

Role of Membranes and Activated Carbon in the Removal of Endocrine Disruptors and Pharmaceuticals during Water Treatment Processes

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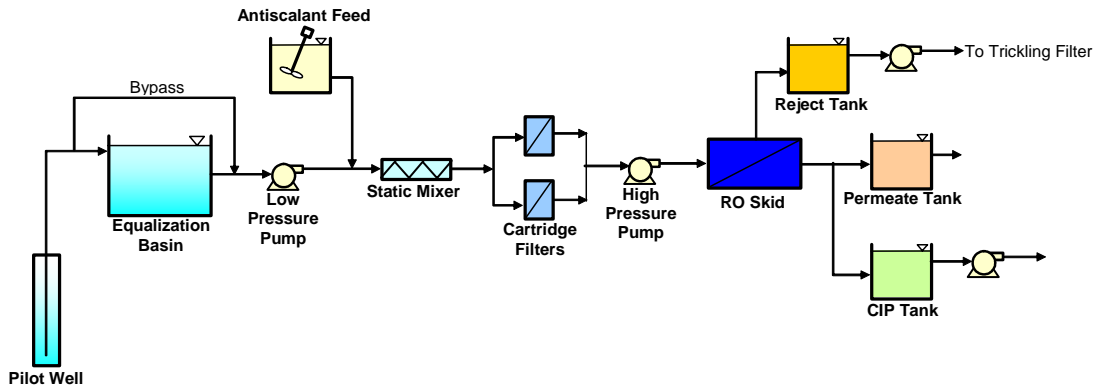
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Introduction: As part of an American Water Works Association Research Foundation (AwwaRF) research project to evaluate conventional and advanced treatment processes for the removal of endocrine disruptors and pharmaceuticals (Project #2758), several experiments were conducted using membranes and activated carbon. A series of dynamic flow-through membrane experiments were performed at pilot- and full-scale to determine the removal of micropollutants. Various membrane configurations were investigated including: reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF), electro dialysis reversal (EDR), and membrane bioreactors. Activated carbon tests were performed at bench-scale using both powdered activated carbon (PAC) and granular activated carbon (GAC). Several full-scale plants were also evaluated as a comparison to predictions from pilot-scale. In general, observations at pilot-scale agreed well with full-scale measurements.

Methods and Observations: The process schematic of an RO Pilot using a shallow saline aquifer is shown in Figure 1. A well was drilled to supply groundwater for the pilot plant. Feedwater was pumped from the equalization basin by a low-pressure pump and dosed with antiscalant ahead of a static mixer. Initial testing for EDC and pharmaceutical target compounds indicated that only one or two compounds were present in the saline groundwater. Therefore, the equalization basin was used as a head tank where target contaminants were spiked and thoroughly mixed before pumping the spiked water through the RO system.

Figure 1. Saline Groundwater RO Pilot Plant Schematic



After the static mixer, the feedwater was filtered through two 5- μm cartridge filters to protect the membranes from damage by debris. After filtration, the feed pressure was boosted by the high-pressure pump for delivery to the first stage of the RO skid. A bypass line on the suction side of the high pressure pump made it possible to bypass the RO skid during initial startup and at any other time when the feed water condition or debris in the feed lines necessitated bypass of the RO membranes.

RO permeate was discharged to a permeate holding tank and used for membrane cleaning and flushing procedures. During normal operation, permeate was discharged to the permeate tank continually. A constant level was maintained in the permeate tank by an overflow orifice, and overflow permeate was discharged by gravity flow to a reject tank.

The pilot skid contained two stages of pressure vessels in a 2:2:1:1 array, as shown in Figure 1. Each vessel contained three 4-inch diameter, 40-inch long RO elements. The elements were Koch model TFC-HR, thin film composite (TFC) polyamide elements. The first stage included the first two pairs of pressure vessels in series and the second stage comprised the last two vessels in series. Flux and recovery were controlled automatically by the operator from a central control panel.

Results from the spiking study using virgin membranes and fouled membranes are shown in Tables 1 & 2. From these data, it appears that all target analytes were well rejected and that membrane fouling played a minimal role in removal. Interestingly, the anti-scalant appeared to removal a significant portion of the phenolic steroids (i.e., estradiol, estrone, ethinylestradiol)

Table 1. RO Removal using Virgin Membranes

| | Feed Tank Post Spike | CF (After cartridge, anti-scale) | FD (Brine recycle) | Final Permeate |
|------------------|----------------------|----------------------------------|--------------------|----------------|
| Analyte | ppt | ppt | ppt | ppt |
| Trimethoprim | 265 | 294 | 268 | <25 |
| Caffeine | 311 | 324 | 344 | 52 |
| Fluoxetine | 263 | 284 | 499 | <25 |
| Pentoxifylline | 458 | 483 | 471 | 45 |
| Dilantin | 259 | 275 | 287 | <25 |
| Oxybenzone | 218 | 176 | 192 | <25 |
| Estriol | 128 | 78 | 58 | <25 |
| Ethinylestradiol | 125 | 65 | 58 | <25 |
| Estrone | 167 | 57 | 78 | <25 |
| Estradiol | 125 | 66 | 57 | <25 |
| Progesterone | 285 | 324 | 312 | <25 |
| Androstenedione | 284 | 306 | 315 | <25 |
| Iopromide | 165 | 170 | 158 | <25 |
| Naproxen | 118 | 129 | 119 | <25 |
| Ibuprofen | 259 | 244 | 251 | <25 |
| Diclofenac | 26 | 32 | 31 | <25 |
| Triclosan | 246 | 185 | 180 | <25 |
| Gemfibrozil | 230 | 211 | 218 | <25 |

