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 disadvantages
• Case study (I)
  – elimination of pharmaceuticals in a laboratory scale MBR (vs CAS)
• Case study (II)
  – elimination of pharmaceuticals 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 with internal vacuum driven membrane filtration

External MBR with external pressure driven membrane filtration

Submerged MBR:
- Primary Treated Wastewater
- Aeration Basin
- Solids Recycle
- Waste Activated Sludge
- Equation: \( Q_R = 3-5 \cdot Q \)

External MBR:
- Primary Treated Wastewater
- Aeration Basin
- Solids Recycle
- Waste Activated Sludge
- Equation: \( Q_R = 20-30 \cdot Q \)
**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).

A layer of proteins and cellular material in the membrane surface change the porosity into \( \approx 0,01 \, \mu m \): Range of filtration change into ULTRAFILTRATION.
**Types of membranes**

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiral wound membrane</td>
<td>NF/RO</td>
</tr>
<tr>
<td>Hollow fibre membrane</td>
<td>MF/UF</td>
</tr>
<tr>
<td>Plate &amp; frame membrane</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>Membrane for nanofiltration</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>(NF) and reverse osmosys (RO)</td>
<td>Microfiltration</td>
</tr>
</tbody>
</table>

**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 m³/h
Maximum daily flow: 1 800 m³/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)

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 membranes (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.


<table>
<thead>
<tr>
<th>Effluent</th>
<th>COD, (mg/l) (C.V.%)</th>
<th>TSS (mg/l) (C.V.%)</th>
<th>NH₄⁺ (mg/l) (C.V.%)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR</td>
<td>42.7 (± 23.3)</td>
<td>7.1 (± 74.85)</td>
<td>8.3 (± 42.4)</td>
<td>7.43</td>
</tr>
<tr>
<td>CAS</td>
<td>80.7 (± 30.3)</td>
<td>24 (± 37.4)</td>
<td>17.8 (± 39.6)</td>
<td>7.27</td>
</tr>
<tr>
<td>Legislation</td>
<td>125</td>
<td>35</td>
<td>25</td>
<td>6-9</td>
</tr>
</tbody>
</table>

COMPARATION OF BASIC PARAMETERS
MBR (72.2 ± 11.7 %)

CAS WWTP (58.90 ± 23.8 %)

Target compounds monitored

<table>
<thead>
<tr>
<th>CLASS</th>
<th>Compounds</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANALGESICS AND ANTI-INFLAMMATORY DRUGS</td>
<td>ibuprofen, indomethacin, ketoprofen, naproxen, diclofenac</td>
<td>To relieve pain, inflammation and fever</td>
</tr>
<tr>
<td>ANTI-ULCER AGENTS</td>
<td>lansoprazole</td>
<td>To prevent and treat ulcers</td>
</tr>
<tr>
<td>PSYCHIATRIC DRUGS</td>
<td>fluoxetine, paroxetine</td>
<td>Antidepressants</td>
</tr>
<tr>
<td>ANTIEPILEPTIC DRUGS</td>
<td>carbamazepine</td>
<td>To treat epileptic attacks</td>
</tr>
<tr>
<td>ANTIBIOTICS</td>
<td>erythromycin, azithromycin, sulfamethoxazole, trimethoprim, ofloxacin</td>
<td>Antibacterial agents</td>
</tr>
<tr>
<td>B-BLOCKERS</td>
<td>atenolol, sotalol, metoprolol, propranolol</td>
<td>Antianginal antihypertensive</td>
</tr>
<tr>
<td>DIURETICS</td>
<td>hydrochlorothiazide</td>
<td>To treat excessive fluid accumulation</td>
</tr>
<tr>
<td>HYPOGLYCAEMIC AGENTS</td>
<td>glibenclamide</td>
<td>To treat type II diabetes</td>
</tr>
<tr>
<td>LIPID REGULATOR AND CHOLESTEROL LOWERING STATIN DRUGS</td>
<td>colestipol acid, gemfibrozil, bezafibrate, pravastatin, mevastatin</td>
<td>To lower fat (lipids) level</td>
</tr>
<tr>
<td>ANTI-HISTAMINICS</td>
<td>famotidine, ranitidine, loratidine</td>
<td>To relieve allergy reactions</td>
</tr>
</tbody>
</table>
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

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

ELIMINATION OF GIBENCLAMIDE

ELIMINATION OF PAROXETINE

ELIMINATION OF NAPROXEN

ELIMINATION OF IBUPROFEN
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).

