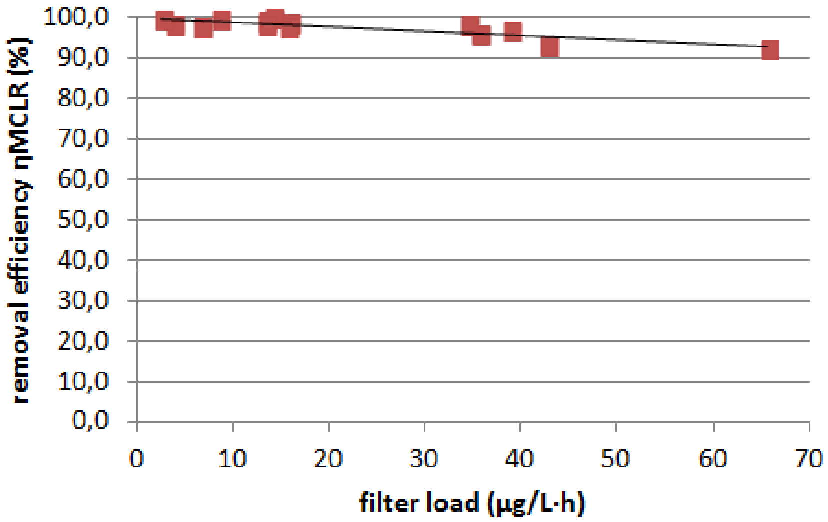
- GAC-filter
  - removal efficiency > 70 % at EBCT ≤ 1 h and $C_0 \leq 30$ µg/L
  - removal efficiency > 70 % at filter load ≤ 30 µg/L·h.



Removal efficiencies of MC-LR

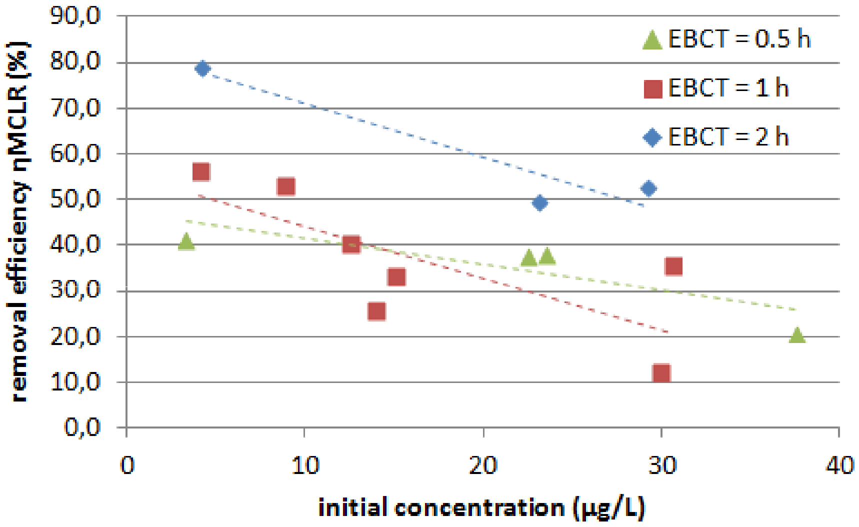
- Lignite-filter
  - removal efficiency > 90 % at EBCT ≤ 2 h and C_0 ≤ 40 µg/L
  - removal efficiency > 90 % at filter load ≤ 70 µg/L·h.

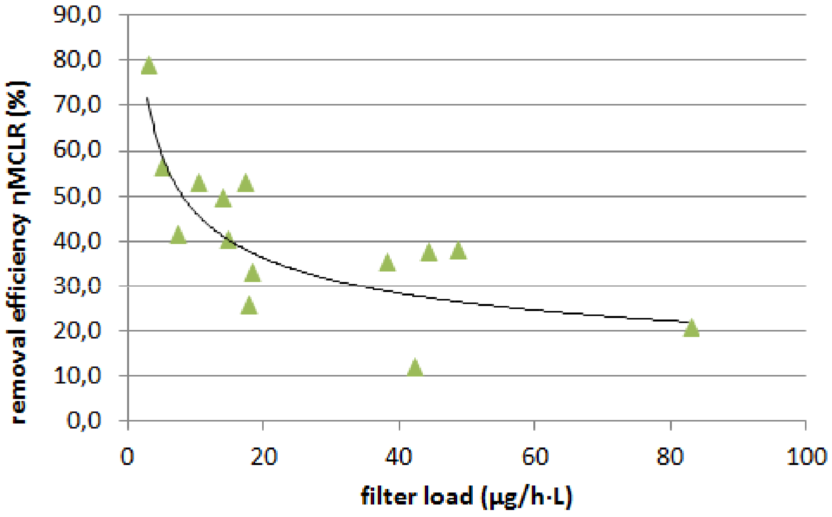




Removal efficiencies of MC-LR

- Basalt-filter
  - Considerably lower removal efficiencies
  - removal efficiency > 50 % only at EBCT = 2 h or filter load ≤ 10 µg/L·h





