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Evaluation of technologies for the removal of pharmaceuticals from wastewaters

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Background

Biological waste water treatment and micropollutants

- Many of them are removed → e.g. ibuprofen and paracetamol >98%
- Some of them are not so easily removed, e.g. diclofenac -40% - 40%, carbamazepine -60%-10%

→ Tertiary treatments are needed!

Technologies for removal of micropollutants

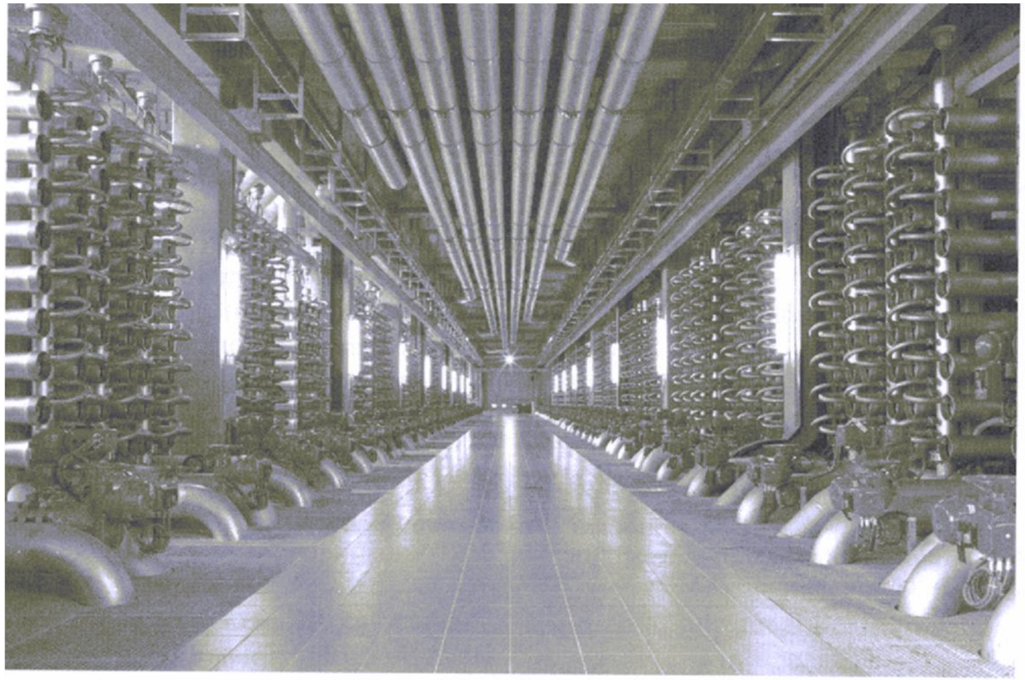
1. Binding (adsorption)
2. Concentrating (membrane filtration)
3. Degrading (oxidation) methods

Switzerland:

- activated carbon, ozone to remove micropollutants

France (Méry-sur-Oise):

- nanofiltration for removal of pesticides (atrazine, simazine)
- 140000 m^3/day (1.6 m^3/second)
- 340000 m^2 membranes



10 Méry-sur-Oise: nanofiltration gallery (Source: SEDIF)

Aim

- To evaluate the efficiency of selected methods in the removal/degradation of pharmaceuticals that are not readily biodegradable

Removed or not?