Table 2. RO Removal using Fouled Membranes

| | Feed Tank Post Spike | CF (After cartridge, anti-scale) | FD (Brine recycle) | Final Permeate |
|------------------|----------------------|----------------------------------|--------------------|----------------|
| Analyte | ppt | ppt | ppt | ppt |
| Trimethoprim | 278 | 309 | 371 | <25 |
| Caffeine | 196 | 193 | 219 | <25 |
| Fluoxetine | 564 | 441 | 451 | <25 |
| Pentoxifylline | 169 | 154 | 160 | <25 |
| Dilantin | 239 | 242 | 225 | <25 |
| Oxybenzone | 221 | 34 | <25 | <25 |
| Estriol | <25 | <25 | <25 | <25 |
| Ethinylestradiol | 51 | <25 | <25 | <25 |
| Estrone | 83 | <25 | <25 | <25 |
| Estradiol | 27 | <25 | <25 | <25 |
| Progesterone | 250 | 251 | 250 | <25 |
| Androstenedione | 247 | 250 | 243 | <25 |
| Iopromide | 125 | 115 | 133 | 72 |
| Naproxen | 91 | 73 | 77 | <25 |
| Ibuprofen | 302 | 275 | 284 | <25 |
| Diclofenac | <25 | <25 | <25 | <25 |
| Triclosan | 166 | 105 | 90 | <25 |
| Gemfibrozil | 234 | 234 | 221 | <25 |

Water Recycling Membrane Bioreactor and Ultrafiltration Pilot: Both membrane bioreactor (MBR) and ultrafiltration (UF) processes were evaluated separately at pilot-scale to assess their ability to prevent EDC/PPCP passage. The pilot-testing site for the study was a full-scale tertiary treatment water reuse facility located in Nevada. Tertiary treatment at the full-scale facility consisted of influent screening, grit removal, chemical coagulation, flocculation, primary sedimentation, aeration, secondary clarification, dual media filtration and UV disinfection. Influent and effluent water quality data are provided in Table 3.

Table 3. Water Quality for at UF/MBR Water Recycling Pilot-Plant

Table -1

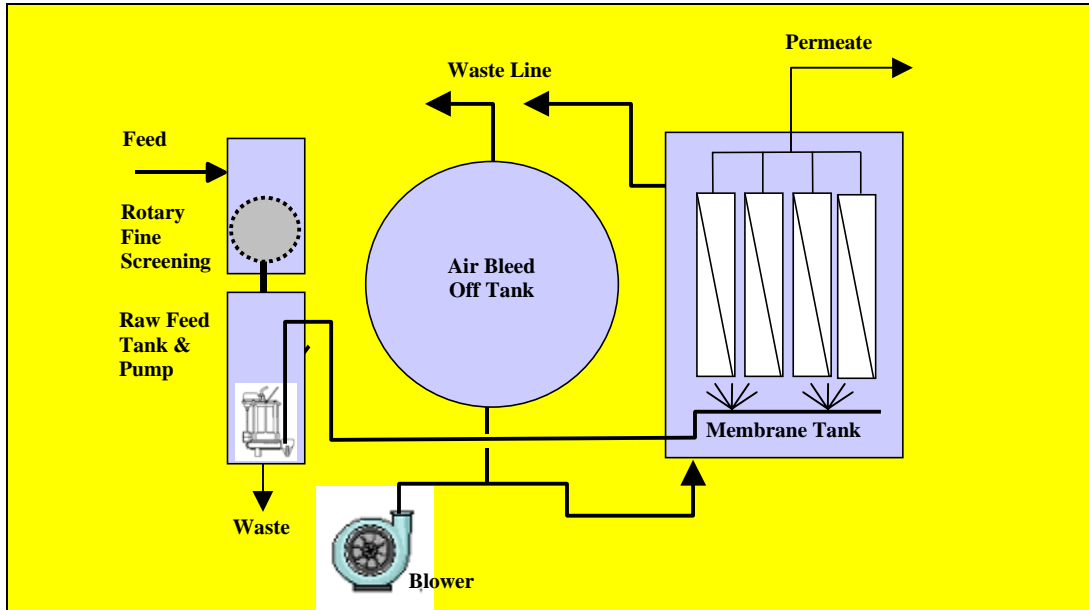
**Plant Influent and
Primary Effluent Water Quality**

| | | | |
|--------------|---------|-------|------|
| BOD | mg/L | 229 | 198 |
| TSS | mg/L | 221 | 98 |
| VSS | mg/L | NT | NT |
| pH | ---- | NT | NT |
| TDS | mg/L | 1,083 | NT |
| Conductivity | umhos/c | NT | NT |
| Turbidity | NTU | NT | NT |
| Ammonia | mg/L | 24 | 19 |
| Nitrate | mg/L | 0.08 | 0.89 |
| Phosphate | mg/L | 2.76 | 1.43 |
| Alkalinity | mg/L | 2.45 | 242 |

