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Retention of nine micropollutants covering a wide range of physical-chemical properties by negatively charged hollow fiber nanofiltration membranes

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Increase of population and living standard lead to increasing amount of micropollutants released into wastewater but actual wastewater treatment plants (WWTP) are not efficient for the removal of such molecules

Great urgency to redefine the technologies employed in WWTP regarding elimination of micropollutants



Laboratoire écologie fonctionnelle et environnement



Institut Européen des Membranes

save

Station Avancée pour la Valorisation des Effluents



nereus
sustainable recycling systems



Toulouse Biotechnology Institute
Bio & Chemical Engineering

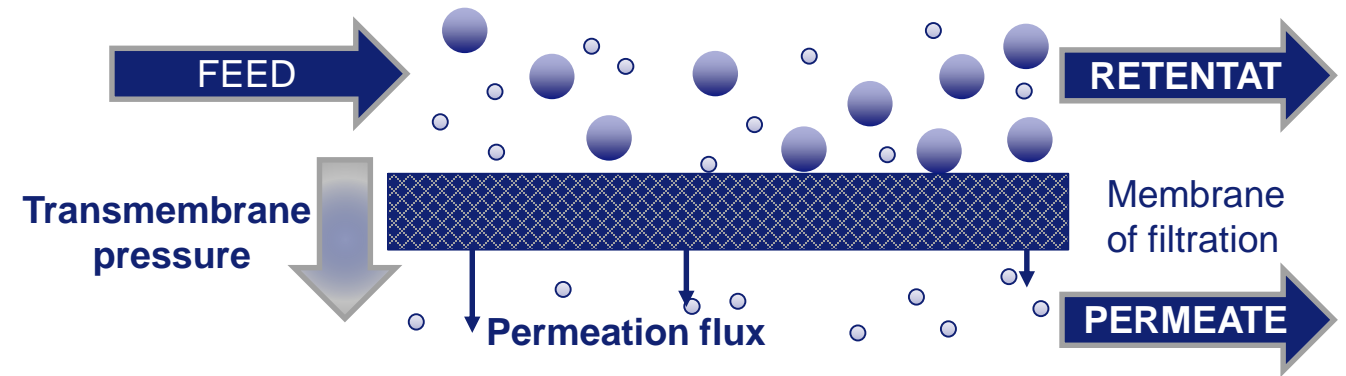


sapoVAL

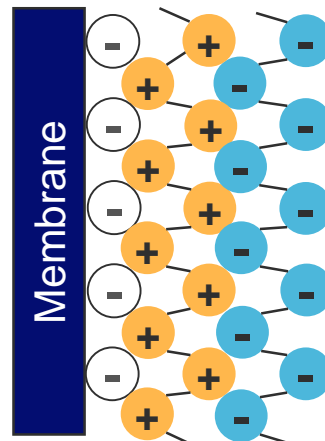


LGC 2

Nanofiltration

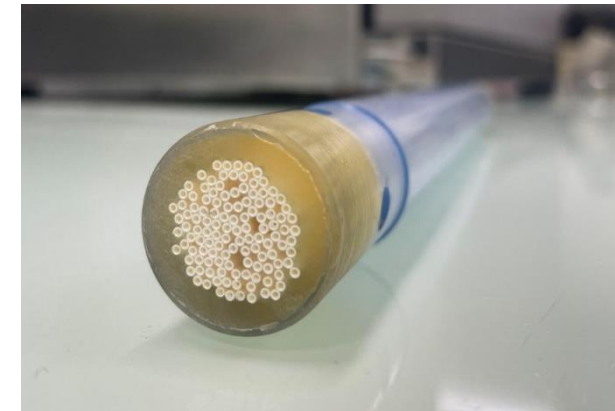


Polyelectrolyte LbL membrane



- ✓ High micropollutants removal
- ✓ Low salts retention

Hollow fiber membrane



- ✓ Low fouling

Impact of physical-chemical properties of micropollutants

Experimental design to determine the micropollutants of the study according to their **molecular weight**, **hydrophobicity** and **charge** at neutral pH

Impact of the membrane properties

Molecular weight cut-off of the membrane (size of the smallest molecule being retained by the membrane) :
400 or 800 Da

Impact of the operation parameters

Volume reduction ratio (volume of feed divide by volume of retentat) :
1, 3 or 6

Impact of the matrix

Content in organic matter of the matrix :
0, 15 or 50 mg.L⁻¹

Performance indicators on
24 h filtration at TMP 3 bar

Permeation flow rate = quantity
of liquid going through the
membrane per time unit

