Elimination of emerging contaminants (surfactants, pharmaceuticals) by membrane bioreactor (MBR) technology

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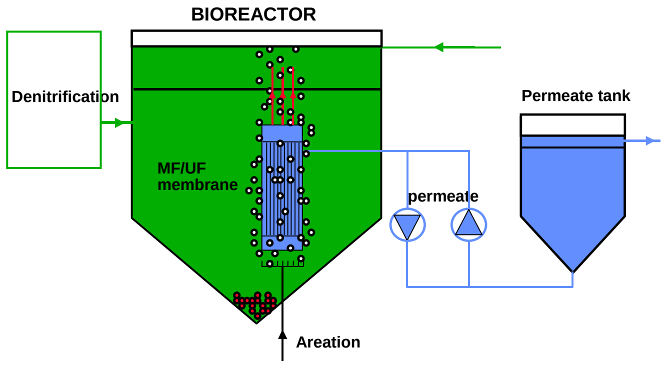
Outline

- **Introduction on MBR**
  - types of membranes
  - types of bioreactors
  - advantages and disadvanteges
- **Case study (I)**
  - elimination of pharmacueticals in a laboratory scale MBR (vs CAS)
- **Case study (II)**
  - elimination of pharmacueticals in a pilot scale MBR (vs CAS)
- **Case study (III)**
  - elimination of surfactants in a laboratory scale MBR (vs CAS)
- Conclusions

Membrane bioreactors (MBRs)

- ✓ Membrane bioreactors (MBRs) combine the use of biological processes and membrane technology to treat wastewater.
- ✓ Within one process unit, a high standard of treatment is achieved, replacing the conventional arrangement of aeration tank, settling tank and filtration that generally produces what is termed as a tertiary standard effluent.

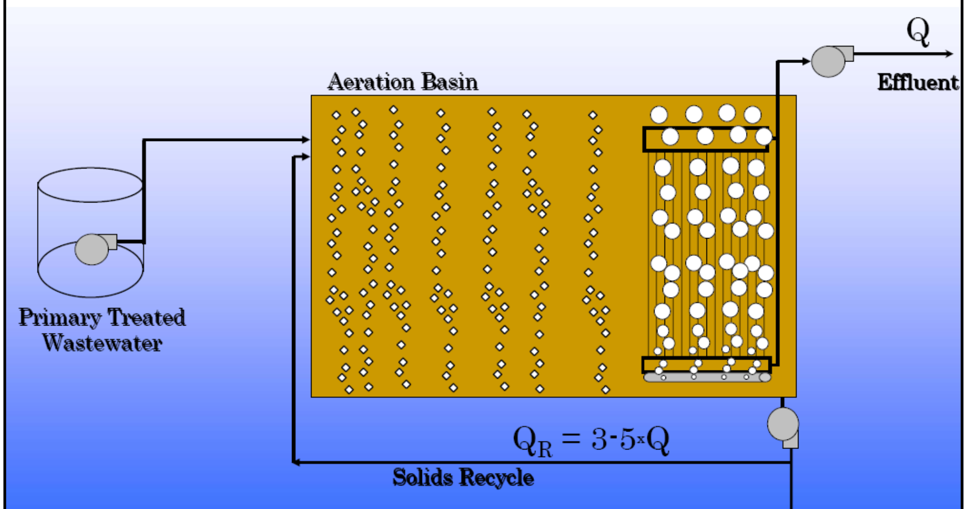


Why MBR?

Technical aspects

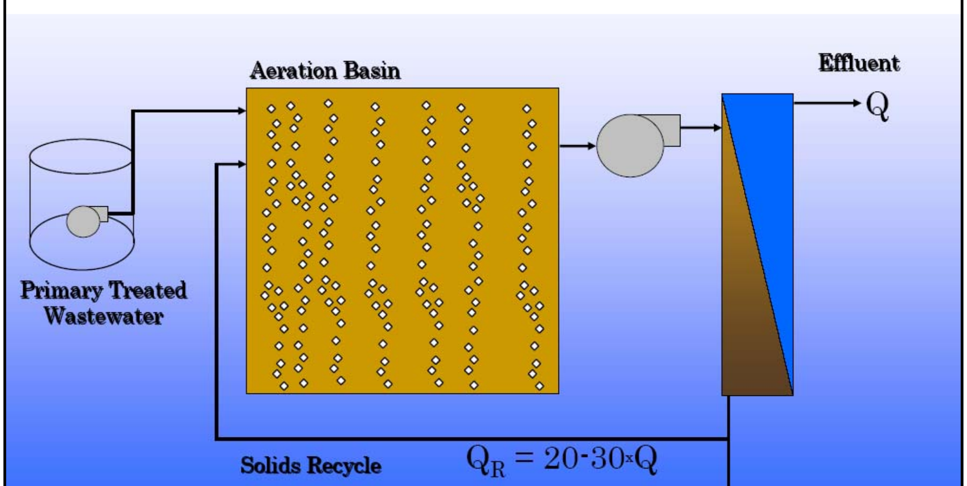
- adsorption, improved physical sludge characteristics, with higher biomass concentration and more effective surface;
- biodegradation, cultivation of metabolic speciation, with high sludge age, low mass organic load favouring biological synthesis of broader substrate spectrum
- direct and complete separation through membrane with entire removal of all contaminants bound to colloids and particulate matter.

Submerged MBR



Submerged MBR with internal vacuum driven membrane filtration

External MBR



Side-stream MBR with external pressure driven membrane filtration

Types of MBR configurations

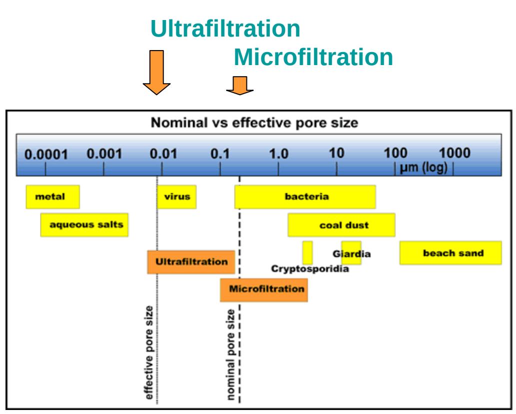
The configurations of MBR are based on either a planar or cylindrical geometry.