NT - Not Tested

A US Filter MBR system was utilized for this testing. A general process flow schematic of the system is provided in Figure 2. The pilot used 3-mm pre-screen, influent holding tank and pumps, membrane tank and backwash tank. The system was also equipped with a self-priming pump, to pump mixed liquor from the full – scale plant aeration basin to the membrane pilot unit. The membranes, under a light suction, filtered a portion of the mixed liquor from the membrane tank with the remaining mixed liquor overflowed back to the feed tank. This operation resulted in a cross flow velocity across the membrane surface to prevent fouling.

Figure 3. Schematic of US Filter Jet Tech MBR Pilot System



Four membrane modules were submerged in the membrane tank. Each membrane module was comprised of hollow fibers with a nominal pore size of 0.2 microns. During operation, air and mixed liquor were continuously pumped into the membrane tank to scrub and shake the membrane fibers. Technical information on the membranes are provided in Table 4.

Table 4. Specifications for US Filter MemJet B10R Microfiltration Membrane

| | Units | Value |
|---|----------------|----------------------|
| Manufacturer | --- | US Filter |
| Approximate Size of Element (L x Dia) | mm | 1850 x 100 |
| Active Membrane Area (outside) per module | m ² | 9.2 |
| Number of Fibers | | ~2000 |
| Inside Diameter of Fiber | mm | 0.65 |
| Outside Diameter of Fiber | mm | 1.0 |
| Approximate Length of Fiber | m | 1.5 |
| Flow Direction | --- | outside-in |
| Nominal Membrane Pore size | micron | 0.08 |
| Absolute Membrane Pore Size | micron | 0.2 |
| Membrane Material/Construction | --- | PV dF / Hollow Fiber |
| Membrane Surface Characteristics | --- | hydrophilic |
| Membrane Charge | --- | Neutral |
| Design Flux | gfd | 14.4 |
| Acceptable Range of Operating pH Values | --- | 2-11 |
| Vacuum Pressure for System | kPa | 50 |
| Chlorine/Oxidant Tolerance | ppm hr/yr | 100,000 |

No significant removal was observed through the UF membranes. Results showing the wastewater treatment plant performance as compared to the MBR are shown in Table 5.

Table 5. Removal during Wastewater Treatment using MBR

| Analyte | WWTP Influent ppt | WWTP Effluent ppt | MBR Effluent ppt |
|---------------------------------|----------------------|----------------------|---------------------|
| Hydrocodone | 118 | 168 | <10 |
| Trimethoprim | 693 | 42 | <10 |
| Acetaminophen | 172000 | <10 | <10 |
| Caffeine | 72200 | 68 | <10 |
| Erythromycin - H ₂ O | 1050 | 800 | 34 |
| Sulfamethoxazole | 1110 | 23 | <10 |
| Fluoxetine | <100 | 44 | <10 |
| Pentoxifylline | <100 | <10 | 30 |
| Meprobamate | 966 | 652 | 1340 |
| Dilantin | 210 | 192 | 184 |
| Carbamazepine | 189 | 281 | <10 |
| DEET | 150 | 213 | 171 |
| Atrazine | <100 | <10 | <10 |
| Diazepam | <100 | <10 | <10 |
| Oxybenzone | 3810 | <10 | <10 |
| Estriol | <250 | <25 | <25 |
| Ethinylestradiol | <100 | <10 | <10 |
| Estrone | <250 | <25 | <25 |
| Estradiol | <100 | <10 | <10 |
| Testosterone | <100 | <10 | <10 |
| Progesterone | <100 | <10 | <10 |
| Androstenedione | 150 | <10 | <10 |
| Iopromide | <100 | <10 | <10 |
| Naproxen | 12500 | 70 | <10 |
| Ibuprofen | 12000 | 27 | 43 |
| Diclofenac | <100 | 16 | <10 |
| Triclosan | 1280 | 17 | <10 |
| Gemfibrozil | 2210 | 74 | <10 |

Ultrafiltration followed by Reverse Osmosis Water Recycling Pilot: A pilot system consisting of UF followed by RO was evaluated for its ability reject EDC/PPCPs. An overall schematic of the pilot treatment train employed during the study is provided in Figure 4. As shown, tertiary wastewater was used as feed water to the pilot systems. Values of general water quality parameters measured at various locations in the pilot train are presented in Table 6.