Retention of micropollutants

Retention of salts



STRATEGY : selection of micropollutants

Experimental design :

to determine the impact of each physical-chemical property of MPs on their retention by NF membranes

3 factors ; 3 levels → 27 micropollutants

Square Latin method :

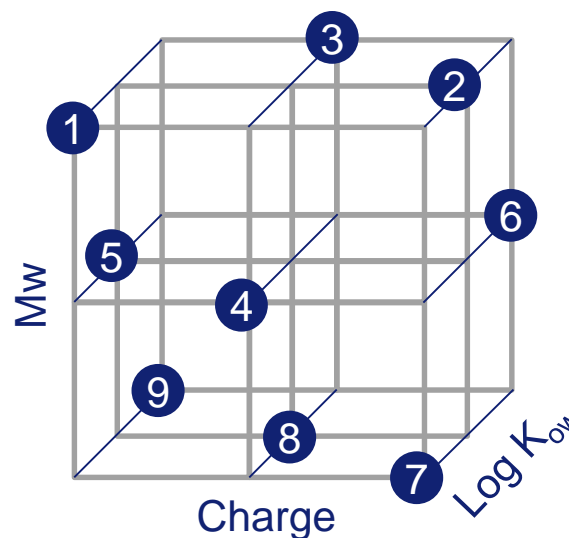
to reduce the number of contaminant from 27 to 9

Technical constraint :

Molecules have to be quantifiable by chromatography with UV detector

→ Content of micropollutants : **10 mg.L⁻¹ each**

#	Charge	Hydrophily	Size
-	Negative	$\text{Log } K_{ow} > 2$	$\text{Mw} < 210 \text{ g.mol}^{-1}$
0	Neutral	$0.5 < \text{Log } K_{ow} < 2$	$230 < \text{Mw} < 280 \text{ g.mol}^{-1}$
+	Positive	$\text{Log } K_{ow} < 0.5$	$\text{Mw} > 300 \text{ g.mol}^{-1}$

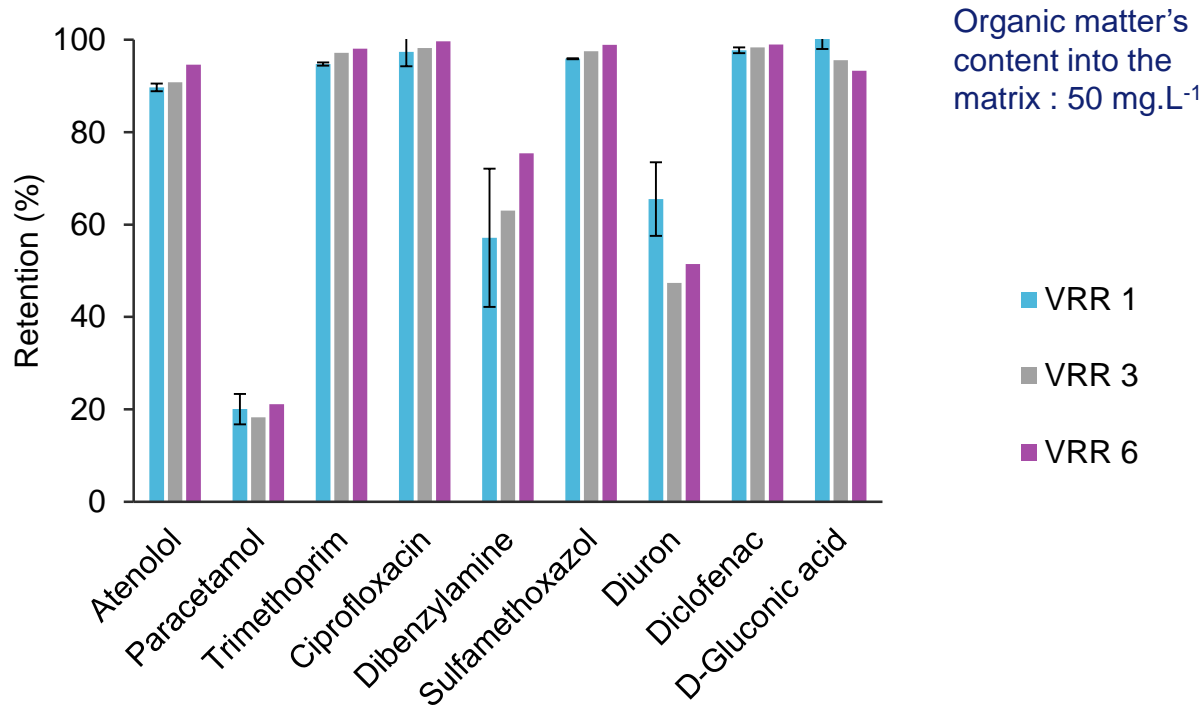


Compounds selected :