CAS: conventional activate sludge process
MBR: membrane bioreactor

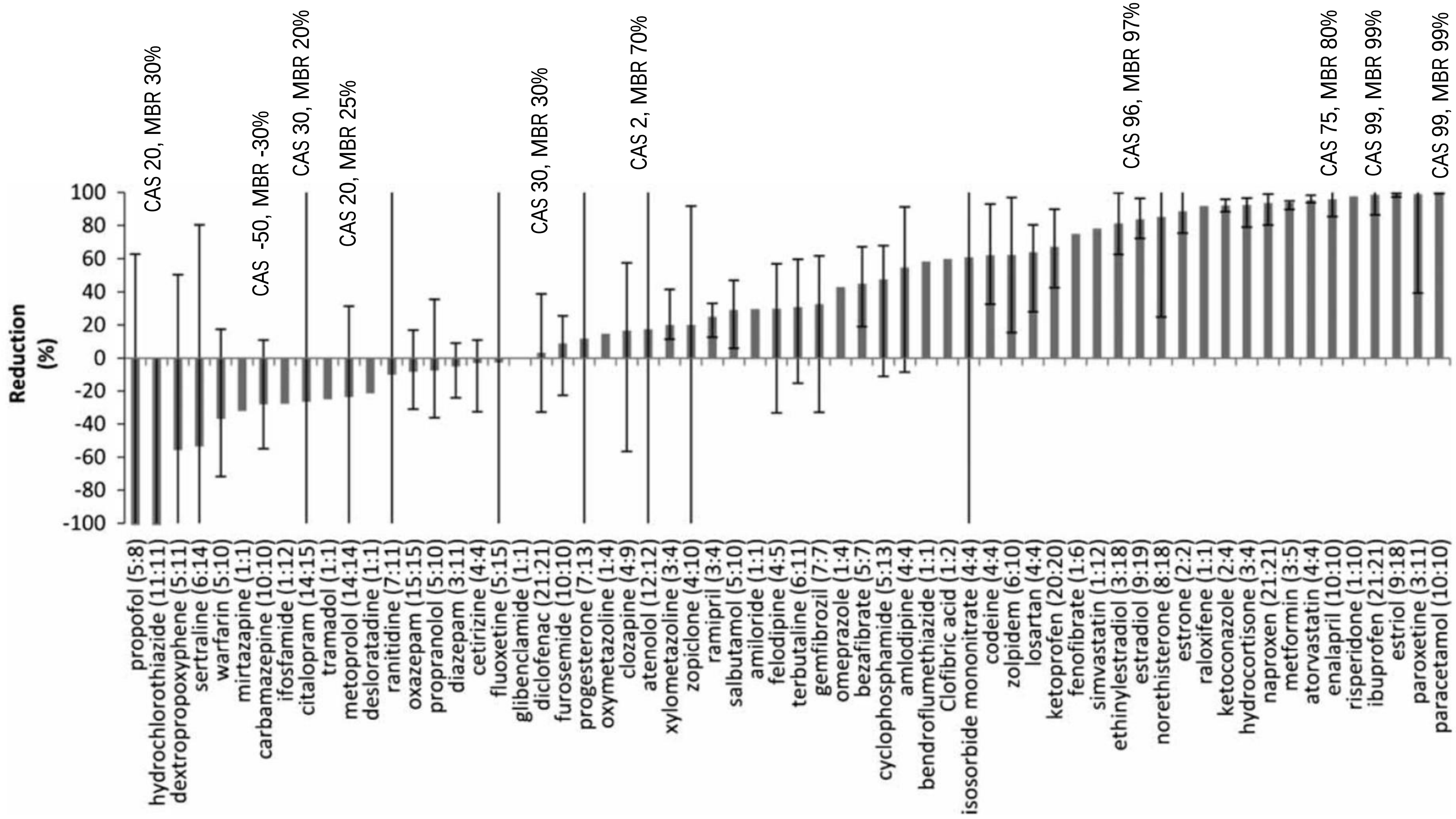


Figure 5 | Median removal efficiency in activated sludge plants with extended nitrogen removal. T-bars indicate standard deviation and numbers within brackets represent – Number of plants used in calculations: Number of plants sampled.

Hydrochlorothiazide
Carbamazepine
Citalopram
Diclofenac
Metoprolol
Atenolol

Sourse: P. Falås, H. R. Andersen, A. Ledin and J. la Cour Jansen, 2012, Occurrence and reduction of pharmaceuticals in the water phase at Swedish wastewater treatment plants Water Science & Technology

Different methods to reduce amount of micropollutants in waste waters

- Novel adsorbing material
- Oxidation (Pulsed corona discharge method)
- Membrane filtration processes

Adsorption

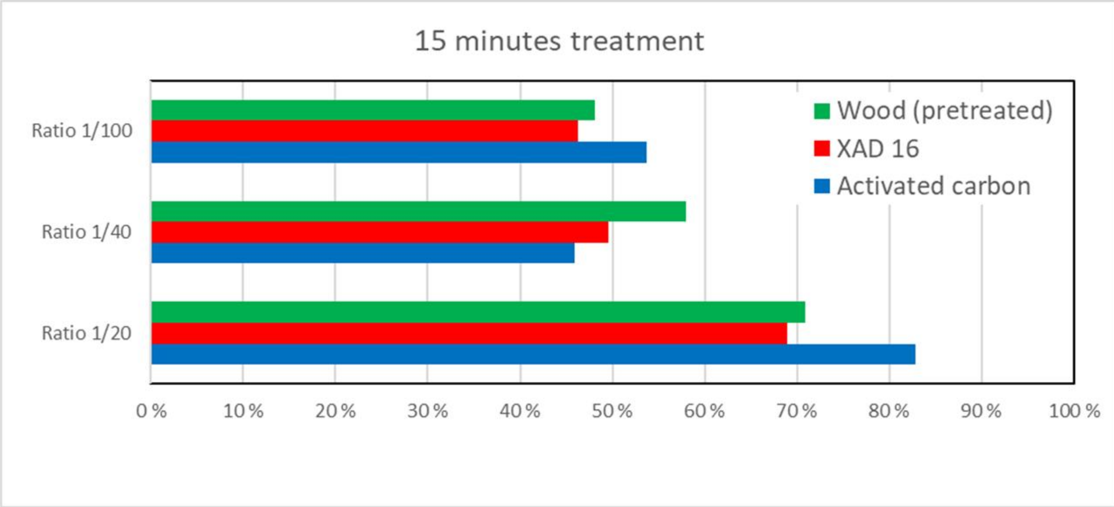
- Huge amount of literature is available on removal of micropollutants with adsorption
- Challenges:
  - Treatment time
  - Tank volumes
  - Regeneration of adsorbents
  - Price of adsorbents