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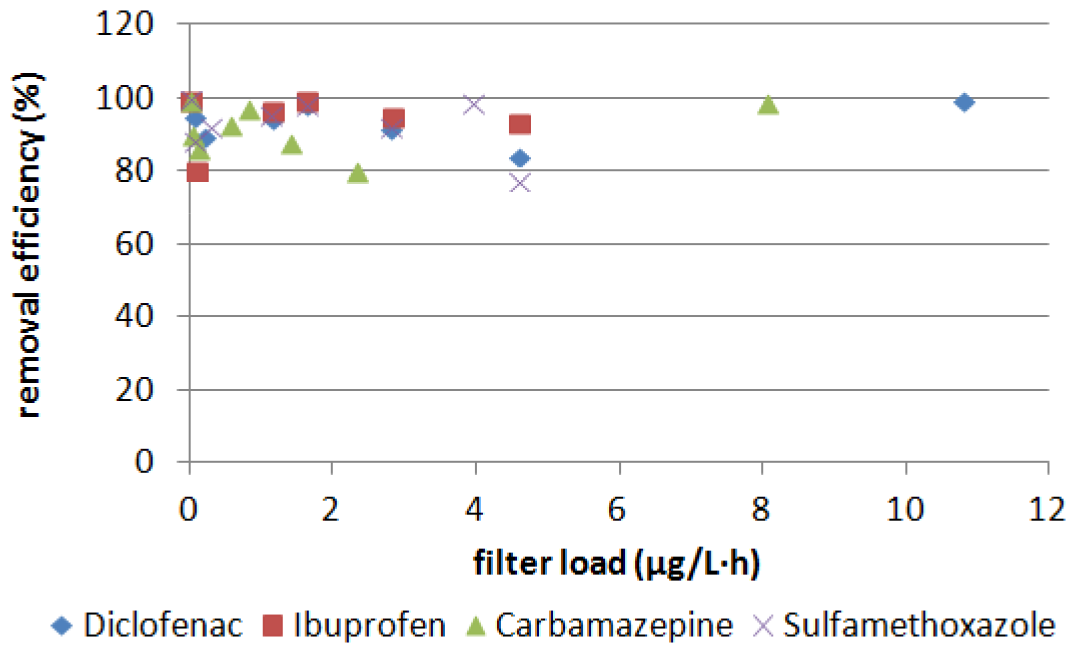
Removal efficiencies of pharmaceutical residues

- GAC-filter
  - Initial concentration: 2 - 15 µg/L
  - EBCT: 1 – 3.5 h
  - removal efficiency > 80 % at filter load ≤ 11 µg/L·h for all four substances



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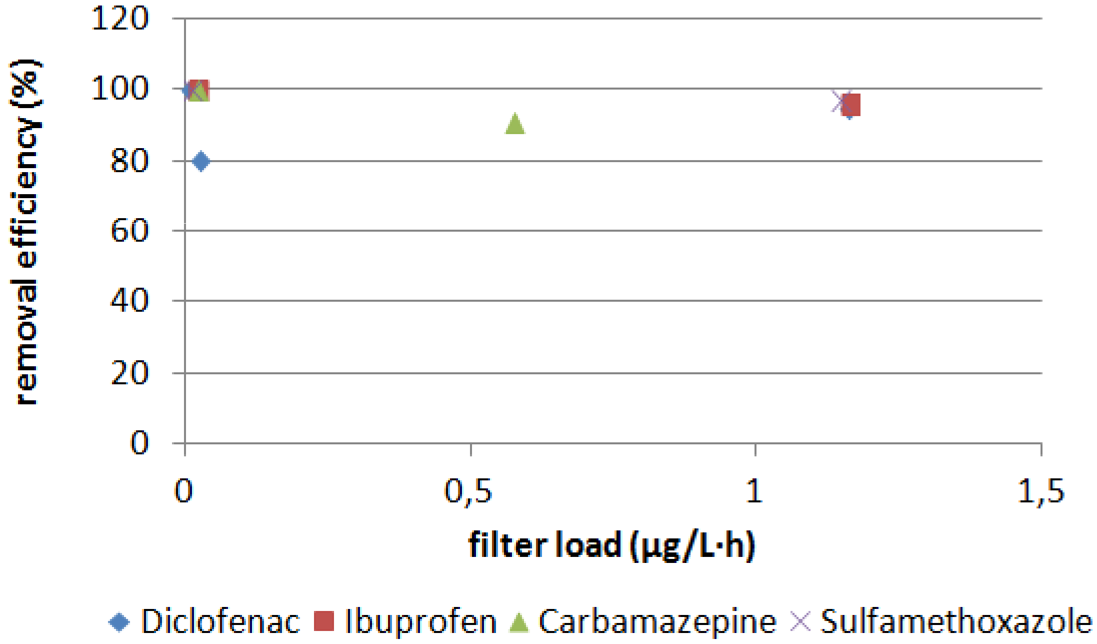
Removal efficiencies of pharmaceutical residues