atenolol,
paracetamol,
trimethoprim,
ciprofloxacin,
dibenzylamine,
sulfamethoxazole,
diuron,
diclofenac
D-gluconic acid

RESULTS : retention of micropollutants on 400 Da MWCO membrane

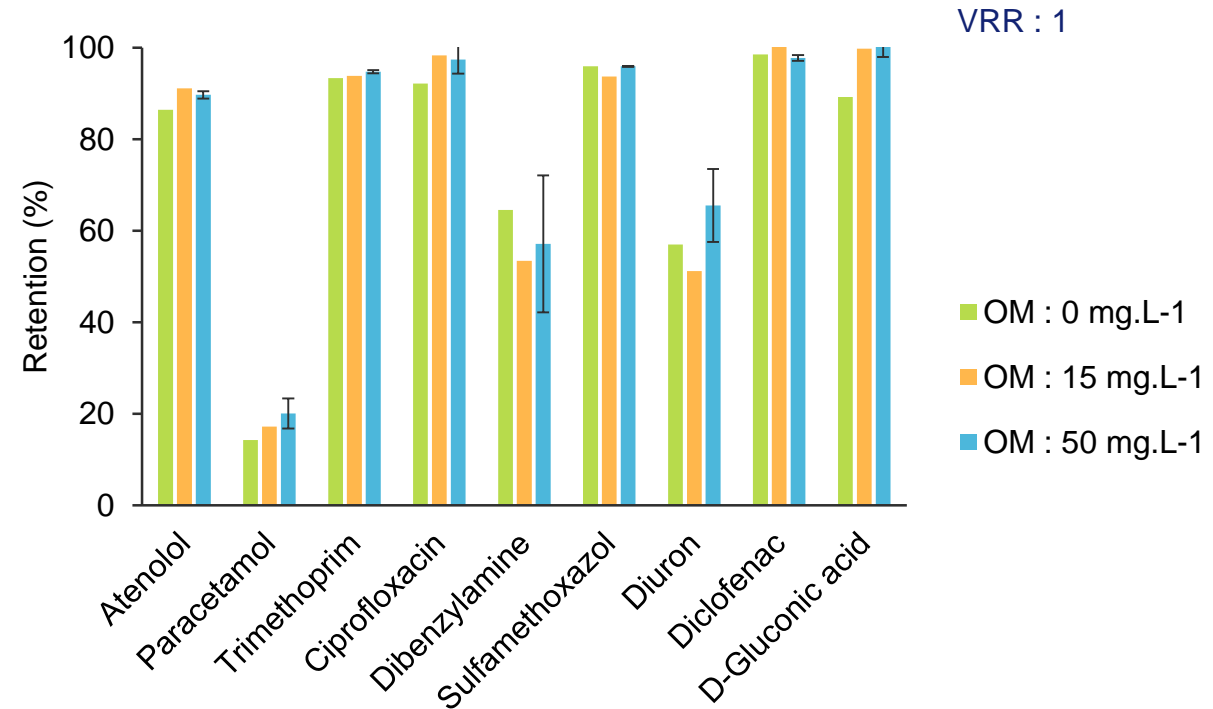
Impact of the volume reduction ratio



With 400 Da membrane :

- High retention ($\geq 90\%$) for six micropollutants
- Moderate retention (between 57 and 65 %) for two micropollutants
- Only one micropollutant with low retention ($\leq 20\%$)