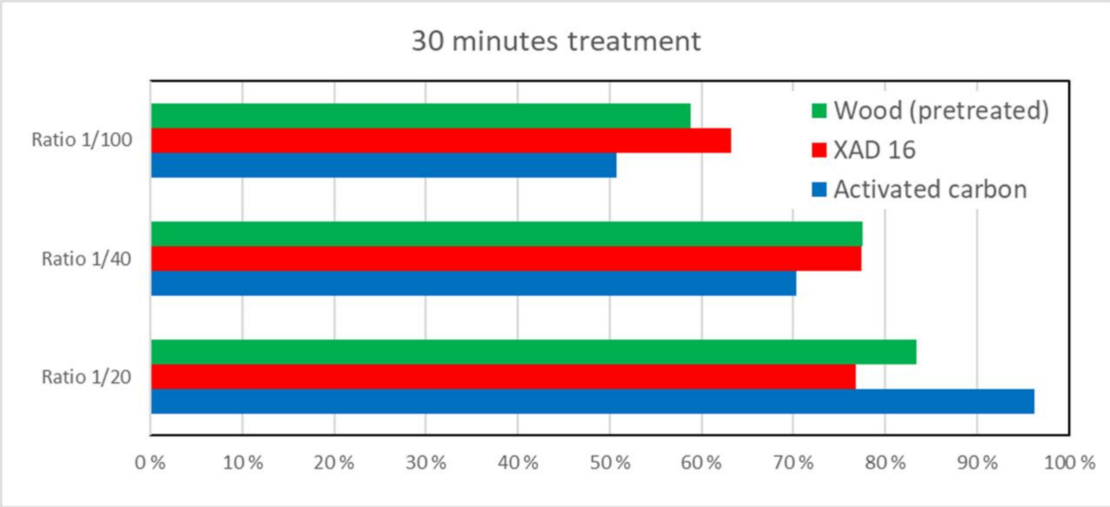
→ utilisation of waste material as an adsorbent?

Adsorption

Carbamazepine

- 11 mg/L
- Mass-ratio adsorbent/water 1/100, 1/40 and 1/20

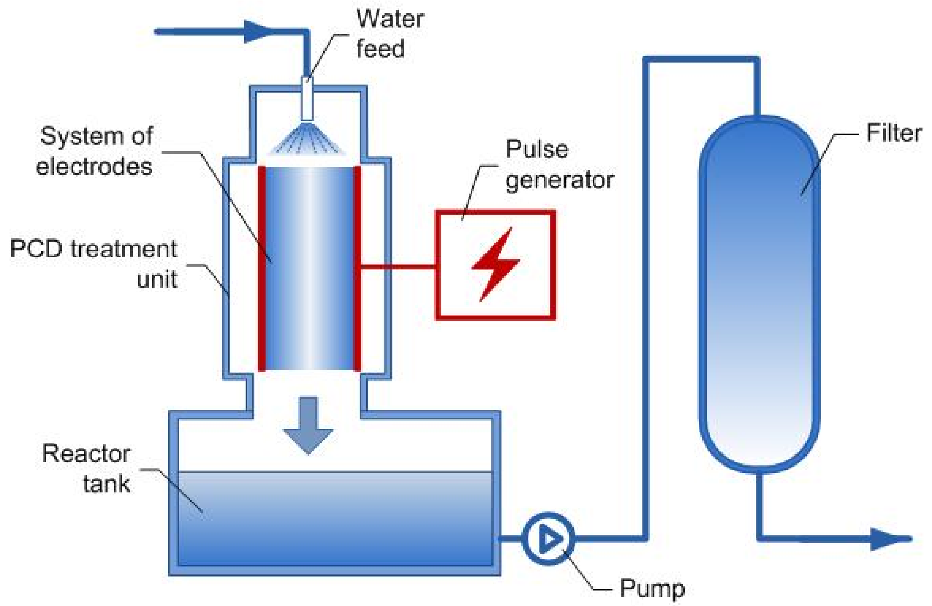




– Wood based adsorbents as efficient as activated carbon or polymeric resins

Oxidation (degradation method)

- Pulsed corona disharge → a cheaper way to create oxidants
- Transformation products mostly unknown