Figure 4. Process Flow Diagram of UF/RO Pilot

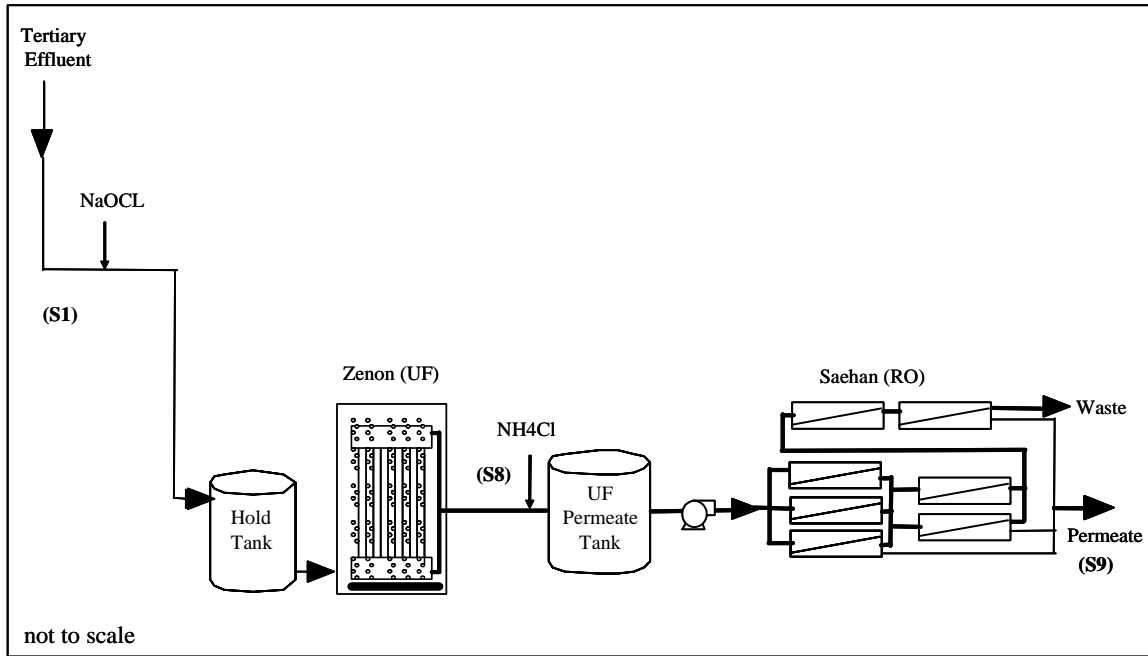


Table 6. Water Quality Measured at UF/RO Pilot

| Parameter | Unit | 3/25/2005 | | | 4/13/2005 | | |
|----------------|-----------|-----------|-------------|-------------|-----------|-------------|-------------|
| | | Tertiary | UF effluent | RO permeate | Tertiary | UF effluent | RO permeate |
| Aluminum | µg/L | 16.4 | 13.3 | ND | 10.7 | 7.89 | ND |
| Alkalinity_tot | mg/L | 146 | 147 | 9.01 | 145 | 143 | 8.49 |
| Arsenic | µg/L | 2.03 | 1.93 | ND | 1.99 | 1.99 | ND |
| Boron | µg/L | 365 | 353 | 283 | 363 | 367 | 301 |
| Chloride | mg/L | 268 | 276 | 7.93 | 248 | 248 | 7.02 |
| Conductivity | µmho/cm | 2420 | 2550 | 0.91 | 1640 | 1660 | 65 |
| Hardness | mg/L | 352 | 356 | 4.4 | 342 | 338 | 5.32 |
| Manganese | µg/L | 119 | 115 | ND | 80 | 74.4 | 1.47 |
| Silica | mg/L | 18.4 | 18.2 | 0.714 | 15.7 | 15.9 | 0.667 |
| Sulfate | mg/L | 233 | 234 | 0.769 | 215 | 214 | 0.679 |
| TOC | mg/L | 8.13 | 7.8 | ND | 7.98 | 7.51 | ND |
| TDS | mg/L | 934 | 1020 | 77 | 960 | 956 | 64 |
| Total Coliform | MPN/100mL | | <2 | 4 | | 8 | ND |
| Turbidity | NTU | | 0.25 | 0.1 | | 0.4 | 0.1 |

- A Zenon ZeeWeed[®] 1000 UF pilot system was used during the study to provide pretreatment to downstream RO membranes. Specifications for the ZW 1000 membrane are provided in Table 7.

Table 7. Specifications of the ZW1000 UF Membrane Pilot

| Parameter | Unit | Value |
|--|-----------------------------------|--|
| Manufacturer | | ZENON Environmental |
| Membrane Model and ID Number | | E1000-0061, 0066 & 0068 |
| Membrane Commercial Designation | | ZeeWeed [®] 1000 |
| Approximate Size of Membrane Element | ft (m) | 2.2 (0.68) x 2.0 (0.62) x 0.34 (0.104) |
| Active Membrane Area per Membrane Element | ft ² (m ²) | 350 ft ² (32.5 m ²) |
| Number of Fibers per Element | | 30,000 |
| Number of Elements (Operational) | | 3 |
| Inside Diameter of Fiber | mm | 0.35 |
| Outside Diameter of Fiber | mm | 0.6 |
| Approximate Length of Fiber | ft (m) | 2 (0.6) |
| Flow Direction | | Outside-in |
| Nominal Molecular Weight Cutoff | Daltons | 100,000 |
| Absolute Molecular Weight Cutoff | Daltons | NA |
| Nominal Membrane Pore Size | micron | 0.02 |
| Absolute Membrane Pore Size | micron | 0.10 |
| Membrane Material/Construction | | PVDF |
| Membrane Surface Characteristics | | Hydrophilic |
| Membrane Charge | | Non-ionic |
| Design Operating Pressure | psi | 1.0 - 10.0 |
| Design Flux at Design Pressure | gfd (l/hr-sq m) | 5 - 50 (8.5 - 85) |
| Maximum Transmembrane Pressure | psi (bar) | 12 (0.83) |
| Standard Testing pH | | 7 |
| Acceptable Range of Operating pH Values | | 2 - 9.5 |
| Standard Testing Temperature | degF (degC) | 77 (25) |
| Acceptable Range of Operating Temperatures | degF (degC) | 33.8 - 95 (1 - 35) |
| Maximum Permissible Turbidity | NTU | > 2,000 |
| Chlorine/Oxidant Tolerance | ppm | > 2,000 |