There are five principal membrane configurations currently employed in practice:

- hollow fiber (HF)
- spiral wound
- plate-and-frame (i.e. flat sheet (FS))
- pleated filter cartridge
- tubular.

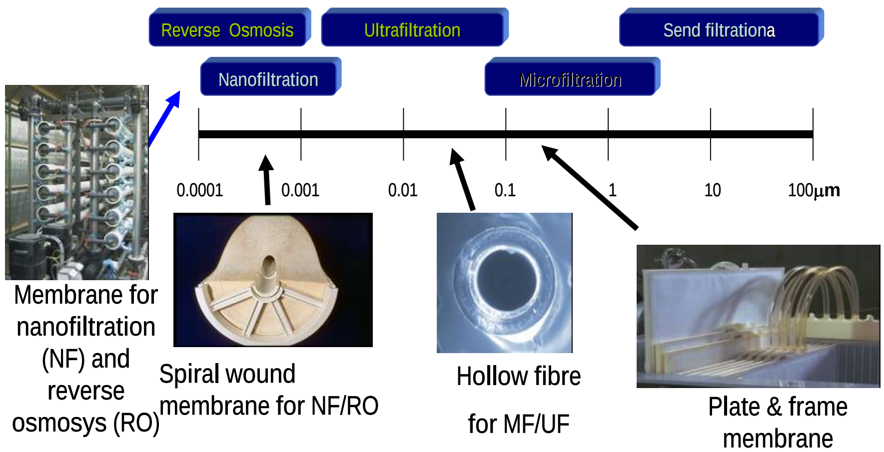
The disinfection depends on the membrane pore size, MICROFILTRATION (elimination of bacteria and pathological organisms) ULTRAFILTRATION (total disinfection including virus elimination).

The pore size of the membrane is 0,4 µm **(microfiltration)**



A layer of proteins and cellular material in the membrane surface change the porosity into ≈ 0,01 µm: Range of filtration change into **ULTRAFILTRATION**

Types of membranes



MEMBRANE PROCESSES

Configurations most frequently used in wastewater treatment are hollow fiber (HF) and flat sheet (FS) MBR

Hollow fiber membranes

Flat sheet membranes

Advantages of MBR

- **Sludge production** is significantly reduced, compared to conventional CAS, as longer sludge ages are achievable
- **Effluent quality** is consistently high and generally independent of the influent quality.
- **Good disinfection capability**, with significant bacterial and viral reductions achievable using UF and MF membranes.
- Longer retention of **nitrifying bacteria** within the bioreactor results in greater nitrification than in a conventional CAS.
- **Denitrification** can be achieved by utilizing a second anoxic vessel.
- **Sludge age** and **hydraulic retention time** are independent
- Growing of **specialized microorganisms**

Disadvantages of MBR

- Higher **energy consumption** (bigger oxygen consume)
- Higher **cost** (membranes and maintenance) (the cost of MBR drop from 2001 to 2004 and is estimated to be from 0.8 $ m-3 to 0.5 $ m-3)
- Higher **initial investment**

Case study (1): elimination of pharmaceuticals in wastewater treatment plant (WWTP) Rubí, Spain

- full scale CAS treatment,
- laboratory scale MBR treatment

Wastewater treatment plant (WWTP) Rubí

Influent type: municipal/hospital/industrial wastewater
Equivalent inhabitants: 125 550
Average daily flow: 1 125 m^3/h
Maximum daily flow: 1 800 m^3/h
Hydraulic retention time: 14 h
Solids retention time: 3 days

Treatment:
1. **Preliminary treatment** (large solids are removed)
2. **Primary treatment** (physical process of settling removes more solids)
3. **Secondary treatment** (removes the demand for oxygen using microbial action) consisting in pre-denitrification (anaerobic) and nitrification (aerobic)

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Laboratory scale submerged plate-and-frame MBR

- Volume: 20-22 l
- Hydraulic retention time (HRT): 14 h
- Solids retention time (SRT): infinite.
- Nominal porosity: 0.4 µm (MF)
- Effective porosity: in the range of UF
- Kubota flat sheet membranes (chlorinated poliethilen): 2 A4 embranes (A=0.3 m²), maximum capacity ~ 6 l/h.

Laboratory-scale membrane bioreactor (MBR) was operating in parallel to a conventional activated sludge (CAS) treatment. Their performance was monitored during a period of approximately two months, during which 28 integrated samples were analyzed.

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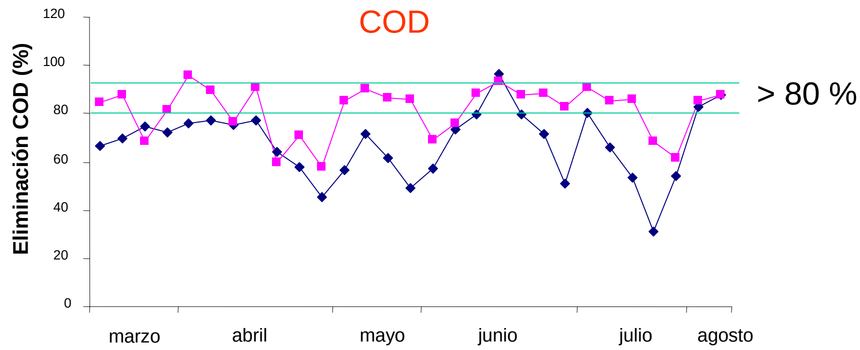
COMPARATION OF BASIC PARAMETERS