- Lignite-filter
  - Initial concentration: 2 - 4 µg/L
  - EBCT: 1 – 3.5 h
  - removal efficiency > 80 % at filter load ≤ 1.5 µg/L·h



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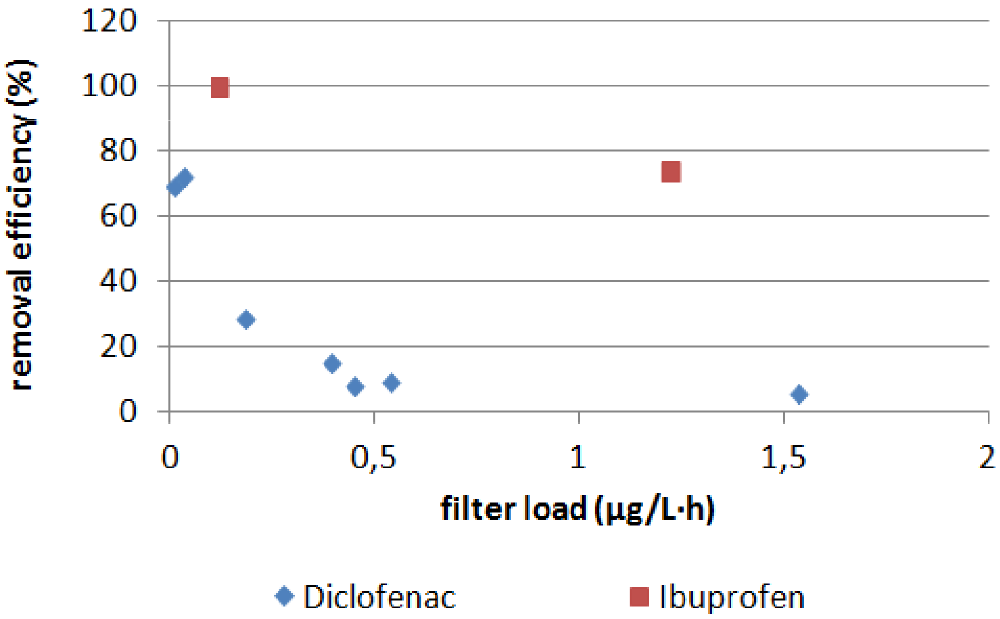
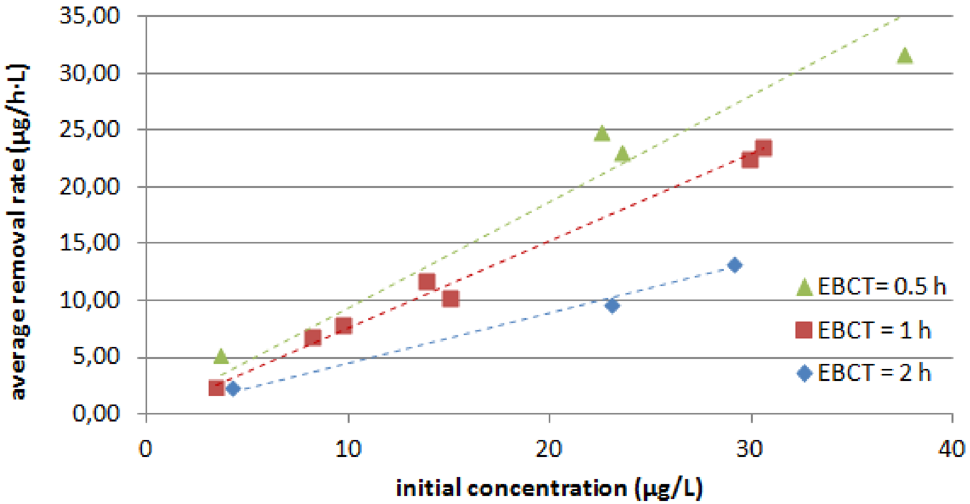
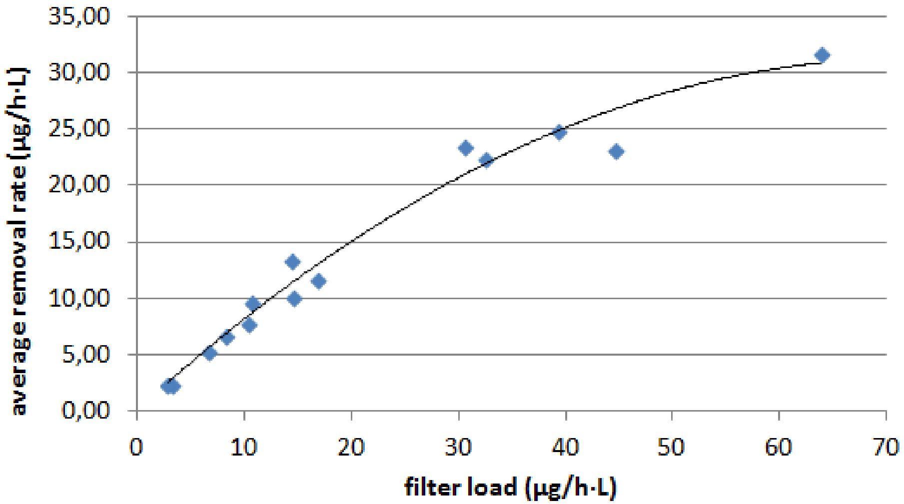
Removal efficiencies of pharmaceutical residues