Impact of the matrix



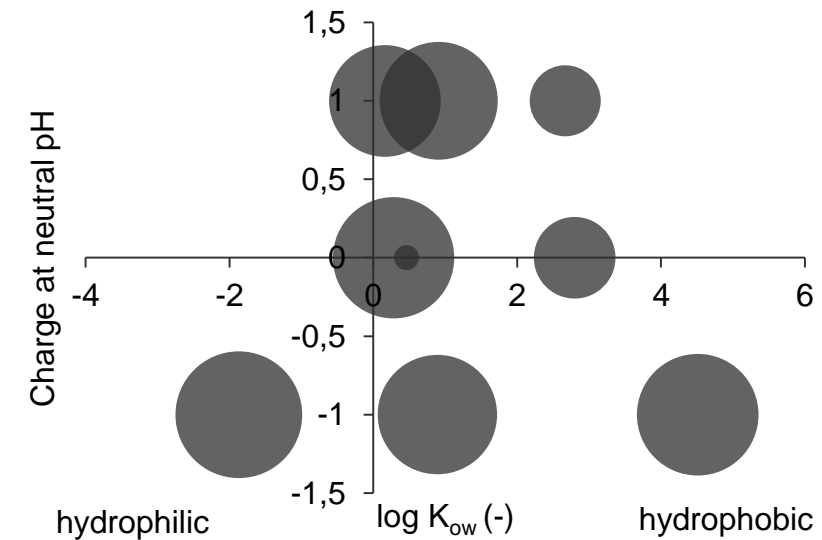
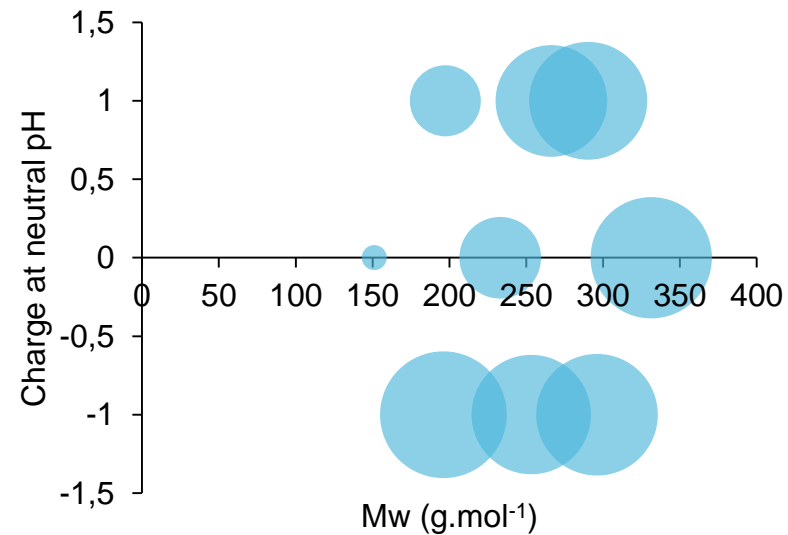
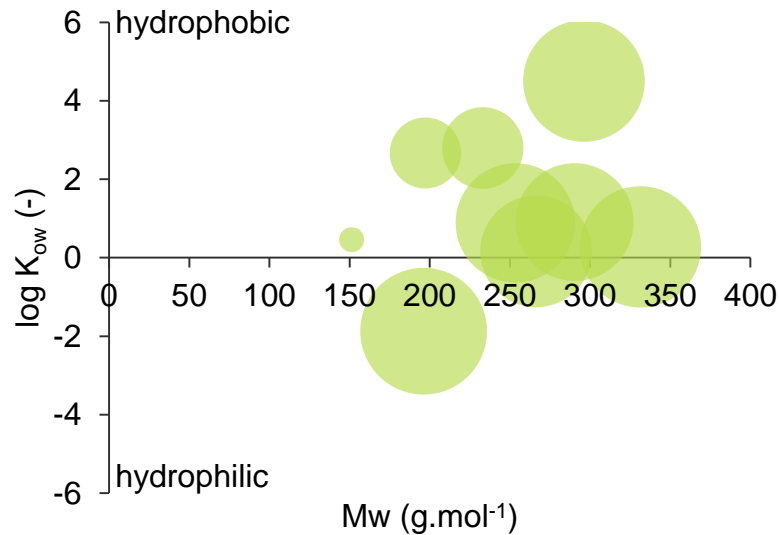
- No effect of organic matter content on micropollutants retention

PEM are efficient to remove most of micropollutants whatever the VRR applied and the content of organic matter into the matrix

RESULTS : retention of micropollutants on 400 Da MWCO membrane

VRR : 1

Organic matter's content into the matrix : 50 mg.L⁻¹



- For small contaminants (Mw < 250 g.mol⁻¹), the highest retentions were observed for hydrophilic molecules
- For large contaminants (Mw > 250 g.mol⁻¹), retention was similar