Effluent	COD, (mg/l) (C.V.%)	TSS (mg/l) (C.V.%)	NH_4^+ (mg/l) (C.V.%)	pH
MBR	42.7 (± 23.3)	7.1 (± 74.85)	8.3 (± 42.4)	7.43
CAS	80.7 (± 30.3)	24 (± 37.4)	17.8 (± 39.6)	7.27
Legislation	125	35	25	6-9



MBR (72.2 ± 11.7 %)

CAS WWTP (58.90 ± 23.8 %)

Target compounds monitored

ANALGESICS AND ANTI-INFLAMMATORY DRUGS	Ibuprofen Indomethacine Ketoprofen Acetaminophen Naproxen Mefenamic acid Diclofenac Propyphenazone	To relief pain, inflammation and fever
ANTI-ULCER AGENTS	Lansoprazole	To prevent and treat ulcers
PSYCHIATRIC DRUGS	Flouxetine Paroxetine	Antidepressants
ANTIEPILEPTIC DRUGS	Carbamazepine	To treat epileptic attacks
ANTIBIOTICS	Erythromycin Azythromycin Sulfamethoxazole Trimethoprim Ofloxacin	Antibacterial agents
B-BLOCKERS	Atenolol Sotalol Metoprolol Propranolol	Antianginal antihypertensive
DIURETICS	Hydrochlorothiazide	To treat excessive fluid accumulation
HYPOGLYCAEMIC AGENTS	Glibenclamide	To treat type II diabetes
LIPID REGULATOR AND CHOLESTEROL LOWERING STATIN DRUGS	Clofibric acid Gemfibrozil Bezafibrate Pravastatin Mevastatin	To lower fat (lipids) level
ANTI-HISTAMINICS	Famotidine Ranitidine Loratidine	To relieve allergy reactions

Out of 31 pharmaceutical products included in the analytical method, 22 were detected in the wastewater entering WWTP Rubí.

Compounds that were found in highest influent concentrations (µg/L) were:

- analgesics and anti-inflammatory drugs: ibuprofen, ketoprofen, naproxen, diclofenac, indomethacin, acetaminophen
- lipid regulator and cholesterol lowering statin drugs: gemfibrozil, bezafibrate
- diuretics: hydrochlorothiazide

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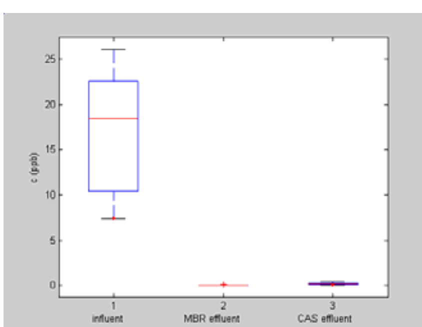
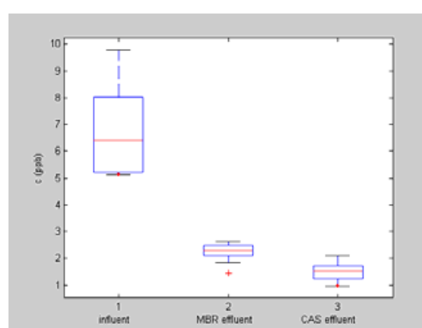
✓ In some cases the removal efficiencies were very similar and high for both treatments (e.g. ibuprofen, naproxen, acetaminophen, hydrochlorothiazide, paroxetine).

Elimination of acetaminophen



Elimination of hydrochlorothiazide



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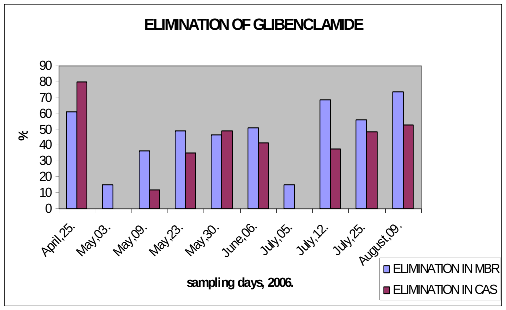
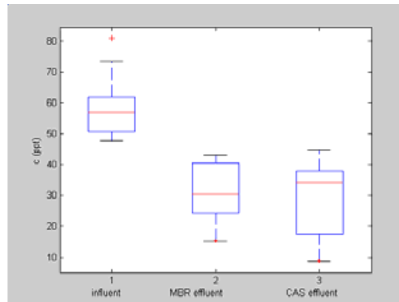
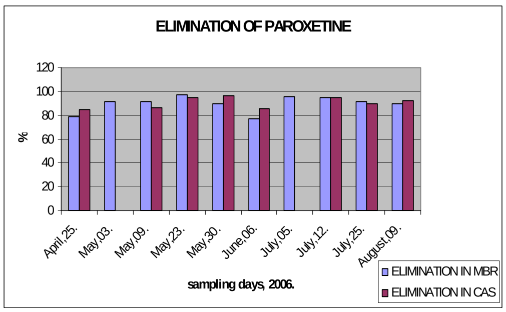
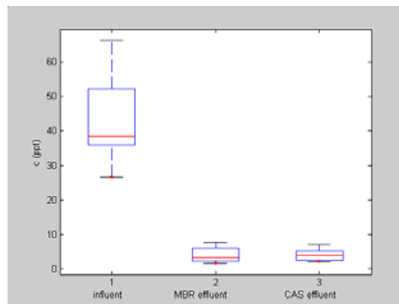