- Basalt-filter
  - Initial concentration: 2 - 4 µg/L
  - EBCT: 1 – 3.5 h
  - Removal efficiency > 60% at filter load < 1.5 µg/L·h for ibuprofen
  - Low removal efficiency < 20% at filter load > 0.5 µg/L·h for diclofenac
  - No removal of carbamazepine and sulfamethoxazol



Influences of influent concentration and EBCT an the removal rates of MC-LR





- GAC-filter
  - High removal rates up to 30 µg/L·h
  - The removal rate increases with the increasing C_0 at a constant EBCT
  - The removal rate increases with the increasing filter load
  - The filter load is the quotient of C_0 and the corresponding EBCT and therefore reflects the combined influence of both parameters

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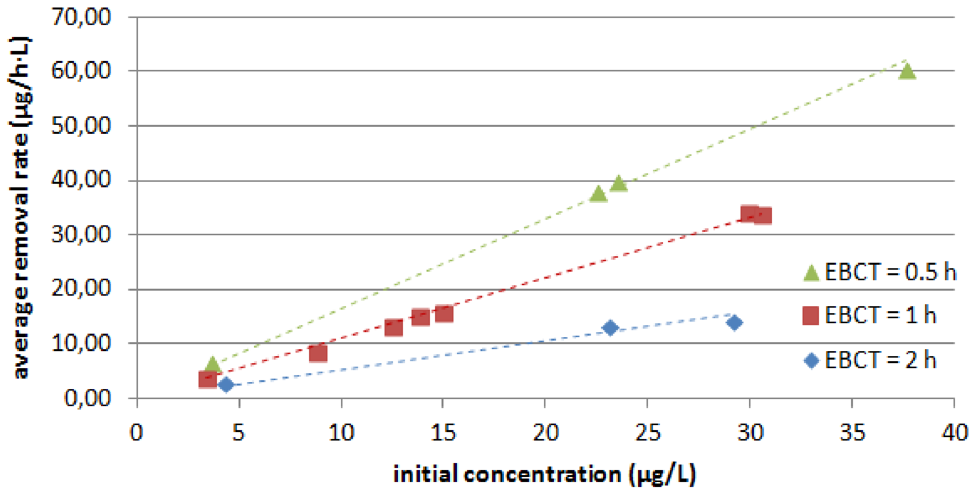
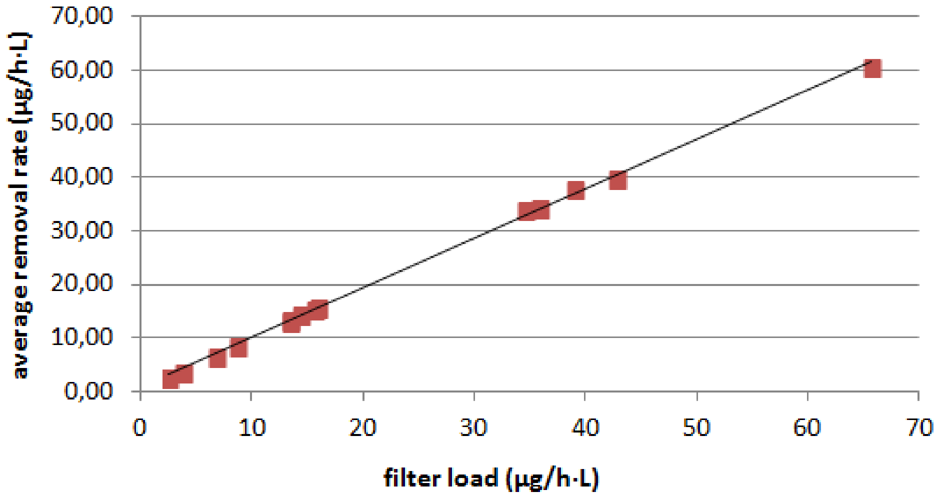
Influences of influent concentration and EBCT an the removal rates of MC-LR