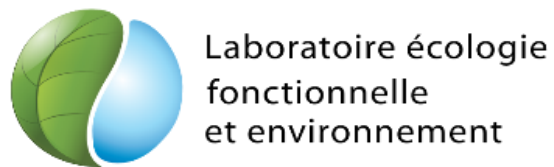
- Retention of contaminants increased when Mw increased
- For small contaminants (Mw < 250 g.mol⁻¹), the highest retention were measured for negatively charged micropollutants
- For large contaminants (Mw > 250 g.mol⁻¹), retention was similar

- For negatively charged contaminants, no differences were measured between hydrophilic and hydrophobic molecules
- For neutral or positively charged molecules, no correlation was observed between retention and hydrophobicity

Size exclusion and electrostatic repulsion seem to be the main mechanisms occurring with the functionalized membranes studied

TAKE HOME MESSAGES

- ❑ **Polyelectrolyte LbL membranes were efficient for the removal of most of the micropollutants with low retention of chloride**
- ❑ **Hollow fiber membranes were efficient to avoid fouling** during 24 h to 96 h of filtration in the conditions studied
- ❑ The influence of size and charge of micropolluants would be studied statistically



Thank you

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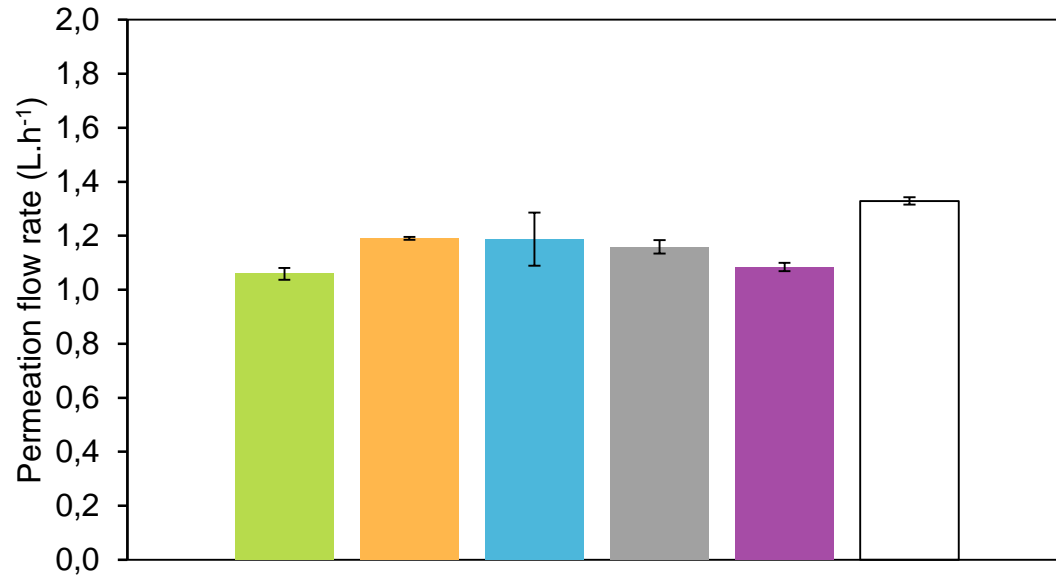