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


<table>
<thead>
<tr>
<th>Compound</th>
<th>Elimination in MBR, %a</th>
<th>Elimination in CAS, %b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Analgesics and anti-inflammatory drugs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>99.3 (1.52) *</td>
<td>85.1 (11.4)</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>91.9 (6.55)</td>
<td>51.5 (22.9)</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>99.8 (0.386)</td>
<td>82.5 (15.8)</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>87.6 (14.1)</td>
<td>50.1 (20.1)</td>
</tr>
<tr>
<td>Indomethacin</td>
<td>46.6 (23.2)</td>
<td>23.4 (22.3)</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>99.6 (0.299)</td>
<td>98.4 (1.72)</td>
</tr>
<tr>
<td>Mefenamic acid</td>
<td>74.8 (20.1)</td>
<td>29.4 (32.3)</td>
</tr>
<tr>
<td>Propyphenzone</td>
<td>64.6 (13.3)</td>
<td>42.7 (19.0)</td>
</tr>
<tr>
<td><strong>Anti-ulcer agents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ranitidine</td>
<td>95.0 (3.74)</td>
<td>42.2 (47.0)</td>
</tr>
<tr>
<td><strong>Psychotropic drugs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paroxetine</td>
<td>89.7 (6.69)</td>
<td>90.6 (4.74)</td>
</tr>
<tr>
<td><strong>Antiepileptic drugs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>no elimination**</td>
<td>no elimination</td>
</tr>
<tr>
<td><strong>Antibiotics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ofloxacine</td>
<td>94.0 (6.51)</td>
<td>23.8 (23.5)</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>60.5 (33.9)</td>
<td>55.6 (35.4)</td>
</tr>
<tr>
<td>Erythromycin</td>
<td>67.3 (16.1)</td>
<td>23.8 (29.2)</td>
</tr>
<tr>
<td><strong>β-blockers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atenolol</td>
<td>65.5 (36.2)</td>
<td>no elimination</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>58.7 (72.8)</td>
<td>no elimination</td>
</tr>
<tr>
<td><strong>Diuretics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrochlorothiazide</td>
<td>66.3 (7.79)</td>
<td>76.3 (6.65)</td>
</tr>
<tr>
<td><strong>Hypoglycemic agents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glibenclamide</td>
<td>47.3 (20.1)</td>
<td>44.5 (19.1)</td>
</tr>
<tr>
<td><strong>Lipid regulator and cholesterol lowering statin drugs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>86.6 (23.3)</td>
<td>38.8 (16.9)</td>
</tr>
<tr>
<td>Bezafibrate</td>
<td>95.8 (8.66)</td>
<td>49.4 (33.8)</td>
</tr>
<tr>
<td>Cilostaric acid</td>
<td>71.8 (30.9)</td>
<td>27.7 (46.9)</td>
</tr>
<tr>
<td>Pravastatin</td>
<td>90.8 (13.2)</td>
<td>61.8 (23.6)</td>
</tr>
</tbody>
</table>

*values are presented as average with relative standard deviation (%) in brackets, for *N=10 and *N=8 samples.

**as “no elimination” were considered all cases with elimination efficiency less than 10%.

Comparison of CAS and MBR performances – elimination of pharmaceutical residues

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 m³/h
- **Maximum daily flow**: 2,500 m³/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

<table>
<thead>
<tr>
<th>MBR</th>
<th>KUBOTA</th>
<th>KOCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration</td>
<td>External membrane module</td>
<td>External membrane module</td>
</tr>
<tr>
<td>Membrane type</td>
<td>Plate-and-frame</td>
<td>Hollow fibre</td>
</tr>
<tr>
<td>Membrane surface active area (m²)</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>Nominal porosity (µm)</td>
<td>0.4 (MF)</td>
<td>0.05 (UF)</td>
</tr>
<tr>
<td>Volume (m³)</td>
<td>4.69</td>
<td>3.6</td>
</tr>
<tr>
<td>Flow (L m⁻² h⁻¹)</td>
<td>10-20</td>
<td>17</td>
</tr>
<tr>
<td>HRT (h)</td>
<td>10-20</td>
<td>7.2</td>
</tr>
<tr>
<td>SRT</td>
<td>infinite</td>
<td>infinite</td>
</tr>
</tbody>
</table>

- ✔ Two pilot-scale membrane bioreactors are operating in parallel to a conventional activated sludge process.
Elimination of target compounds in CAS and two pilot-plant MBRs in WWTP Terrassa

Pharmaceuticals with elimination during conventional treatment > 80%

- **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

Pharmaceuticals with elimination during conventional treatment < 80%

- **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 indomethacin and glibencamide 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

- 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 pathway of NPEOs

Increasing toxicity
Increasing persistence
Increasing bioconcentration
Increasing polarity

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Secondary effluent (µg/L)</th>
<th>Sludge (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPEO</td>
<td>&lt;LOD-80 up to 330*</td>
<td>10-2400</td>
</tr>
<tr>
<td>NPEC</td>
<td>1-115 up to 1120*</td>
<td>&lt;LOD-65</td>
</tr>
<tr>
<td>NP</td>
<td>&lt;LOD-33 up to 225*</td>
<td>&lt;LOD-825</td>
</tr>
<tr>
<td>CAPEC</td>
<td>levels of 10-40 µg/L</td>
<td>No data</td>
</tr>
</tbody>
</table>

* WWTP receiving industrial WW

The relative estrogenic potency (relative to 17β-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.

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