- Lignite-filter
  - High removal rates up to 60 µg/L·h
  - The removal rate increases with the increasing C_0 at a constant EBCT
  - The removal rate increases with the increasing filter load

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Model description for the removal of MC-LR

By combining the reaction kinetics between zero- and first-order (zero-order when C >> k, first-order when C << k)

$$v = v_{max} \cdot \frac{C}{k + C}$$

and a plug-flow model

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial H} + v$$

with	v	reaction rate [µg/L·h]
	v_{max}	maximal reaction rate [µg/L·h]
	c	substrate concentration [µg/L]
	k	constant [µg/L]
	t	time [h]
	H	distance in the vertical direction of the filter [cm]

Model description for the removal of MC-LR

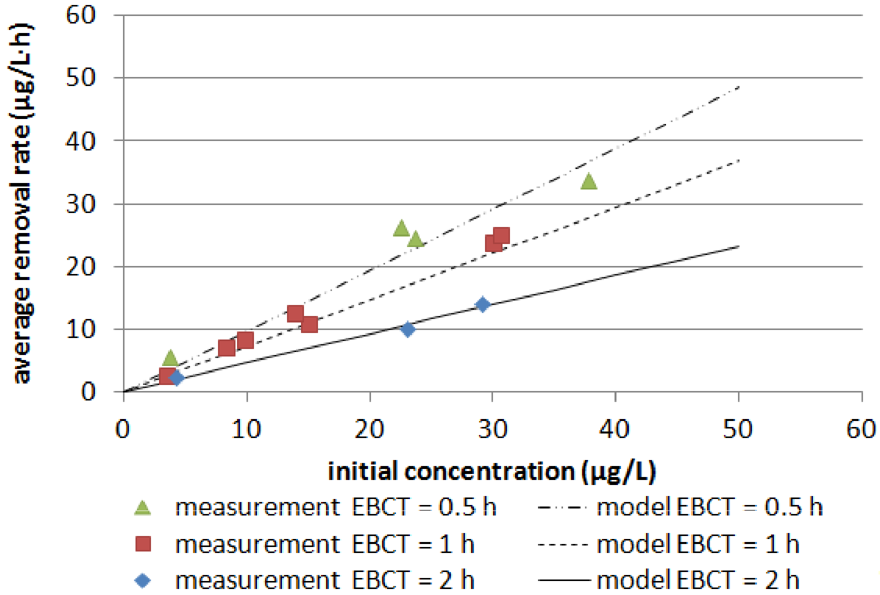
- GAC-Filter:

