Elimination of emerging contaminants (pharmaceuticals) by membrane bioreactor (MBR)

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Outline

✓ Introduction on MBR
  • types of membranes
  • types of bioreactors
  • advantages and disadvantages

✓ Case study (1)
  • elimination of pharmaceuticals in a laboratory scale MBR (vs CAS)

✓ Case study (2)
  • elimination of pharmaceuticals in a pilot scale MBR (vs CAS)
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.
Microfiltration

Ultrafiltration

The pore size of membranes used in wastewater treatment by MBR is usually 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
External MBR

Side-stream MBR with external pressure driven membrane filtration

Introduction on MBR

Side-stream MBR with external pressure driven membrane filtration

Aeration Basin

Primary Treated Wastewater

Solids Recycle

$Q_R = 20-30 \times Q$

Effluent

Waste Activated Sludge
Submerged MBR

Submerged MBR with internal vacuum driven membrane filtration

$Q_R = 3.5 \times Q$

Effluent
The more common configuration is this one, with immersed membranes, although a side-stream one is also used (it has higher energy consumption).
CID, 20/11/2007
Configurations most frequently used in wastewater treatment are hollow fiber (HF) and flat sheet (FS) MBR.
Introduction on MBR

Why MBR?

✓ Direct separation of suspended solids by membrane, with a complete removal of all contaminants bound to colloids and particulate matter (100% of turbidity removal).

✓ Enhanced phosphorus removal can be achieved by intermittent aeration of the MBR.

✓ Complete removal of bacteria and high removal of phages, spores and viruses (biofilm formed on the membrane surface decreases the effective pore size to the UF range!).

✓ Increased solids retention time (SRT)

The higher the biomass concentrations is, the lower the sludge loading, i.e. Food to Microorganisms (F/M) ratio becomes lower (gCOD gTSS⁻¹ day⁻¹). When the sludge loading becomes low enough, little or no excess sludge is produced.

Long SRTs applied in MBR prevent nitrifying bacteria from being washed out from the bioreactor, thus improving the nitrification capability of activated sludge.

→ Enhanced removal of organic micropollutants with longer SRT!

Higher sludge ages that are accomplished by high SRTs allow more complete mineralization of raw water organics (usually 90%), but also adaptation of microorganisms to less degradable compounds.

Higher sludge age means smaller sludge particles, i.e. greater specific surface, thus improved adsorption to biosolids.
Dado que el crecimiento celular de las bacterias nitrificantes es muy lento, la nitrificación es normalmente lo que limita la velocidad del proceso biológico de tratamiento de agua residual. Eliminación de materias en suspensión y de materia orgánica expresada como demanda química de oxígeno (COD) son prácticamente independientes del tiempo de retención de sólidos (SRT).

CID, 16/01/2008
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): ~3 months.
Nominal porosity: 0.4 µm (MF)
Effective porosity: in the range of UF
Kubota flat sheet membranes (chlorinated poliethilen): 2 A4embranes (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.

## COMPARATION OF BASIC PARAMETERS

<table>
<thead>
<tr>
<th>Effluent</th>
<th>COD, (mg/l) (C.V.%)</th>
<th>TSS, (mg/l) (C.V.%)</th>
<th>NH$_4^+$, (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>
<tr>
<td>Category</td>
<td>Compounds</td>
<td>Uses</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>------------------------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ANALGESICS AND ANTI-INFLAMMATORY DRUGS</strong></td>
<td>Ibuprofen, Indomethacin, Ketoprofen, Acetaminophen, Naproxen, Mefenamic acid, Diclofenac, Propyphenazone</td>
<td>To relieve pain, inflammation and fever</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ANTI-ULCER AGENTS</strong></td>
<td>Lansoprazole</td>
<td>To prevent and treat ulcers</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>PSYCHIATRIC DRUGS</strong></td>
<td>Fluoxetine, Paroxetine</td>
<td>Antidepressants</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ANTIEPILEPTIC DRUGS</strong></td>
<td>Carbamazepine</td>
<td>To treat epileptic attacks</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ANTIBIOTICS</strong></td>
<td>Erythromycin, Azithromycin, Sulfamethoxazole, Trimethoprim, Ofloxacin</td>
<td>Antibacterial agents</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>B-BLOCKERS</strong></td>
<td>Atenolol, Sotalol, Metoprolol, Propranolol</td>
<td>Antianginal antihypertensive</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DIURETICS</strong></td>
<td>Hydrochlorothiazide</td>
<td>To treat excessive fluid accumulation</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HYPOGLYCAEMIC AGENTS</strong></td>
<td>Glibenclamide</td>
<td>To treat type II diabetes</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LIPID REGULATOR AND CHOLESTEROL LOWERING STATIN DRUGS</strong></td>
<td>Clofibric acid, Gemfibrozil, Bezafibrate, Pravastatin, Mevastatin</td>
<td>To lower fat (lipids) level</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ANTI-HISTAMINICS</strong></td>
<td>Famotidine, Ranitidine, Loratidine</td>
<td>To relieve allergy reactions</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Case study (1)