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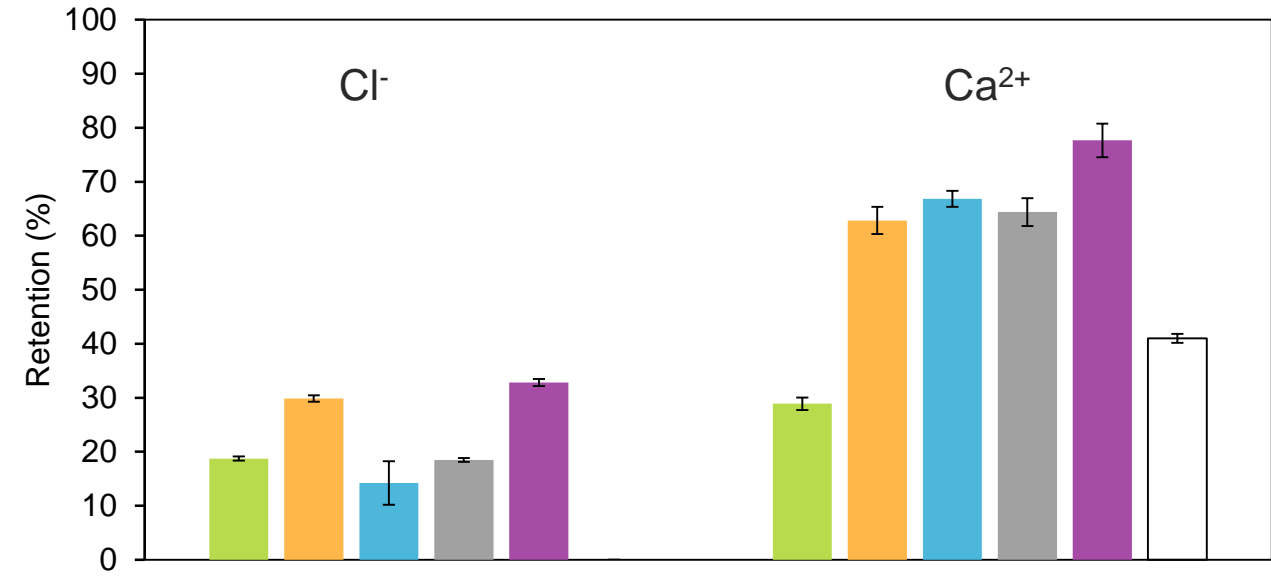
RESULTS : permeation flux & salts retention

Permeation flow rate



- Small increase of permeation with the MWCO of the membrane
- No effect of VRR applied on permeation
- No effect of organic matter content on permeation

Salts retention



- Decrease of the salts retention when MWCO of the membrane increase
- Low retention of chloride (< 30 %)
- Increase of chloride retention when VRR increase
- Increase of calcium retention when the organic matter content increase

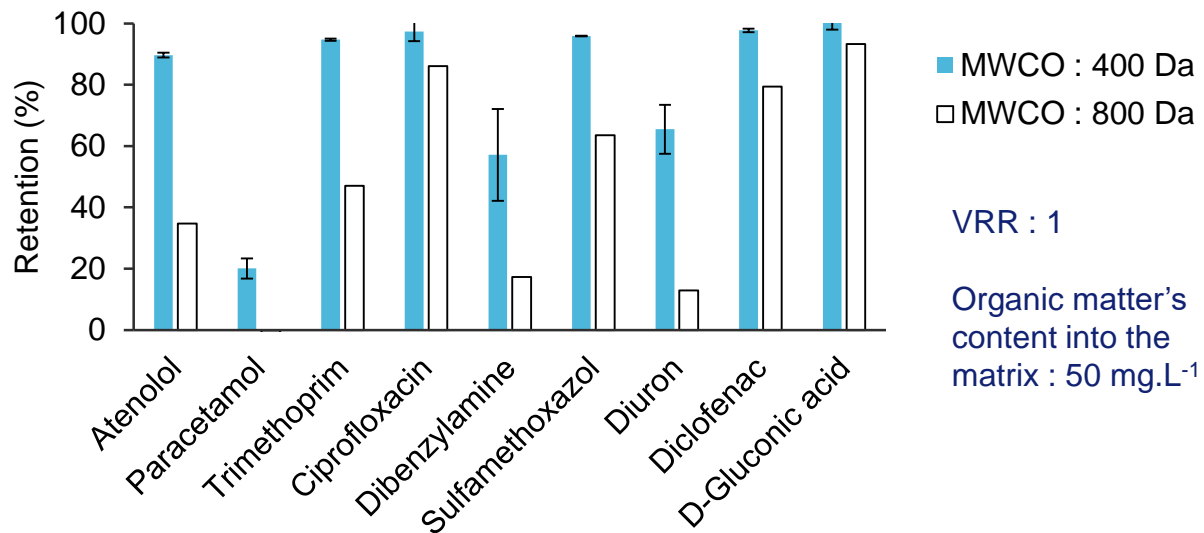
No fouling on 24 h filtration in the study conditions