ELIMINATION OF GLIBENCLAMIDE
%
90
80
70
60
50
40
30
20
10
0
April,25.
May,03.
May,09.
May,23.
May,30.
June,06.
July,05.
July,12.
July,25.
August,09.
sampling days, 2006.
ELIMINATION IN MBR
ELIMINATION IN CAS


c (ppt)
80
70
60
50
40
30
20
10
1
influent
2
MBR effluent
3
CAS effluent


ELIMINATION OF PAROXETINE
%
120
100
80
60
40
20
0
April,25.
May,03.
May,09.
May,23.
May,30.
June,06.
July,05.
July,12.
July,25.
August,09.
sampling days, 2006.
ELIMINATION IN MBR
ELIMINATION IN CAS


c (ppt)
60
50
40
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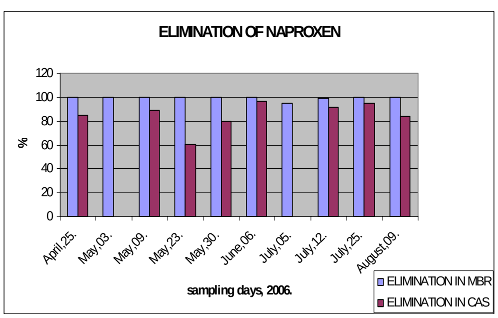
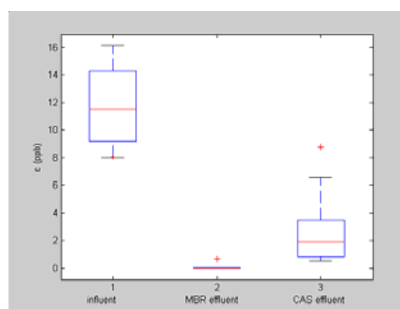
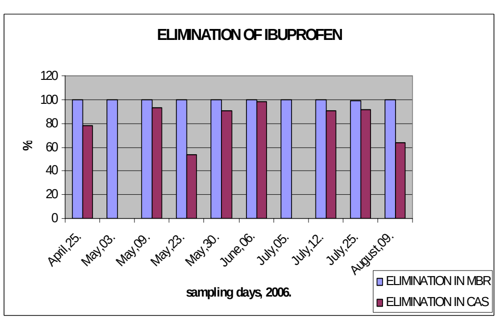
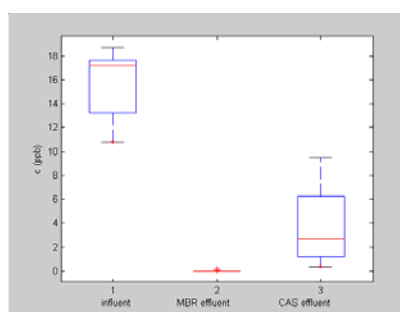
10
0
1
influent
2
MBR effluent
3
CAS effluent

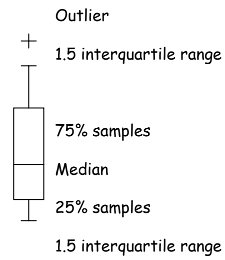

ELIMINATION OF NAPROXEN
%
120
100
80
60
40
20
0
April,25.
May,03.
May,09.
May,23.
May,30.
June,06.
July,05.
July,12.
July,25.
August,09.
sampling days, 2006.
ELIMINATION IN MBR
ELIMINATION IN CAS

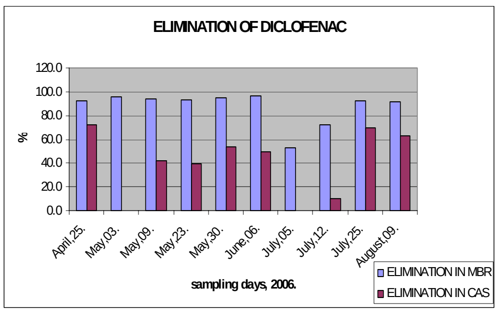

c (ppb)
16
14
12
10
8
6
4
2
0
1
influent
2
MBR effluent
3
CAS effluent

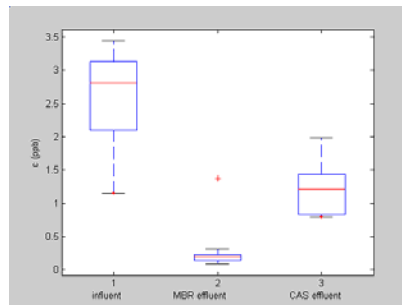

ELIMINATION OF IBUPROFEN
%
120
100
80
60
40
20
0
April,25.
May,03.
May,09.
May,23.
May,30.
June,06.
July,05.
July,12.
July,25.
August,09.
sampling days, 2006.
ELIMINATION IN MBR
ELIMINATION IN CAS


c (ppb)
18
16
14
12
10
8
6
4
2
0
1
influent
2
MBR effluent
3
CAS effluent

✓For most of the investigated compounds MBR treatment had better performance (removal rates>80%) and steadier effluent concentrations than the conventional system (e.g. diclofenac, ketoprofen, gemfibrozil, bezafibrate, ranitidine, pravastatin, ofloxacin).







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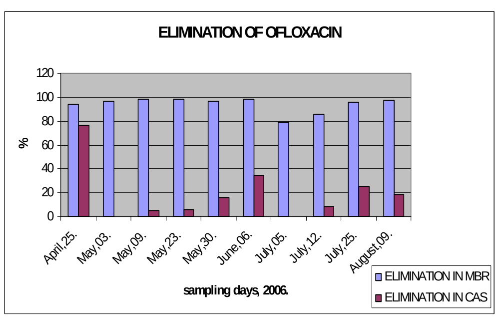
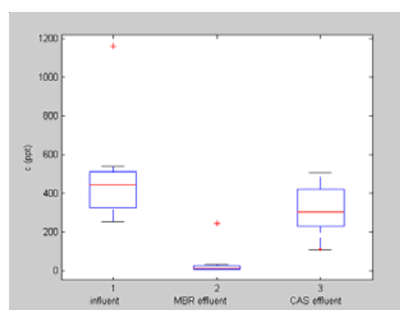
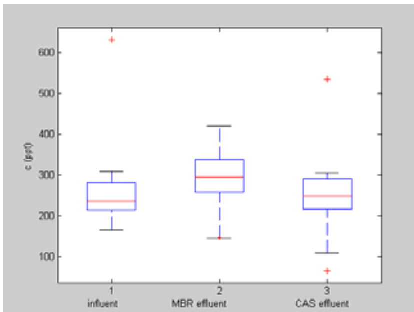


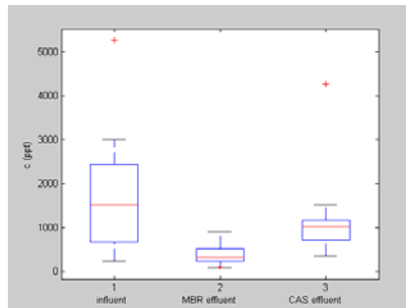


✓ The antiepileptic drug carbamazepine turned out to be the most persistent pharmaceutical as it passed both through MBR and CAS system untransformed.