Sample layout of WAPULEC water treatment device

Principle

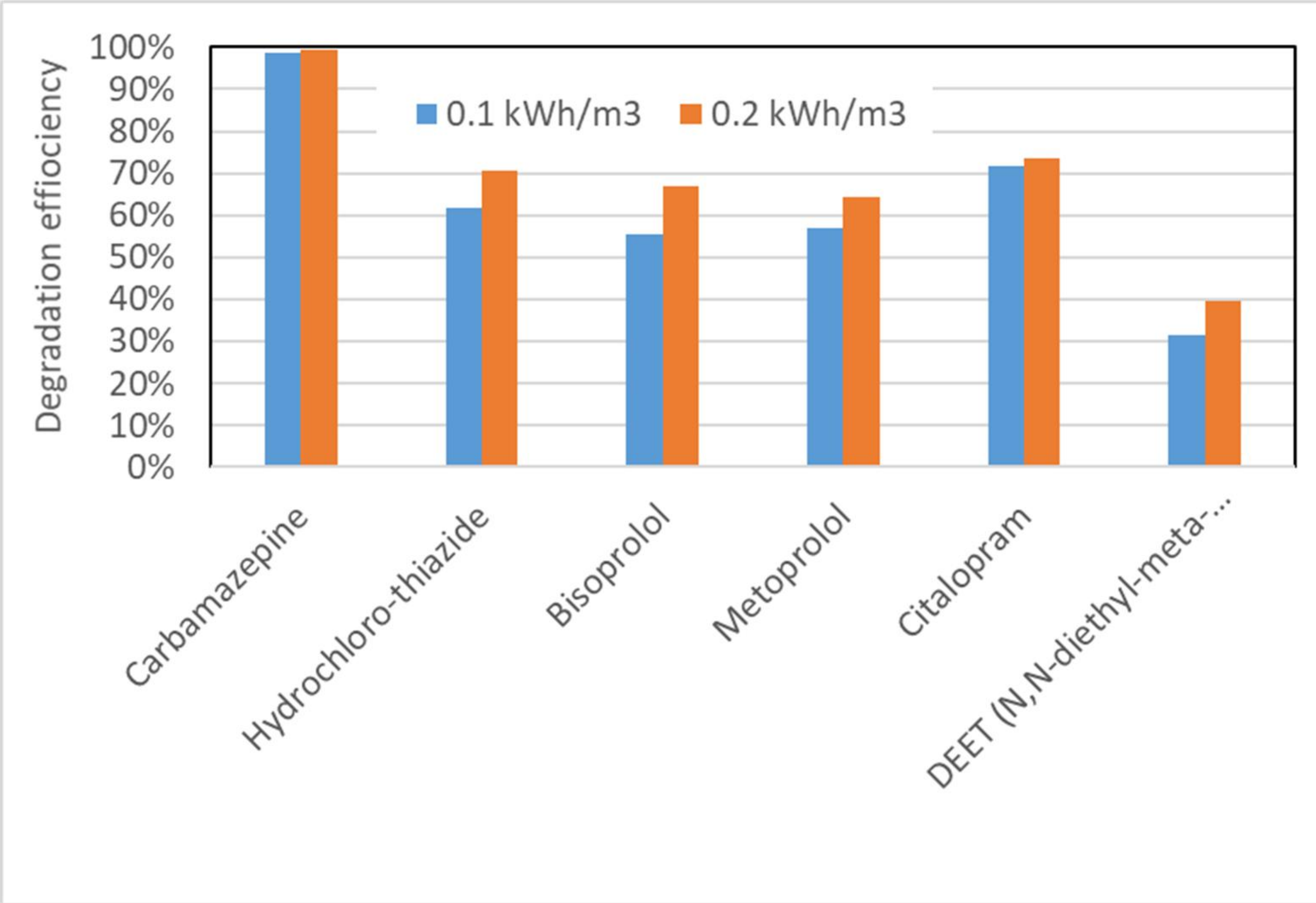
active oxidant species, such as hydroxyl radical, atomic oxygen, and ozone, are produced by gas-phase pulsed electric discharge directly on the surface of treated water in air or oxygen atmosphere.

http://www.wapulec.com/

Oxidation of micropollutants

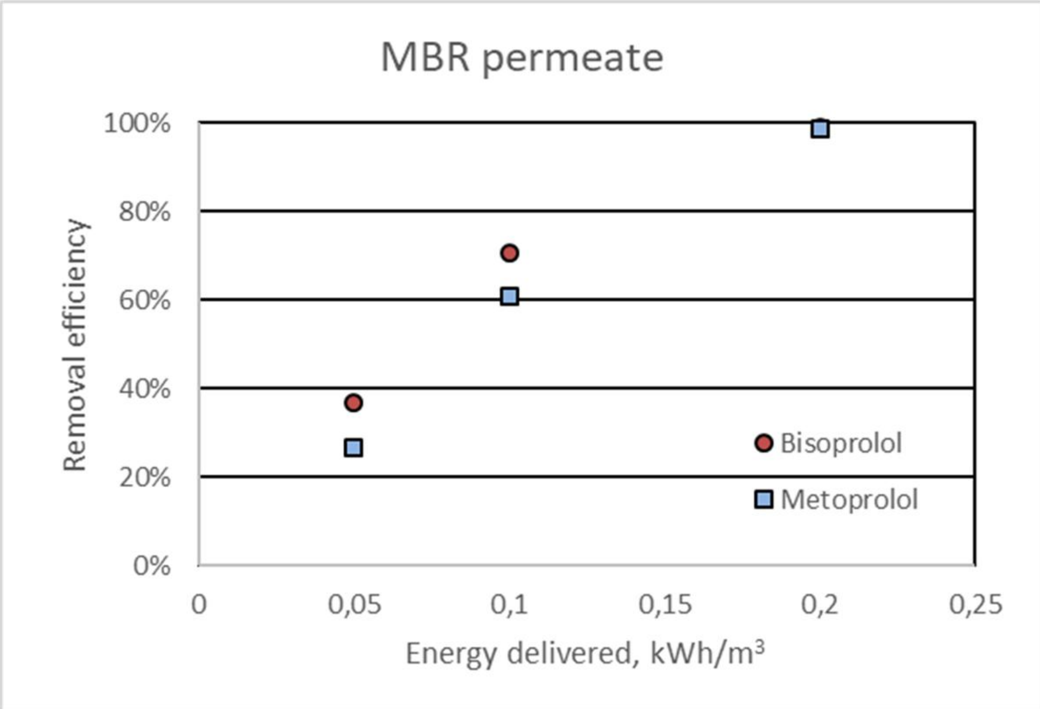
Discharge water from activated sludge plant