$$C_0 = e^{\left(1.33 \cdot \frac{V}{Q}\right)} \cdot C_e$$

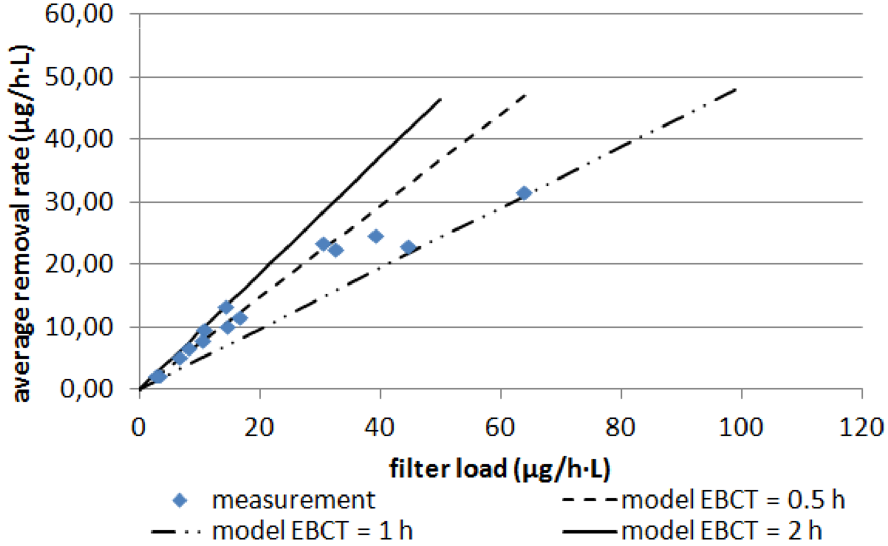
- Lignite-Filter:

$$C_0 = e^{\left(4.47 \cdot \frac{V}{Q}\right)} \cdot C_e$$

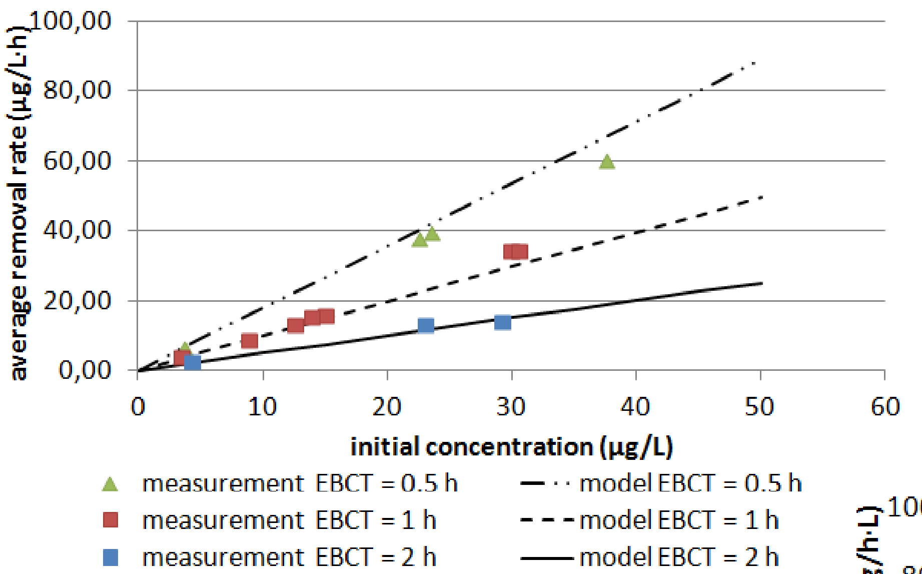
Verification of the model description for the removal of MC-LR



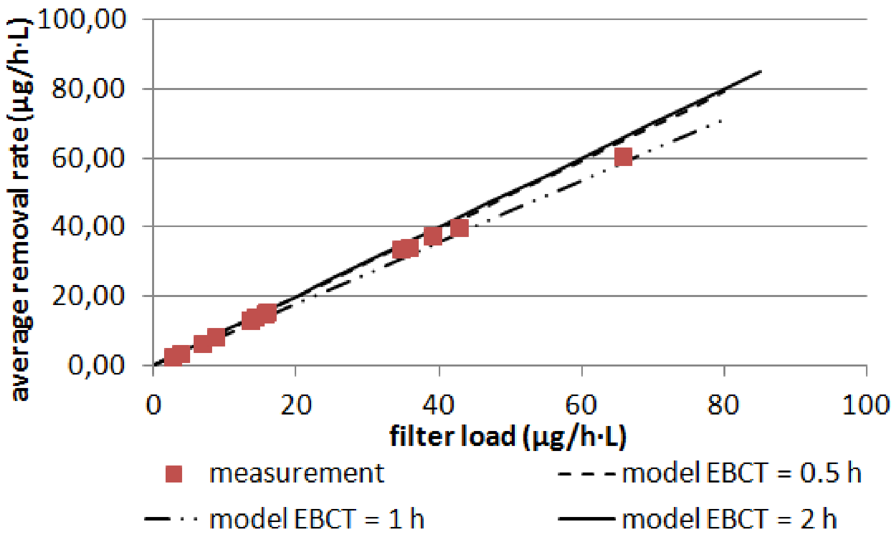
- GAC-filter
  - The model reflects experimental result with sufficient accuracy
  - the removal rate of is rather influenced by C_0 and EBCT separately, instead of solely by the filter load as the combination of both parameters