Elimination of carbamazepine



Elimination of atenolol



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Compound	Elimination in MBR, %[a]	Elimination in CAS,%[b]
Analgesics and anti-inflammatory drugs		
Naproxen	99.3 (1.52) *	85.1 (11.4)
Ketoprofen	91.9 (6.55)	51.5 (22.9)
Ibuprofen	99.8 (0.386)	82.5 (15.8)
Diclofenac	87.4 (14.1)	50.1 (20.1)
Indomethacin	46.6 (23.2)	23.4 (22.3)
Acetaminophen	99.6 (0.299)	98.4 (1.72)
Mefenamic acid	74.8 (20.1)	29.4 (32.3)
Propyphenazone	64.6 (13.3)	42.7 (19.0)
Anti-ulcer agents		
Ranitidine	95.0 (3.74)	42.2 (47.0)
Psychiatric drugs		
Paroxetine	89.7 (6.69)	90.6 (4.74)
Antiepileptic drugs		
Carbamazepine	no elimination**	no elimination
Antibiotics		
Ofloxacin	94.0 (6.51)	23.8 (23.5)
Sulfamethoxazole	60.5 (33.9)	55.6 (35.4)
Erythromycin	67.3 (16.1)	23.8 (29.2)
ß-blockers		
Atenolol	65.5 (36.2)	no elimination
Metoprolol	58.7 (72.8)	no elimination
Diuretics		
Hydrochlorothiazide	66.3 (7.79)	76.3 (6.85)
Hypoglycemic agents		
Glibenclamide	47.3 (20.1)	44.5 (19.1)
Lipid regulator and cholesterol lowering statin drugs		
Gemfibrozil	89.6 (23.3)	38.8 (16.9)
Bezafibrate	95.8 (8.66)	48.4 (33.8)
Clofibric acid	71.8 (30.9)	27.7 (46.9)
Pravastatin	90.8 (13.2)	61.8 (23.6)

*values are presented as average with relative standard deviation (%) in brackets, for [a]N=10 and [b]N=8 samples.
**as “no elimination” were considered all cases with elimination efficiency less than 10%.

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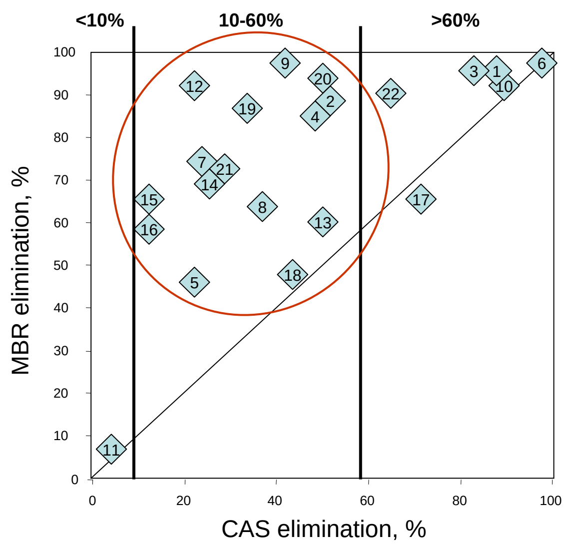
Comparison of CAS and MBR performances – elimination of pharmaceutical residues



1-naproxen,
2-ketoprofen,
3-ibuprofen,
4-diclofenac,
5-indomethacin,
6-acetaminophen,
7-mefenamic acid,
8-propyphenazone,
9-ranitidine,
10- paroxetine,
11-carbamazepine,
12- ofloxacin,
13- sulfamethoxazole,
14- erythromycin,
15- atenolol,
16- metoprolol,
17- hydrochlorothiazide,
18- glibenclamide,
19- gemfibrozil,
20- bezafibrate,
21- clofibric acid,
22- pravastatin

Case study (2): elimination of pharmaceuticals in wastewater treatment plant (WWTP) Terrassa, Spain

- full scale CAS treatment,
- two pilot scale MBR treatments

Wastewater treatment plant (WWTP) Terrassa

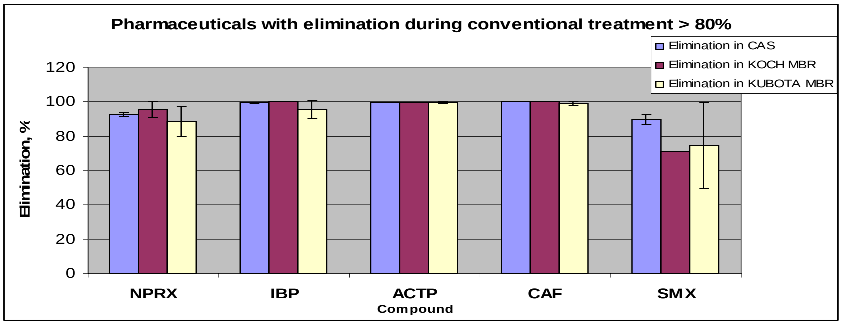
- Influent type: industrial (mostly pharmaceutical and textile industry)/ municipal wastewater
- Equivalent inhabitants: 277 000
- Average daily flow: 2 000 m^3/h
- Maximum daily flow: 2 500 m^3/h
- Hydraulic retention time: 11.5 h
- Solids retention time: 12 days
- Treatment:
  1. **Preliminary treatment**
  2. **Primary treatment**
  3. **Secondary treatment** (pre-denitrification and nitrification).