Conductivity	432 µs/cm
COD	33 mg/L
TOC	11 mg/L
Total phosphorous	0.1 mg/L
Total nitrogen	3.3 mg/L

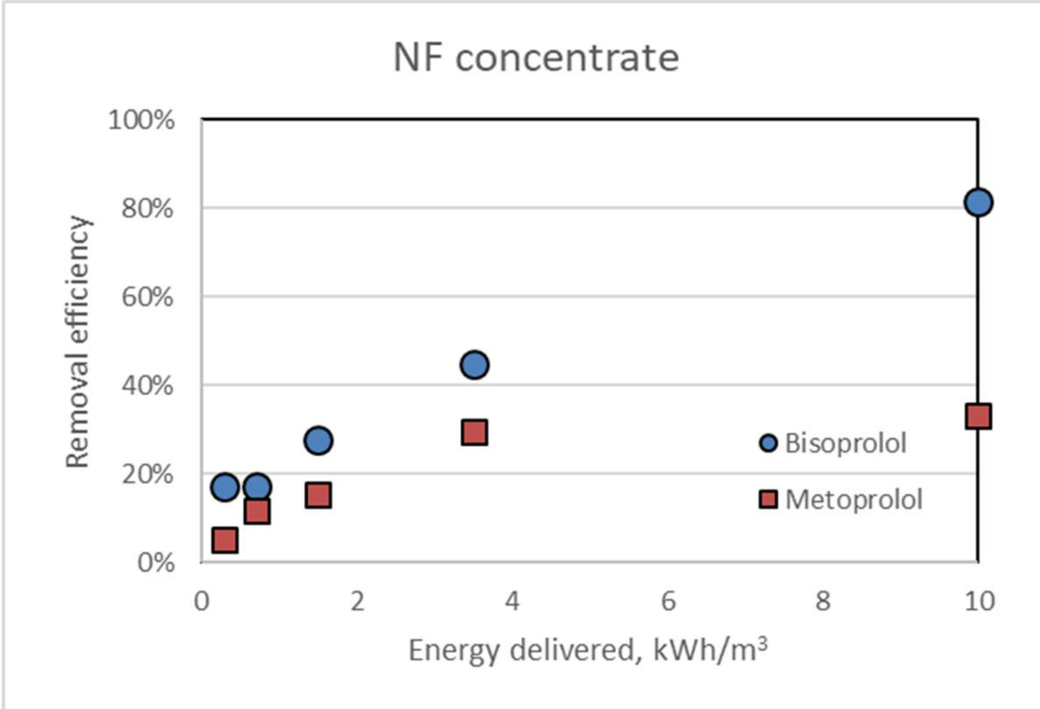


Oxidation of beta blockers

MBR permeate and NF concentrate (VRF 300)



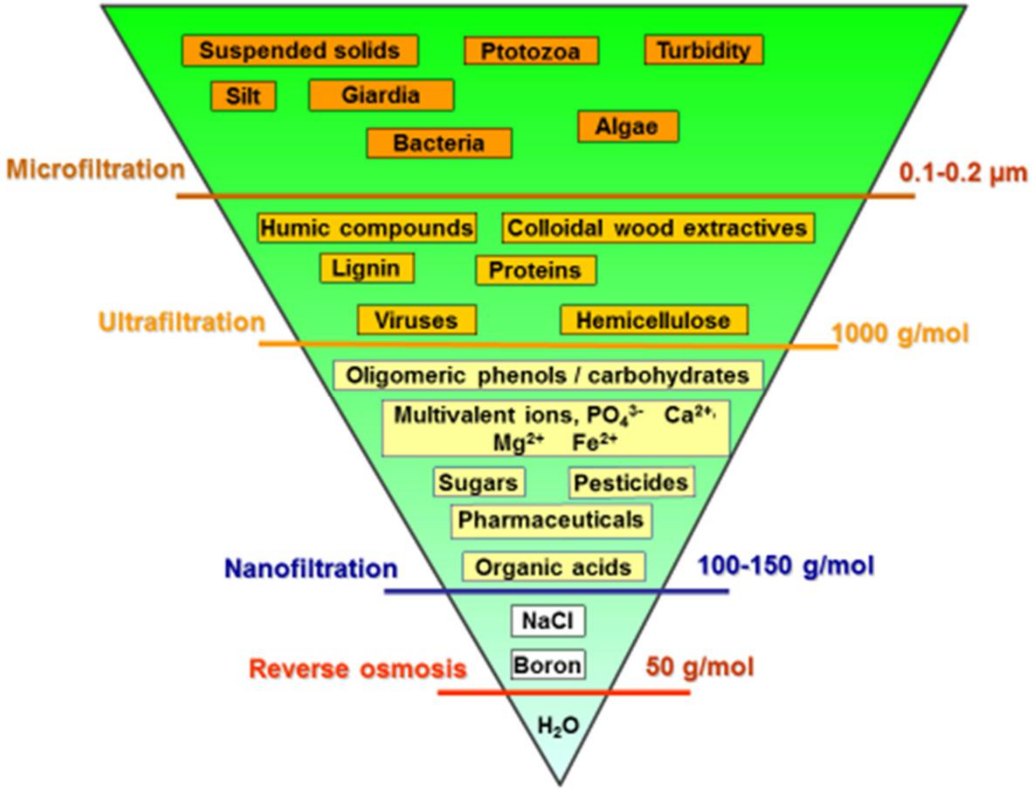
Conductivity 530 µS/cm, TOC 10 mg/L, COD 22 mg/L, P_{tot} 4.4 mg/L, N_{tot} 23 mg/L, metoprolol 1,2 µg/L