Low VRR appears to be preferred

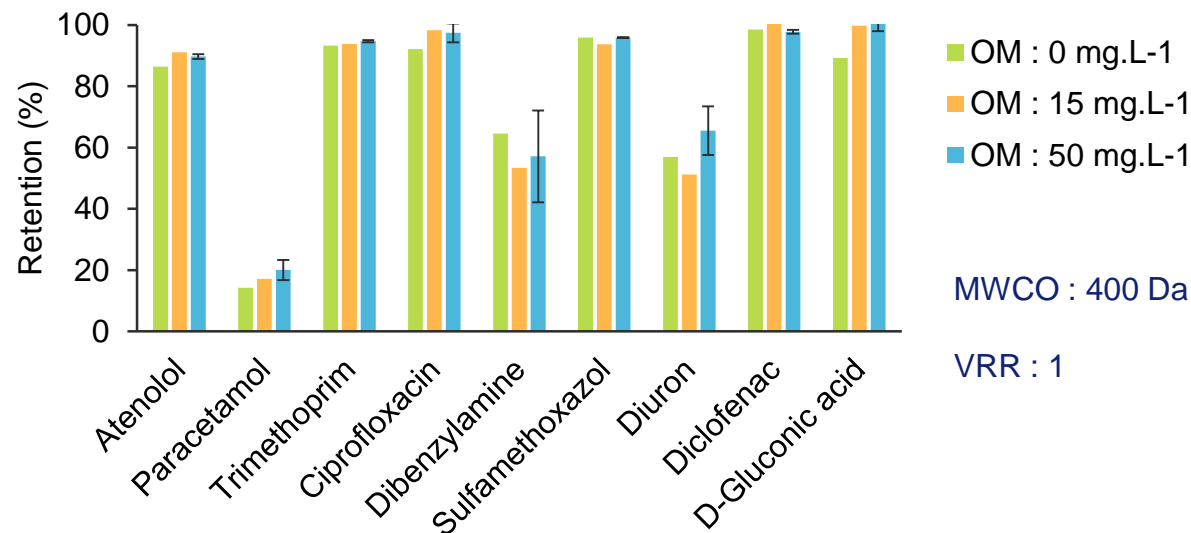
	■	■	■	■	■	□
MWCO (Da)	400	400	400	400	400	800
VRR	1	1	1	3	6	1
OM (mg.L ⁻¹)	0	15	50	50	50	50

RESULTS : retention of micropollutants

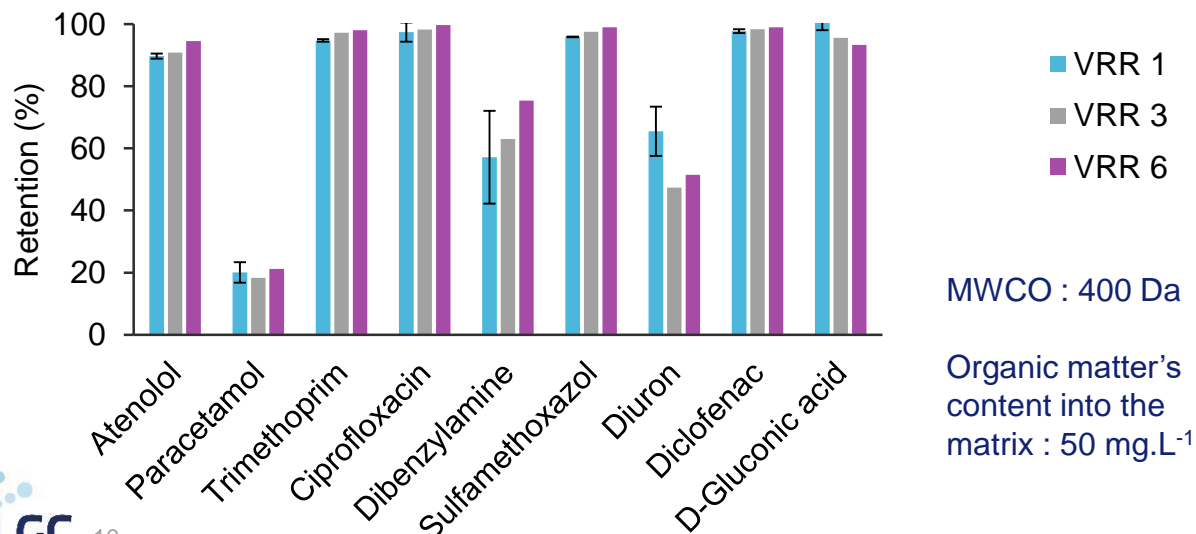
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Impact of the operation parameters



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- Only one micropollutant with low retention ($\leq 20\%$)
- Decrease of the micropollutants retention when MWCO of the membrane increase
- No effect of VRR applied on micropollutants retention
- No effect of organic matter content on micropollutants retention

Low MWCO membrane appears to be preferred