Pilot scale MBRs with external membrane module:
plate-and-frame vs. hollow-fibre membranes

MBR	KUBOTA	KOCH
Configuration	External membrane module	External membrane module
Membrane type	Plate-and-frame	Hollow fibre
Membrane surface active area (m^2)	40	30
Nominal porosity (µm)	0.4 (MF)	0.05 (UF)
Volume (m^3)	4.69	3.6
Flow ($L\ m^{-2}\ h^{-1}$)	10-20	17
HRT (h)	10-20	7.2
SRT	infinite	infinite

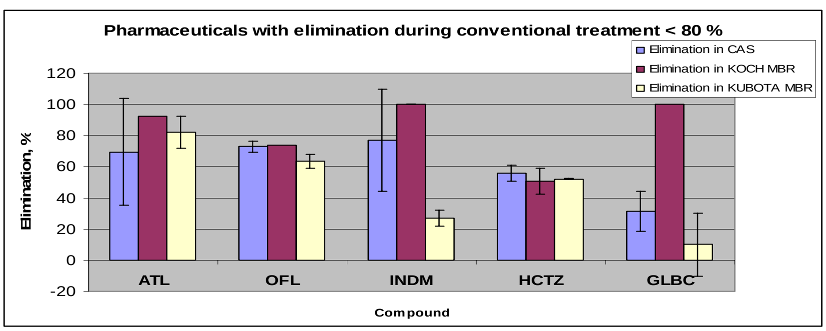
✓ Two pilot-scale membrane bioreactors are operating in parallel to a conventional activated sludge proces.

Elimination of target compounds in CAS and two pilot-plant MBRs in WWTP Terrassa



NPRX: Naproxen, Influent conc. range= 3.9-5 µg/ L.
IBP: Ibuprofen, Influent conc. range= 51-57 µg/ L.
ACTP: Acetaminophen, Influent conc. range= 35-36 µg/ L.
CAF: Caffeine, Influent conc. range= 3.5-5.9 µg/ L.
SMX: Sulfamethoxazole, Influent conc. range= 1.4-1.6 µg/ L.

Elimination of target compounds in CAS and two pilot-plant MBRs in WWTP Terrassa



ATL: Atenolol, Influent conc. range=1.2-1.6 µg/ L.
OFL: Ofloxacin, Influent conc. range= 2.1-3.0 µg/ L.
INDM: Indomethacin, Influent conc. range= 42-98 ng/ L.
HCTZ: Hydrochlorothiazide, Influent conc. range= 2.9-5.0 µg/ L.
GLBC: Glibenclamide, Influent conc. range= 130-295 ng/ L.

Conclusions (I):

- ✓ **Several pharmaceuticals (e.g. ibuprofen, naproxen, acetaminophen, ketoprofen, diclofenac, bezafibrate, gemfibrozil, ranitidine, ofloxacin, hydrochlorothiazide and paroxetine) with high attenuation rates can be expected to be completely removed from wastewater during membrane treatments by sorption, degradation or combination of both.**

- ✓ **Some substances were not removed neither in MBR nor in CAS process (e.g. carbamazepine).**

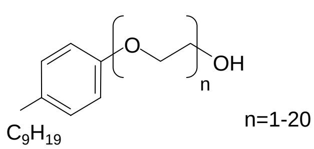
- ✓ **Performances of two types of MBR configuration, plate-and-frame and hollow fiber, were very similar for most of the pharmaceutical residues detected. Only for indomethacine and glibenclamide significantly higher reduction was noted for KOCH hollow fiber MBR.**

- ✓ **Range of variation of removal rates of MBR system was small for most of the compounds, while in the conventional treatment stronger fluctuations were observed and it turned out to be a lot more sensitive to changes in operational parameters (temperature, flow rate, etc).**

- ✓ **Further studies on the occurrence and fate of selected compounds in pilot-scale membrane bioreactors will be conducted, which will provide additional information on the behavior of these compounds during advanced membrane wastewater treatments.**

Example: Non ionic surfactants

Alkylphenol ethoxylates



Nonylphenol ethoxylates (NPEOs)

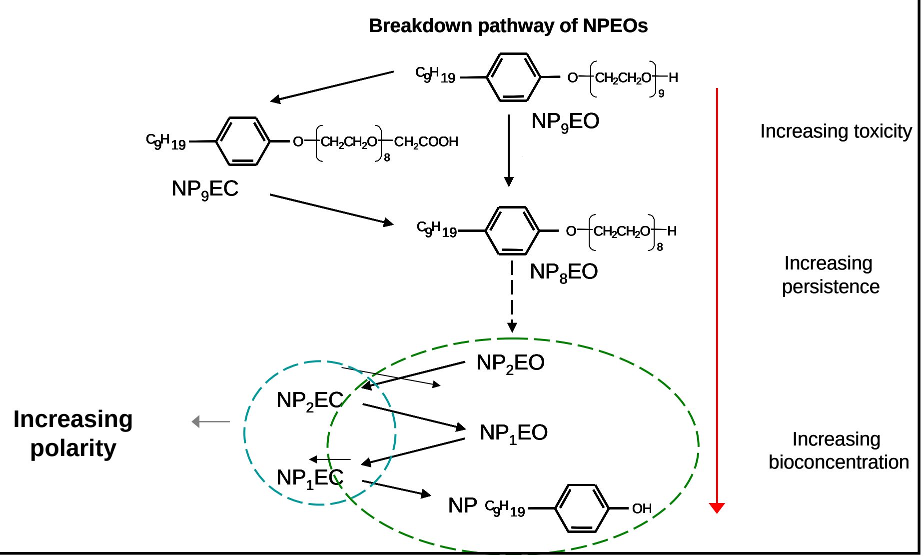
- **Non-ionic surfactants**
  industrial formulation (textile, tannery, pulp and paper industries)
- **Pesticides adjuvants**
- **Paint ingredients**
- **Wetting agents**