Conductivity 12700 µS/cm, TOC 2130 mg/L, COD 5930 mg/L, P_{tot} 380 mg/L, N_{tot} 190 mg/L, metoprolol 78 µg/L

Arola, K., et al. 2017, Advanced treatment of membrane concentrate with pulsed corona discharge, *Separation and Purification Technology*, 198 121-127.

Membrane filtration processes



Nanofiltration (NF)

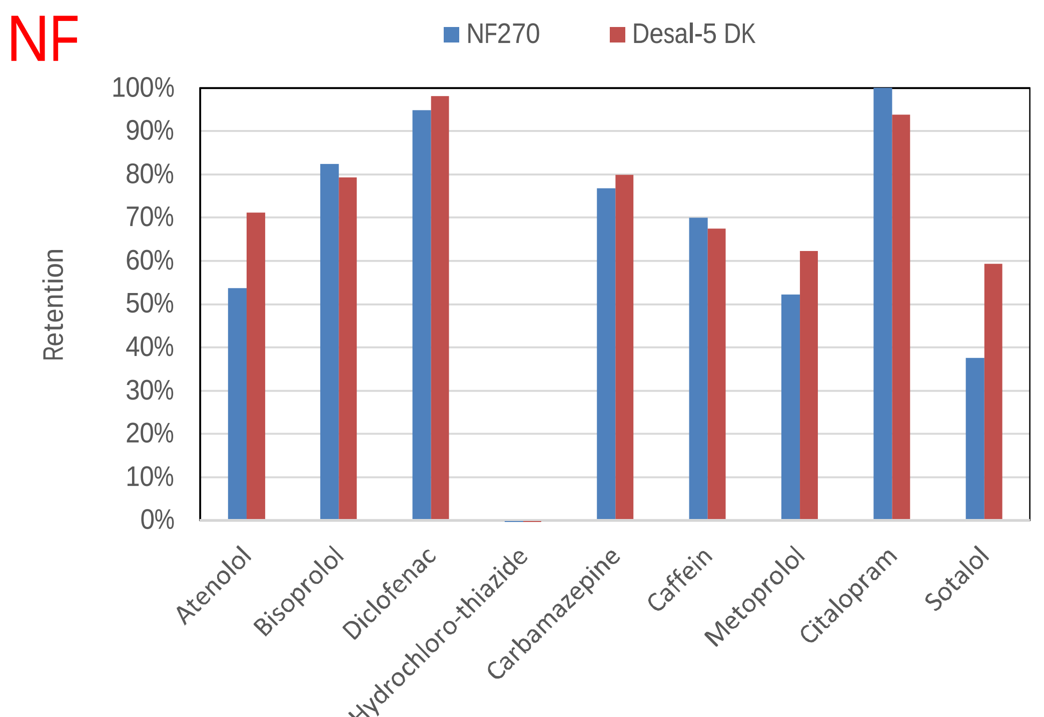
- cut-off value typically about 300 g/mol (pore size around nanometer)
- changes in feed composition and filtration conditions affects separation efficiency
- Significantly higher (2-10x) water permeability than in RO
- Osmotic pressure lower than in RO due to permeation of monovalent ions

Reverse osmosis (RO)

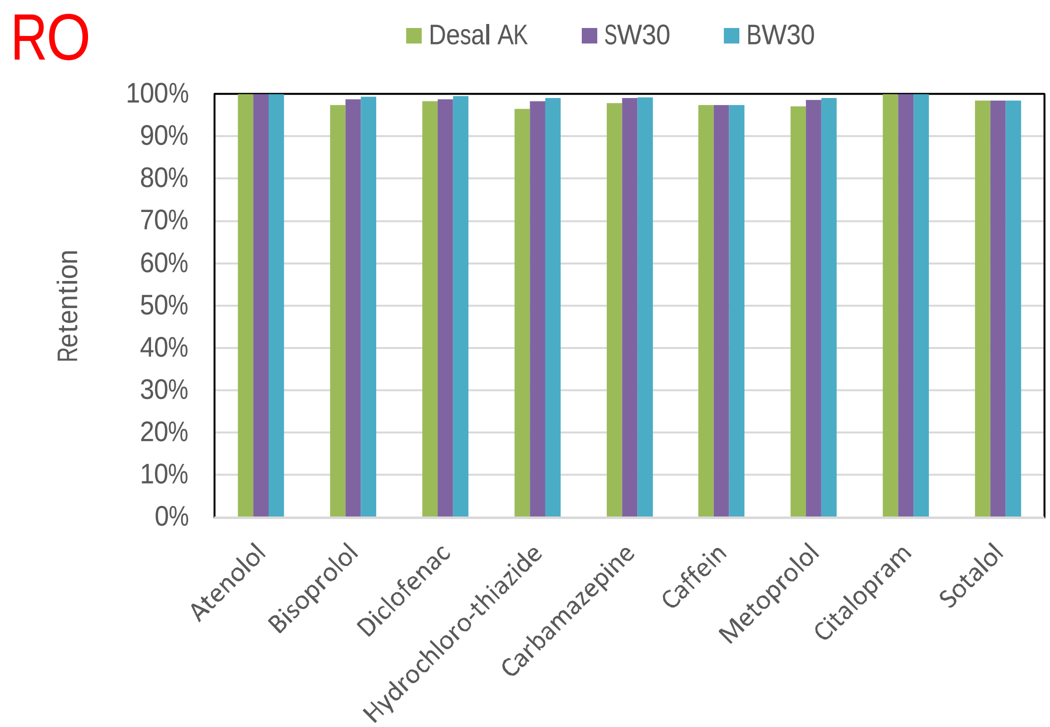
- Dense membrane → solution-diffusion
- Separate water from salt → desalination process
- Not so sensitive to filtration conditions