A multi-stage RO pilot system was utilized during this study. The system was configured as a 2-1 array. Stage 1 consisted of four pressure vessels arranged as two parallel 1-1 arrays. Stage 2 contained two single vessels arranged in series. Each vessel houses 3 RO elements with nominal dimensions of 4" x 40". The stages were arranged in series, to allow concentrate from Stage 1 to serve as feed water for Stage 2. Operating conditions for the UF and RO pilot systems are shown in Table 8. Results of contaminant removal using this pilot are shown in Table 9.

Table 8. Operating Parameters for UF/RO Pilot Systems

| Process | Operating Parameters |
|-------------------------------|--|
| <u>Ultrafiltration</u> | Flux = 35 gfd @ 20°C |
| | Transmembrane pressure = 1 -10 psi |
| | Backwash frequency = 30 min |
| | Backwash pressure = 90 psi (Air) |
| | Flow mode = direct flow (no recirculation) |
| | Free chlorine dose = 1 - 2 mg/L |
| | Free chlorine dose during backwash = 0 mg/L |
| | Chemical cleaning: when $P_{tm} = 7$ psi |
| | |
| <u>Reverse Osmosis</u> | Flux = 12 gfd @ 25 °C |
| | Recovery 85% |
| | Feed pH = 7 - 8 |
| | Antiscalant dose = 2 mg/L |
| | ¹ Combined chlorine dose = 1-2 mg/L |
| | Chemical cleaning (per mfg recommendation) |

1 Formed by dosing ammonium chloride and sodium hypochlorite; no chlorine used during EDC/PCPP sampling.

Table 9. Results from UF/RO Testing

| Units = ng/L | Secondary Feed Effluent | UF Effluent/RO Feed | Stage 1A - RO Permeate | Stage 6 - RO Permeate | RO Reject (Retentate) |
|-------------------------------|-------------------------|---------------------|------------------------|-----------------------|-----------------------|
| Hydrocodone | 87 | 89 | <1.0 | <1.0 | 215 |
| Trimethoprim | 186 | 158 | <1.0 | <1.0 | 403 |
| Acetaminophen | <20 | <10 | <1.0 | <1.0 | 16 |
| Caffeine | <20 | 14 | <1.0 | 1.8 | 298 |
| Erythromycin-H ₂ O | 336 | 357 | <1.0 | <1.0 | 940 |
| Sulfamethoxazole | 90 | 56 | 1.2 | 1.2 | 121 |
| Fluoxetine | <20 | <10 | <1.0 | <1.0 | 17 |
| Pentoxifylline | <20 | <10 | <1.0 | <1.0 | <10 |
| Meprobamate | 693 | 715 | <1.0 | <1.0 | 1610 |
| Dilantin | 126 | 191 | <1.0 | <1.0 | 416 |
| TCEP | 189 | 219 | <1.0 | 1.4 | 426 |
| Carbamazepine | 110 | 147 | <1.0 | <1.0 | 278 |
| DEET | 104 | 103 | <1.0 | <1.0 | 293 |
| Atrazine | <20 | <10 | <1.0 | <1.0 | <10 |
| Diazepam | <20 | <10 | <1.0 | <1.0 | <10 |
| Oxybenzone | 48 | 26 | <1.0 | <1.0 | 20 |
| Estriol | <100 | <50 | <5.0 | <5.0 | <50 |
| Ethinylestradiol | <20 | <10 | <1.0 | <1.0 | <10 |
| Estrone | 35 | <10 | <1.0 | <1.0 | 78 |
| Estradiol | <20 | <10 | <1.0 | <1.0 | <10 |
| Testosterone | <20 | <10 | <1.0 | <1.0 | <10 |
| Progesterone | <20 | <10 | <1.0 | <1.0 | <10 |
| Androstenedione | <20 | <10 | <1.0 | <1.0 | <10 |
| Iopromide | <20 | 58 | <1.0 | 1.1 | 89 |
| Naproxen | <20 | 17 | <1.0 | <1.0 | 33 |
| Ibuprofen | <20 | <10 | <1.0 | <1.0 | <10 |
| Diclofenac | <20 | 37 | <1.0 | <1.0 | 59 |
| Triclosan | 29 | <10 | <1.0 | <1.0 | 14 |
| Gemfibrozil | 100 | 142 | <1.0 | <1.0 | 329 |
| Galaxolide | 968 | 816 | <10.0 | <10.0 | 2180 |
| Musk Ketone | 97 | 106 | <10.0 | <10.0 | 329 |