Results of the case study (1):

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

Case study (1)

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

Elimination of acetaminophen

~100 % removal

Elimination of hydrochlorothiazide

~70 % removal

✓ Case study (1)

**Elimination of Naproxen**

- Sampling days, 2006.
- ~93% removal

**Elimination of Ibuprofen**

- Sampling days, 2006.
- ~90% removal
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).

✓ Case study (1)

**Elimination of Ofloxacine**

![Graph showing elimination of Ofloxacine over different sampling days, 2006.]

**Elimination of Bezafibrate**

![Graph showing elimination of Bezafibrate over different sampling days, 2006.]

**Case study (1)**

- **April, 25, 2006:**
  - Sample Day: 25 April, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **May, 03, 2006:**
  - Sample Day: 03 May, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **May, 09, 2006:**
  - Sample Day: 09 May, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **May, 23, 2006:**
  - Sample Day: 23 May, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **May, 30, 2006:**
  - Sample Day: 30 May, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **June, 06, 2006:**
  - Sample Day: 06 June, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **July, 05, 2006:**
  - Sample Day: 05 July, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **July, 12, 2006:**
  - Sample Day: 12 July, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **July, 25, 2006:**
  - Sample Day: 25 July, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%

- **August, 09, 2006:**
  - Sample Day: 09 August, 2006
  - Elimination in MBR: 24%
  - Elimination in CAS: 94%
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

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Comparison of CAS and MBR performances – elimination of pharmaceutical residues

Case study (1)

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-clofibrac acid, 22-pravastatin
On one side, compounds that are very well removed in CAS (e.g. ibuprofen, naproxen etc.) are also successfully eliminated in MBR. The same goes for poorly degradable compounds, such as carbamazepine (less than 10% elimination). On the other side, the study showed that removal of pharmaceutical residues that are not so readily degraded in CAS treatment (e.g. atenolol, metoprolol, mfenamic acid, gemfibrozil, etc.) can be enhanced by applying MBR technology. They are removed from wastewater during membrane treatment by sorption, degradation or combination of both. Better removal of readily biodegradable micropollutants in the MBR could be due to smaller flock size of sludge, which enhances mass transfer by diffusion and therefore increases the elimination. Considering the composition of sludge originating from a membrane bioreactor (specialized microorganisms, large portion of active biomass in suspended solids) improved removal is to be expected. In general, no relationship has been found so far between the structures of micropollutants and their removal during wastewater treatments.

CID, 20/11/2007
Case study (2): elimination of pharmaceuticals in wastewater treatment plant (WWTP) Terrassa, Spain

- full scale CAS treatment,
- two pilot scale MBR treatments
Case study (2)

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).
**Case study (2)**

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 (Flat sheet)</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>2 months</td>
<td>2 months</td>
</tr>
</tbody>
</table>

Two pilot-scale membrane bioreactors are operating in parallel to a conventional activated sludge process.
**Compounds with MBR removal (Koch+Kubota), R ≥ 75 %**

- **Lab-scale MBR**: 94.0 % (RSD 6.5)
- **CAS Rubí**: 23.8 % (RSD 23.5)
- **CAS Terrassa**: 67.4 % (RSD 33.7)

- **Lab-scale MBR**: 47.3 % (RSD 20.1)
- **CAS Rubí**: 44.5 % (RSD 19.1)
- **FS Kubota**: 89 % (RSD:16.7)
- **HF Koch**: 95 % (RSD: 7.7)

**Case study (2)**

ACTP-acetaminophen
SMX-sulfamethoxazole
OFL-ofloxacin
PVST-pravastatin
GLBC-glibenclamide
NPX-naproxen
IBP-ibuprofen
**Case study (2)**

**Compounds with MBR removal (Koch+Kubota), 50 ≤ R < 75 %**

**CAS Rubí: no elimination**

CAS Terrassa: 56.9 % (RSD 22.8)

CAS Rubí: no elimination

CAS Terrassa: 60.1 % (RSD 22.3)

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**Bar Graph**

- **ATL-atenolol**
- **RNTD-ranitidine**
- **FMTD-famotidine**
- **MTPL-metoprolol**
- **TMP-trimethoprim**
- **PPZ-propyphenazone**
- **LRTD-loratidine**
- **MF AC-mefenamic acid**
- **BZF-bezafibrate**