Nanofiltration and reverse osmosis in the removal of pharmaceutical compounds

Discharge water from membrane bioreactor



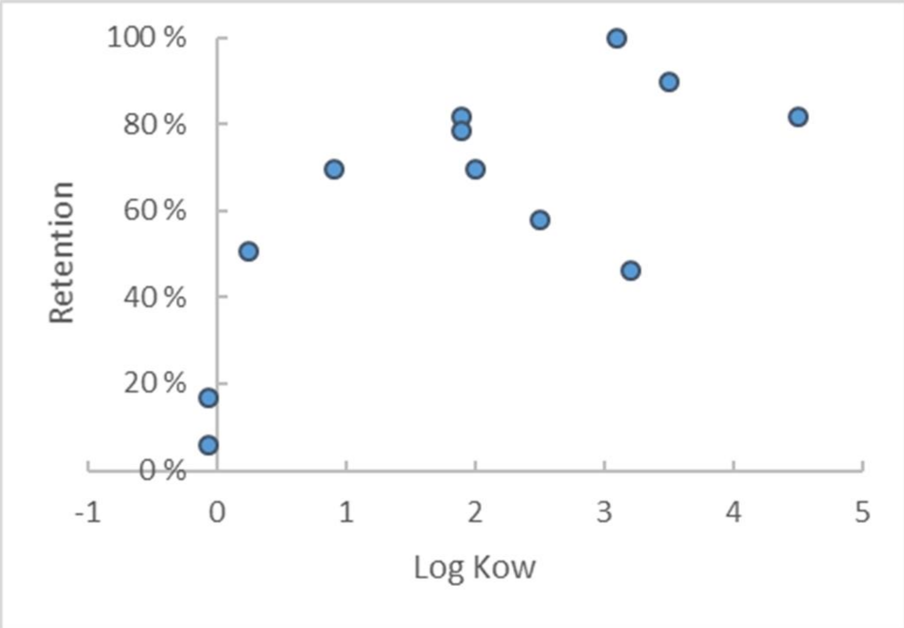
MM, g/mol	266	325	296	298	236	194	267	324	272
Log Kow	0.16	1.9	4.5	-0.07	2.6	-0.07	1.9	3.5	0.24