- Global production is well over 500.000 tons
- Use restricted in many countries
- Throughout northern Europe (Scandinavian countries, England, Germany) a voluntary ban on NPEO use in household cleaning products began in 1995, and restrictions on industrial cleaning applications in 2000
- Spain – use in industrial formulations **not restricted**

Main concern:

Poor ultimate biodegradability

Reproductive toxicity of some degradation products



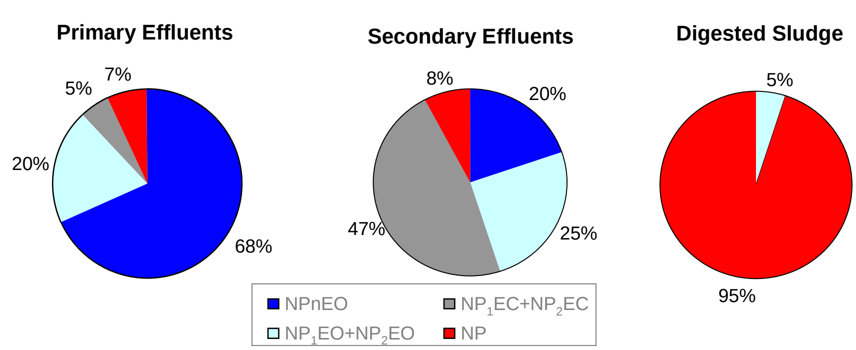
Breakdown during sewage treatment (AST)

(according Ahel, *Wat. Res. 1995*)

Ultimate biodegradation of NPEOs <40%

40-45% ends up in secondary effluent

20 % in sludge



Concentration levels in WWTP effluents

Compound	Secondary effluent (µg/L)	Sludge (mg/kg)
NPEO	**<LOD-**60 **up to 330***	10-2400
NPEC	**1-**115 **up to 1120***	**<LOD-**65
NP	**<LOD-**33 **up to 225***	**<LOD-**825
CAPEC	**levels of 10-40 µg/L**	**No data**

* WWTP receiving industrial WW

The relative estrogenic potency (relative to 17b-estradiol) *in-vitro*
(according Jobling and Sumpter, *Aquatic. Toxicol. 1993*)

NP	9.0 x 10-6
OP	3.7 x 10-5
NP1EC	6.3 x 10-6
NP2EO	6.0 x 10-6
NP10EO	2.0 x 10-7

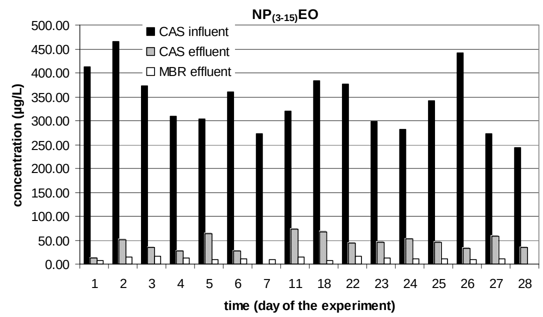
Biologically active concentrations: as low as **1-20 µg/L**

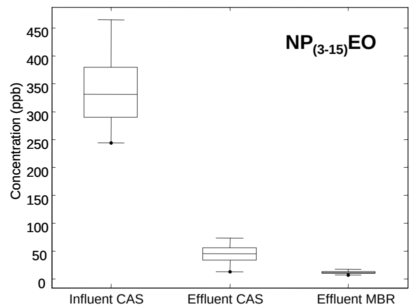
Source: Knepper, Barcelo, de Voogt (Eds) Analysis and fate of surfactants in the aquatic environment, Elsevier 2003

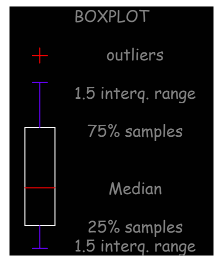
Case study (3): elimination of surfactants in wastewater treatment plant (WWTP) Rubí, Spain