Verification of the model description for the removal of MC-LR



- Lignite-filter
  - The model reflects experimental result with sufficient accuracy
  - the removal rate is influenced by C_0 and EBCT separately, however, at a certain given filter load, the alteration of EBCT between 0.5 and 2 h affects the removal rate only insignificantly



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Economical aspects in the removal of pharmaceutical residues from the wastewater using biofilter

- An inevitable part of the decision making process, when an advanced treatment process should be chosen and implemented to remove emerging pollutants in an existing plant

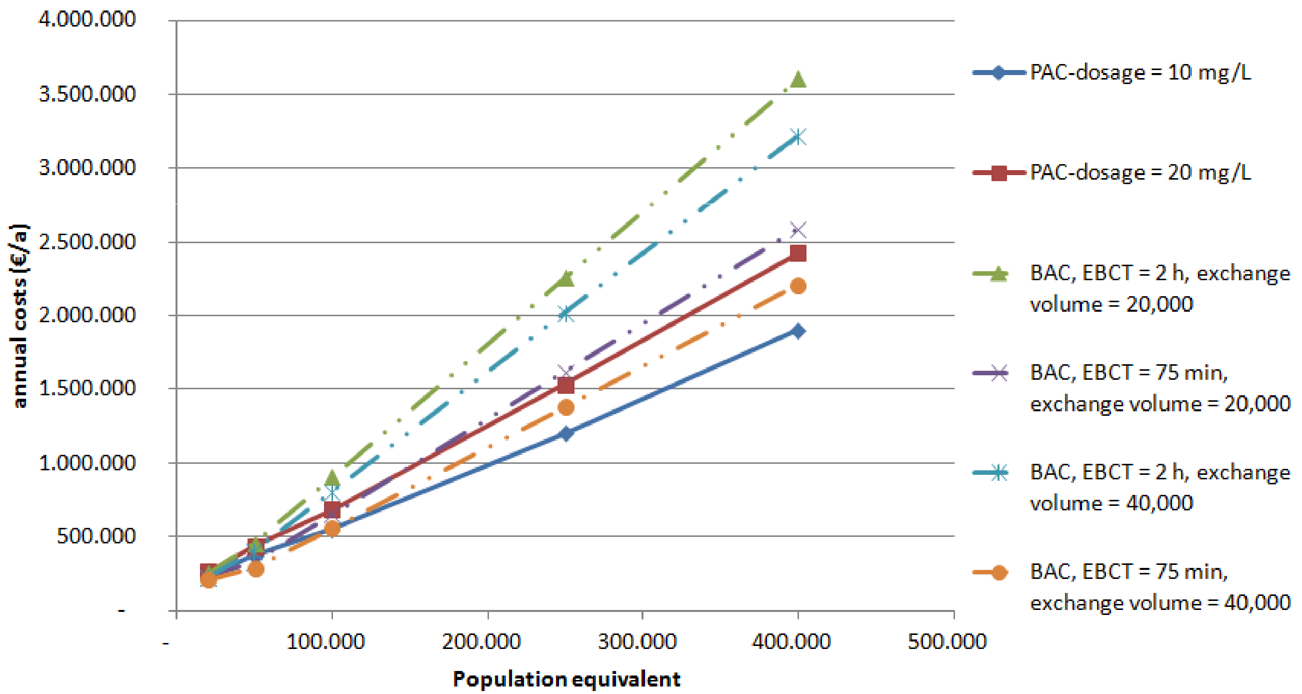
- Advanced treatment stages specifically for the elimination of MC-LR are still absent in the practice of the drinking water treatment, whereas in many WWTPs they have already been set up or are planned to eliminate pharmaceutical residues from the wastewater

- Comparison of the biofiltration process using activated carbon as filter material (BAC) with treatment processes using powered activated carbon (PAC) or granular activated carbon (GAC) to remove pharmaceutical residues from the wastewater

- Relevant operational parameters are chosen as follows:
  - EBCT of the BAC filter: 2 h or 75 min
  - Exchange volume of the BAC filter: 20,000 or 40,000
  - PAC-dosage: 10 or 20 mg/L
  - EBCT of the GAC filter: 75, 30 or 15 min
  - Exchange volume of the GAC filter: 9000