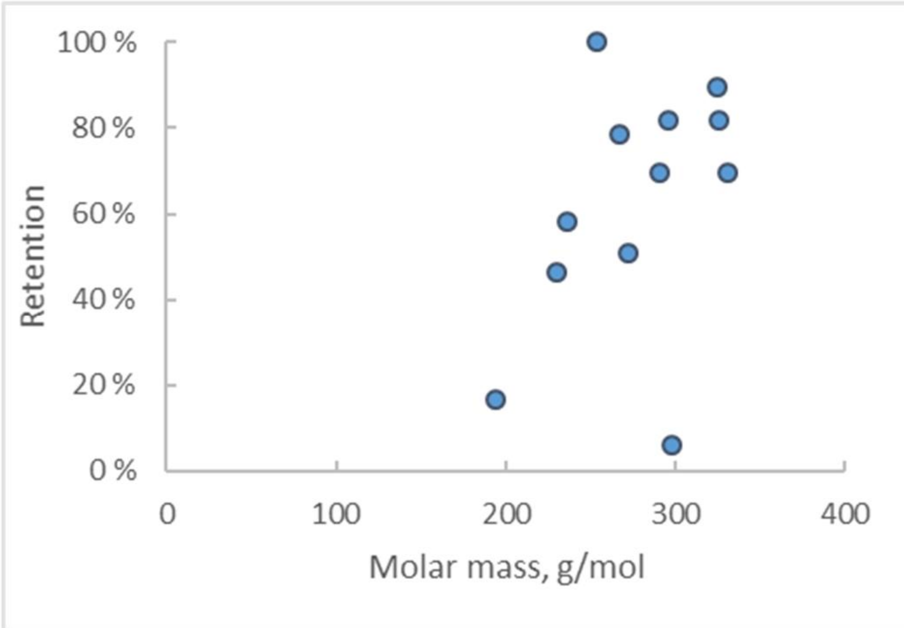


Nanofiltration of pharmaceuticals

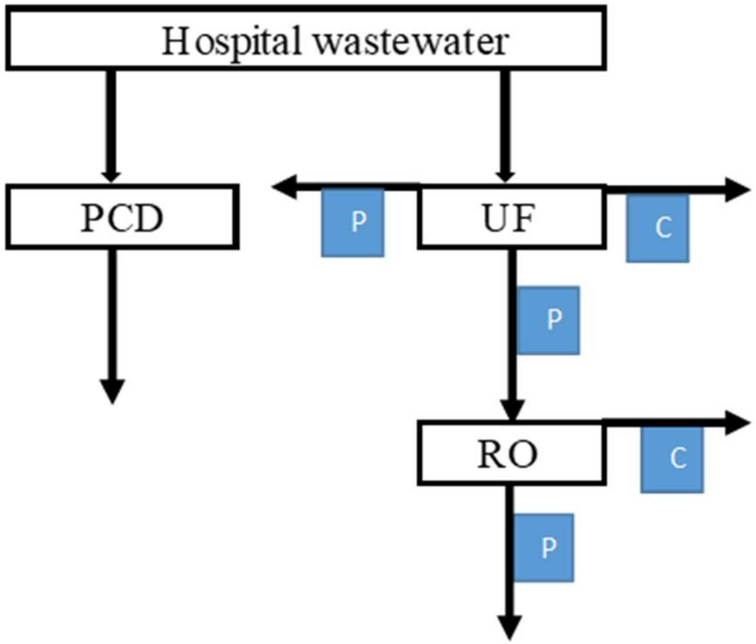
Discharge water from activated sludge plant

Conductivity	432 µs/cm
COD	33 mg/L
TOC	11 mg/L
Total phosphorous	0.1 mg/L
Total nitrogen	3.3 mg/L





Do we need biological processes to purify waste waters?



Direct treatment of hospital waste water

	Concentration, mg/L
Phosphorous	5,5
Nitrogen	63
COD	793
TOC	200

Hospital waste water

	Raw wastewater	UF	RO	Removal efficiency at a	PCD 250 W	PCD 30 W
	mg/L	mg/L	mg/L	water recovery of 82% (UF+RO)	1 kwh/m^3	1 kwh/m^3
P_{tot}	5.5	3.9	0.1	98.2 %	7 %	16 %
N_{tot}	63	54	6	90.5 %	0 %	2 %
COD	793	500	21	97.4 %	13 %	16 %
DOC	200	140	3	98.5 %	12 %	11 %
		Citolapram		95 %	100 %	100 %
		Carbamazepine		95 %	75 %	100 %
		Diclofenac		93 %	86 %	100 %
		Metoprolol		92 %	30 %	100 %
		Bispropol		93 %	53 %	100 %
		Ibuprofein		94 %	7 %	50 %
		Hydrochlorothiazide		94 %	-2 %	48 %
		Enalapril		95 %	19 %	39 %
		Metronidazole		98 %	6 %	18 %
		Caffeine		92 %	-2 %	19 %
		Hydrocortisone		90 %	22 %	18 %

Ajo P., et al. 2018, Hospital wastewater treatment with pilot-scale pulsed corona discharge for removal of pharmaceutical residues, Journal of Environmental Chemical Engineering 6(2) 1569-1577.

Conclusion

- Conventional (biological) waste water treatment degrades many micropollutants but not all
- Oxidation, adsorption and membrane filtration are potential methods to remove residual micropollutants

- Oxidation
  - PCD oxidation degraded most of residual pharmaceuticals with as low energy consumption as 0.1-0.2 kWh/m^3 water when waste waters was pretreated by activated sludge process
  - Direct oxidation of waste waters or membrane concentrates obviously needs more energy
  - Not so readily oxidized compounds: Hydrochloro-thiazide, metronidazole, enalapril, hydrocortisone and pesticide (DEET) and betablockers (Atenol, Bisoprolol, Metoprolol, Sotanol)

Conclusion

- Membrane filtration
  - Retention in nanofiltration depends on the molar mass of pharmaceutical compounds and also molecular and membrane properties as well as filtration conditions
  - Reverse osmosis retained more that 95% of almost all pharmaceutical compounds
  - In membrane processes higher feed concentration lead to lower purity in permeate
  - Nutrients and DOC are also removed

- Adsorption
  - Cheap wood based adsorbent can be used to remove pharmaceuticals

- Not only pharmaceuticals but also nutrients, organic compounds, salts etc. need to be taken into account when advanced purification process is selected

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Efficient Treatment of Pharmaceutical Residue at Source - EPIC

Tekes

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VESIENSUOJELUA vuodesta 1963
Vantaanjoen ja Helsingin seudun vesiensuojeluyhdistys ry

Vesihuoltolaitosten kehittämisrahasto

Kymen Vesi Oy

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Lappeenrannan energia oy

Turun seudun puhdistamo Oy

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VARSINAIS-SUOMEN SAIRAANHOITOPIIRI

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WAPULEC
Water and air treatment

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