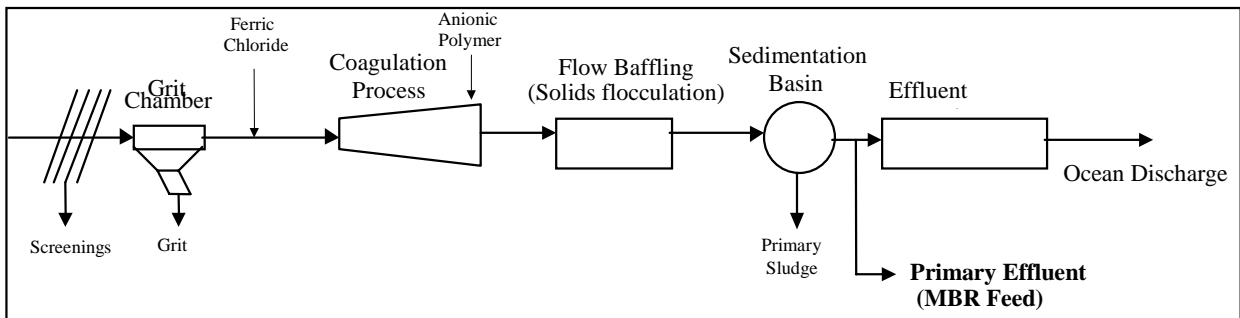
Membrane Bioreactor followed by Reverse Osmosis Pilot: The ability of a pilot scale MBR followed by RO to reduce EDC/PPCP concentrations was evaluated at one treatment facility in Southern California and one facility in New Mexico. Table 10 summarizes the influent source water and pilot equipment installed at each participating location.

Table 10. Source Water and Treatment Systems for Pilot Installation Locations

| | Southern California | New Mexico |
|--------------|---|--|
| Source water | Advanced Primary | Raw wastewater |
| MBR System | Zenon ZW 500D and Mitsubishi Sterapore HF | Zenon ZW 500C |
| RO System | Saehan 4040 FL Dual stage operated at a 75% feed water recovery rate | Osmonics AK4040 Dual stage operated at a 75% feed water recovery rate |

The advanced primary treatment in the Southern California full-scale facility consisted of influent screening, grit removal, chemical coagulation, flocculation, and sedimentation as shown in Figure 5. Chemical addition consisted of ferric chloride (27 mg/L, average dose) and a long chain, high molecular weight anionic polymer (Polydyne Inc., Riceboro, GA at 0.15 mg/L, average dose).

Figure 5. Advanced Primary Treatment in Southern California Full-Scale Facility



A schematic of the Zenon MBR pilot unit is shown in Figure 6 and the Mitsubishi pilot unit is shown in Figure 7. The Zenon MBR pilot unit was equipped with one membrane cassette, composed of three submerged UF membrane elements. An anoxic tank for denitrification was included in the process train installed in New Mexico. Only an aerobic tank for nitrification was included in the process train in Southern California. The MBR samples were obtained for the following range of MBR operating conditions: flux range of 15-22 gfd; HRT of 2-6 hours and MLSS range of 4,000-13,000 mg/L.

Figure 6. Zenon MBR: Side View (Top); Plan View (Bottom)