- full scale CAS treatment,
- laboratory scale MBR treatment

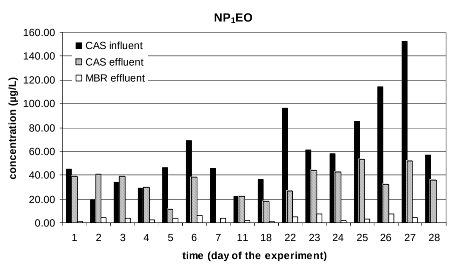
Long ethoxy chain NPEO

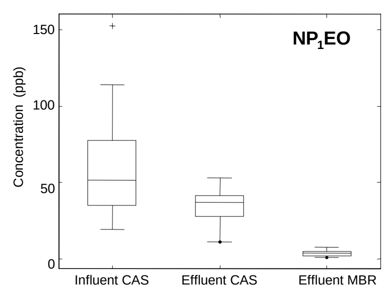


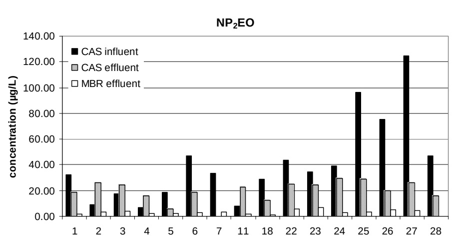


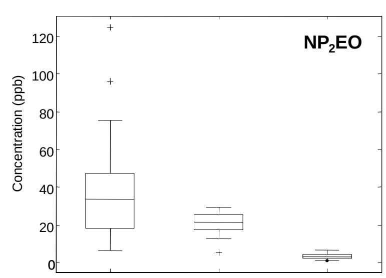


Short ethoxy chain NPEO

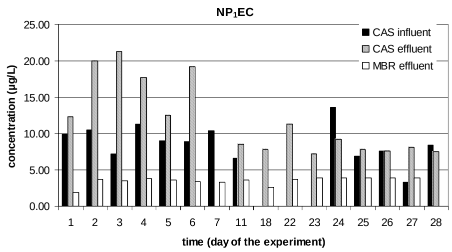


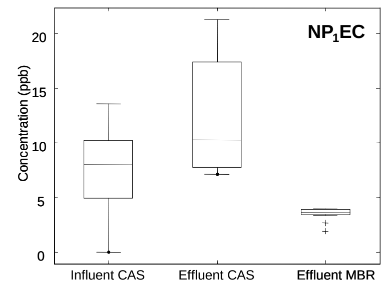


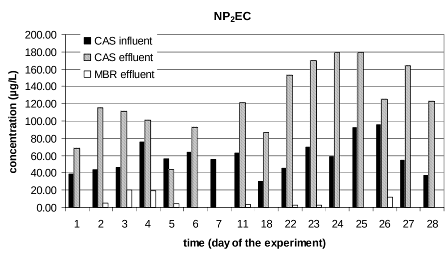


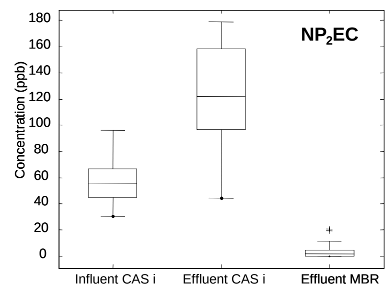


Nonylphenoxy carboxylates

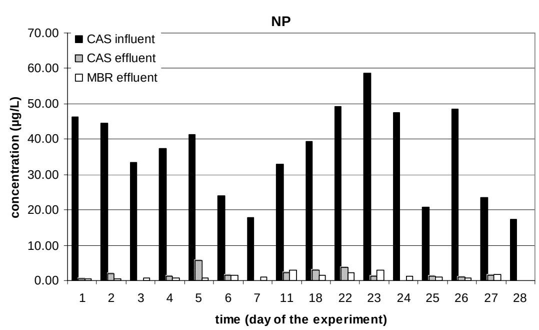


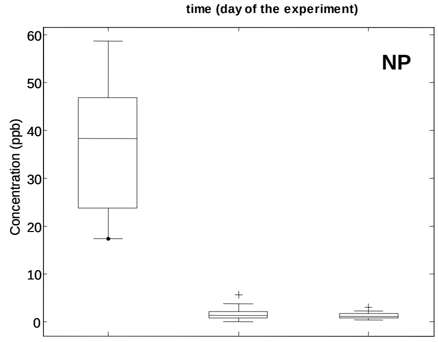




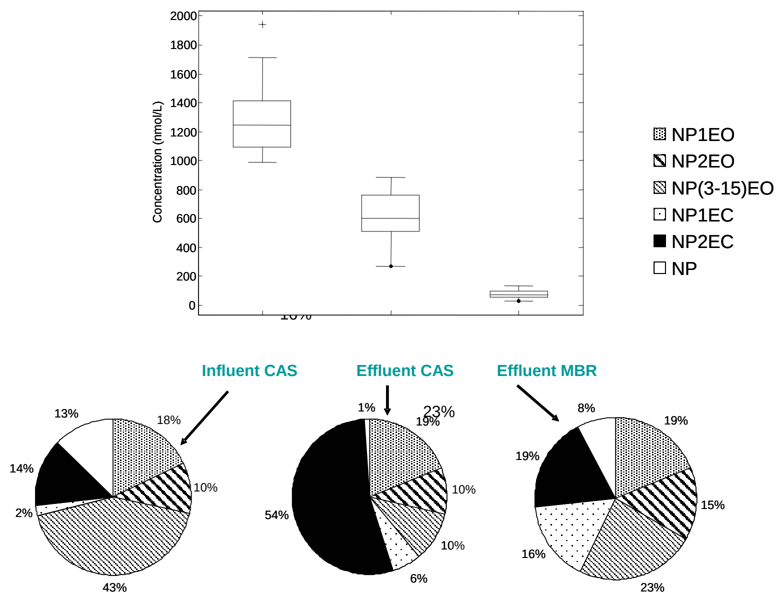


Nonylphenol

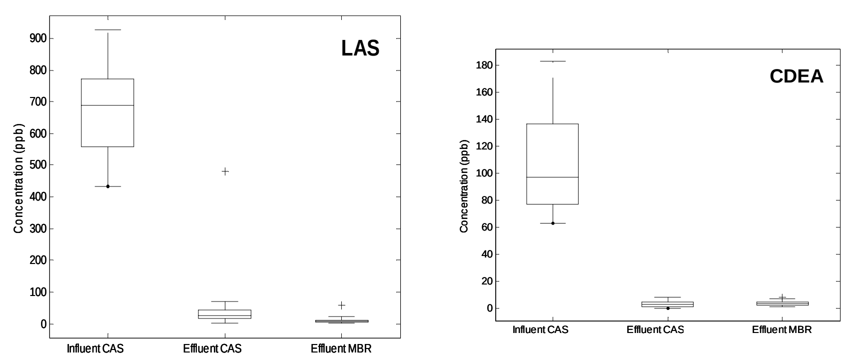




Total nonylphenolic compounds



LAS and CDEA



Conclusions (II)

- MBR treatment retained and degraded alkyphenolic compounds with an overall **efficiency of 94%,** which represented a significant improvement in comparison to the CAS treatment where **only 54%** of the total nonylphenolic compounds were removed.
- MBR is very efficient in removal of **acidic metabolites** (NP1EC and NP2EC) which are the most abundant biodegradation products formed in CAS.

Acknowledgements

This work has been supported by:

EU project **EMCO** (INCO CT 2004-509188)
(Reduction of environmental risks, posed by Emerging Contaminants, through advanced treatment of municipal and industrial wastes)

EU project AquaTerra (GOCE-CT-505428)
Integrated modelling of the river-sediment-soil-groundwater system; Advanced tools for the management of catchment areas and river basins in the context of global change

Spanish Ministerio de Ciencia y Tecnologia
Project CTM2004-06255-CO3-01