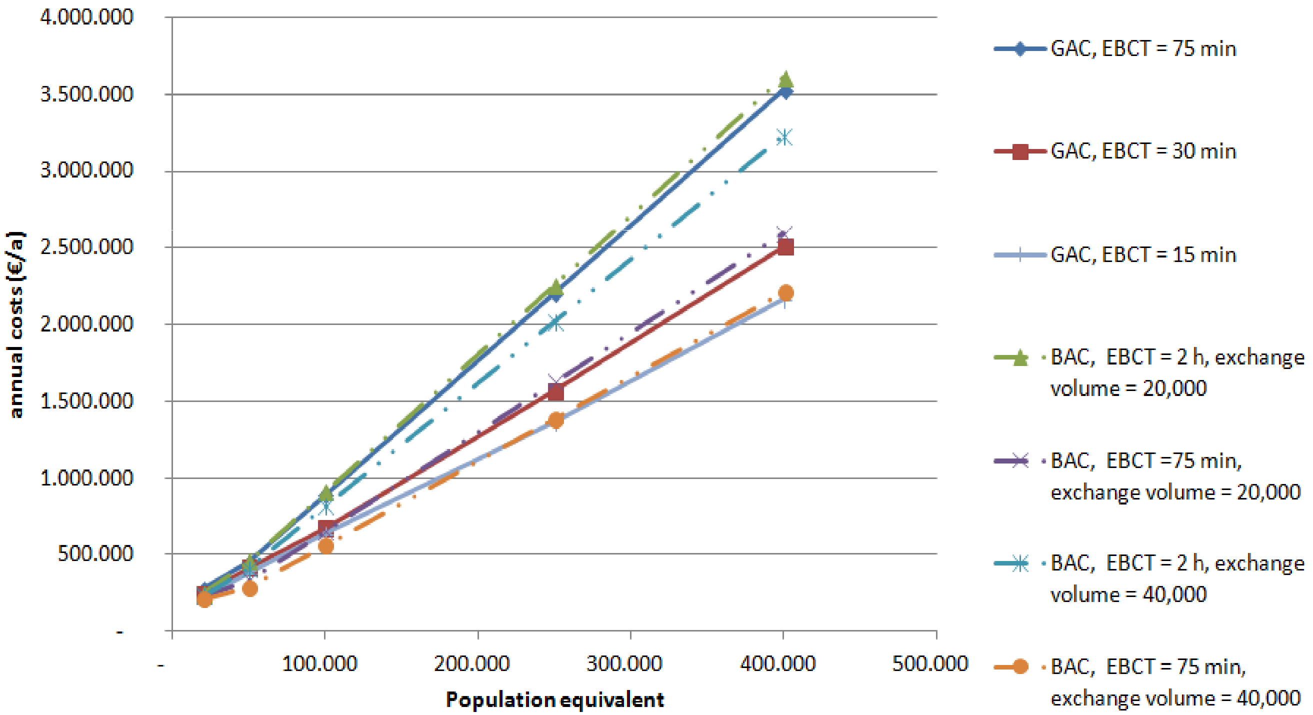
Economical aspects in the removal of pharmaceutical residues from the wastewater

- Compared to the treatment process using PAC
  - The selection of the EBCT affects the annual costs of the BAC process magnificently
  - an economical advantage of the BAC process compared to the PAC process can be given, if the BAC facility can be operated at an EBCT ≤ 75 min and an exchange volume of ≥ 40.000.



Economical aspects in the removal of pharmaceutical residues from the wastewater

- Compared to the treatment process using GAC
  - economically of clear advantage compared to a GAC plant operated with an EBCT ≥ 75 min
  - can be economically competitive to a GAC process operated with EBCT ≤ 30 min, if the BAC process itself can be operated at EBCT ≤ 75 min and an exchange volume of ≥ 40.000



Conclusions

- The biofiltration process shows promising results for the removal of MC-LR and pharmaceutical residues.
- GAC and lignite filters show considerably higher elimination efficiencies for both groups of substances than basalt and prove to be the more suitable filter materials.
- The elimination of MC-LR using GAC or lignite filter can be described as reaction of first-order. Two models were developed with sufficient accuracy to describe the processes.
- As the model predictions reveal, the elimination of MC-LR in both GAC and lignite filters are rather influenced by the influent concentration of MC-LR and the EBCT separately, instead of solely by the filter load as the combination of both parameters.