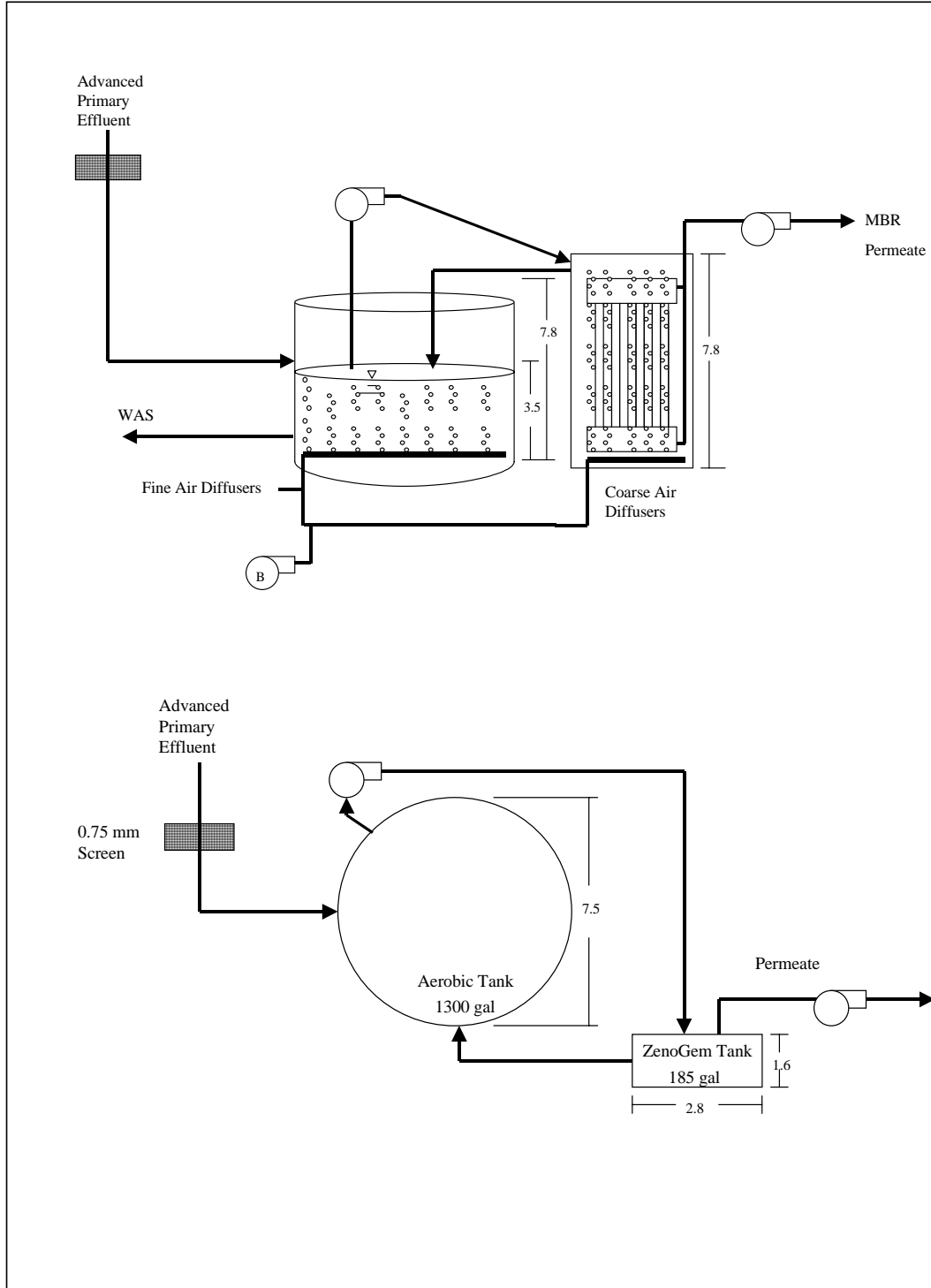
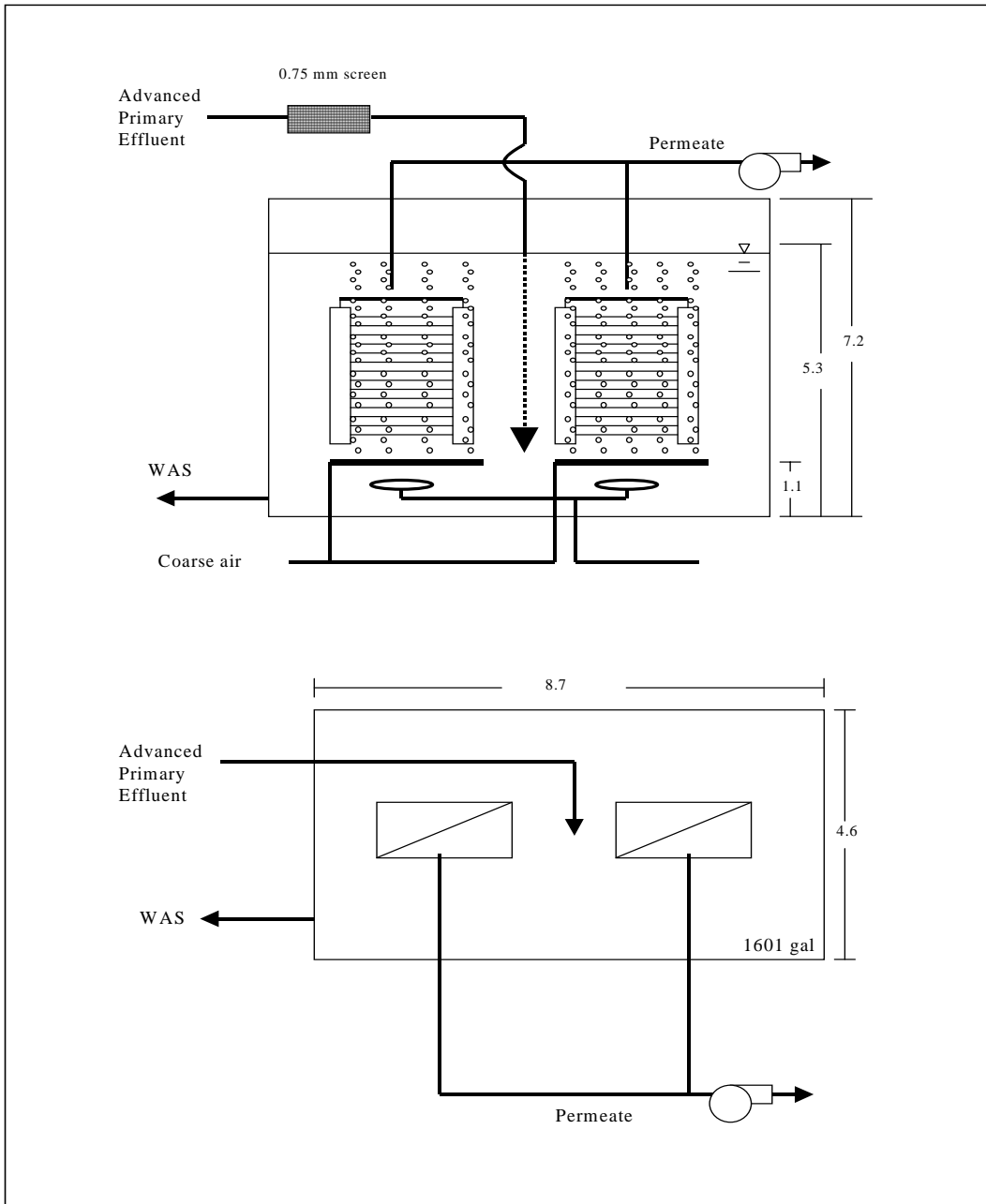