**Legend**

- CAS
- HF KOCH MBR
- FS KUBOTA MBR
IN RED: cases where elimination in CAS Terrassa is better than in CAS Rubi
CID, 31/03/2008
Case study (2)

Compounds with MBR removal (Koch+Kubota), $50 \leq R < 75\%$

**Lab-scale MBR: 95.0 % (RSD 3.7)**
- FS Kubota: 51.4 % (RSD 33.0)
- HF Koch: 61.5 % (RSD 20.4)

**Lab-scale MBR: 95.8 % (RSD 8.6)**
- FS Kubota: 75.4 % (RSD 13.8)
- HF Koch: 72.6 % (RSD 18.0)

**CHEMICALS**
- ATL-atenolol
- RNTD-ranitidine
- FMTD-famotidine
- MTPL-metoprolol
- TMP-trimethoprim
- PPZ-propyphenazone
- LRTD-loratidine
- MF AC-mefenamic acid
- BZF-bezafibrate
IN RED: cases where elimination in lab-scale MBR is greater than in pilot-scale MBRs
CID, 31/03/2008
Compounds with MBR removal (Koch+Kubota), R < 50 %

Lab-scale MBR: 67.3 % (RSD 16.1)
CAS Rubí: 23.8 % (RSD 23.5)

Lab-scale MBR: 87.4 % (RSD 14.1)
CAS Rubí: 50.1 % (RSD 20.1)

NEGATIVE REMOVAL

FS Kubota: 31.5 % (RSD 38.3)
HF Koch: 21.7 % (RSD 51.3)
CAS Terrassa: 8.5 % (RSD 47.2)

STL-sotalol
CBZP-carbamazepine
PPL-propranolol
ERTR-erythromycin
HCTZ-hydrochlorothiazide
KTP-ketoprofen
GMFB-gemfibrozil
DCF-diclofenac
INDM-indomethacine
Case study (2)

Compounds with MBR removal (Koch+Kubota), R < 50%

Lab-scale MBR: 66.3 % (RSD 7.7%)
CAS Rubí: 76.3 % (RSD 6.8)

NO REMOVAL

- STL-sotalol
- CBZP-carbamazepine
- PPL-propranolol
- ERTR-erythromycin
- HCTZ-hydrochlorothiazide
- KTP-ketoprofen
- GMFB-gemfibrozil
- DCF-diclofenac
- INDM-indomethacine
Conclusions from case studies (1,2):

Comparision of LAB-SCALE MBR and PILOT-SCALE MBRs:

✓ Several pharmaceuticals (e.g., ibuprofen, naproxen, acetaminophen, ranitidine, bezafibrate, ofloxacin, atenolol) with high attenuation rates ($R \geq 75\%$) in both laboratory-scale and pilot-scale MBRs can be expected to be completely removed from wastewater during membrane treatments by sorption, degradation or combination of both. The eliminations of these and most of other compounds were always better in MBR than in CAS treatment.

✓ In pilot-scale Koch and Kubota MBRs glibenclamide, pravastatin and sulfamethoxazole were efficiently removed ($R \geq 75\%$), whereas their eliminations were lower in laboratory-scale MBR ($R=47$-$62\%$).

✓ Compounds that were better removed in laboratory-scale MBR than in pilot-scale MBRs were ketoprofen, ranitidine, bezafibrate, gemfibrozil, diclofenac, and erythromycin. This was probably a consequence of a very long SRT applied in a laboratory-scale MBR, whereas in pilot-scale MBRs SRT was shorter and sludge more “stressed” due to frequent sludge wasting and dilution, additions of anti-foaming and anti-fouling agents.

✓ Performances of two types of MBR configuration, flat-sheet and hollow fiber, were very similar for most of the pharmaceutical residues detected. Famotidine, ranitidine, propranolol, and atenolol were better removed by HF Koch MBR than by FS Kubota MBR. This could be explained by more complex foaming problems exhibited in MBR with flat sheet membranes.
Comparision of two full-scale CAS treatments:

✓ Some substances were not removed in any of the full-scale CAS treatments (e.g., carbamazepine, erythromycin).

✓ Other were not removed in full-scale CAS in WWTP Rubí (e.g., atenolol, metoprolol, indomethacin, and ofloxacin), but they were removed in CAS at WWTP Terrassa (50-67 %). This was again probably a consequence of longer SRT applied in WWTP Terrassa when compared to WWTP Rubí (i.e., 12 days vs. 3 days).

✓ Generally, pharmaceuticals were better eliminated in CAS at WWTP Terrassa. However, hydrochlorothiazide and diclofenac were better eliminated in CAS at WWTP Rubí. There is no plausible explanation for this. Also, literature data on the elimination of diclofenac is very variable (0-69 %).
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Thank you for your attention!