Figure 7. Mitsubishi MBR: Side View (Top); Plan View (Bottom)



The Osmonics and Saehan RO membranes are both made of polyamide thin-film composite material with similar spiral wound configurations as shown in the specifications provided in Table 11. The RO systems were operated in a 2-1 array at a flux range of 10-12 gfd and a 75% feed water recovery rate. Samples were collected from the MBR influent, MBR effluent, and RO effluent and analyzed for a full suite of EDC and PPCP compounds. Table 12 presents the results from this MBR/RO investigation

Table 11. RO Membrane Specifications

| | OSMONICS | SAEHAN |
|--|-----------------------|-----------------------|
| Commerical designation | AK4040 | RE 4040-FRM |
| Membrane material | Polyamide | Polyamide |
| | (thin-film composite) | (thin-film composite) |
| Operating pH range | 4-11 | 3-10 |
| Maximum feedwater turbidity | 1 NTU | < 1 NTU |
| Maximum feedwater chlorine concentration | <0.1 ppm | <0.1 ppm |
| Maximum operating pressure | 600 psig | 600 psig |
| Nominal membrane surface area | 85 ft ² | 85 ft ² |
| Configuration | Spiral wound | Spiral wound |
| Element length | 40.0 inches | 40.0 inches |
| Element diameter | 4.0 inches | 4.0 inches |

Table 12. Results from MBR/RO Pilot

| Units = ng/L | WWTP Influent | Primary Effluent | MBR A Effluent | MBR B Effluent | RO Feed | RO Permeate |
|-------------------------------|---------------|------------------|----------------|----------------|---------|-------------|
| Hydrocodone | <100 | 32 | 46 | 39 | 44.5 | <1.0 |
| Trimethoprim | 699 | 144 | 14.5 | 7.4 | <1.0 | <1.0 |
| Acetaminophen | 21950 | 4095 | <1.0 | <1.0 | 11.4 | <1.0 |
| Caffeine | 58550 | 6775 | 7.6 | 2.4 | 16.5 | <1.0 |
| Erythromycin-H ₂ O | 479 | 9.4 | 96 | 54 | 42 | <1.0 |
| Sulfamethoxazole | 234 | 103 | 265 | 33 | 15.5 | <1.0 |
| Fluoxetine | <100 | 4.35 | 4.8 | 9.8 | 6.85 | <1.0 |
| Pentoxifylline | <100 | 6.85 | <1.0 | <1.0 | <1.0 | <1.0 |
| Meprobamate | 520 | 91.5 | 236 | 216 | 238 | 1.3 |
| Dilantin | 143 | 21 | 72 | 67 | 72 | <1.0 |
| TCEP | 464 | 151 | 185.5 | 171 | 186 | 6.5 |
| Carbamazepine | 299 | 137.5 | 205 | 171 | 181 | <1.0 |
| DEET | 690 | 168 | 37 | 46 | 45 | 2.3 |
| Atrazine | <100 | <1 | <1.0 | <1.0 | <1.0 | <1.0 |
| Diazepam | <100 | 1.1 | 2.75 | 2.4 | 2.55 | <1.0 |
| Oxybenzone | 896 | 181 | 3.1 | 9.4 | 4.9 | <1.0 |
| Estriol | 226 | 67 | <1.0 | <1.0 | <1.0 | <1.0 |
| Ethinylestradiol | <100 | <1 | <1.0 | <1.0 | <1.0 | <1.0 |
| Estrone | <100 | 36 | 8.45 | <1.0 | 6 | <1.0 |
| Estradiol | <100 | <1 | <1.0 | <1.0 | <1.0 | <1.0 |
| Testosterone | <100 | 23 | <1.0 | <1.0 | <1.0 | <1.0 |
| Progesterone | <100 | 21.5 | <1.0 | <1.0 | <1.0 | <1.0 |
| Androstenedione | <100 | 60 | <1.0 | <1.0 | <1.0 | <1.0 |
| Iopromide | <100 | <1 | 4.05 | 3.5 | 2.6 | <1.0 |
| Naproxen | 21000 | 599 | 26 | 1.3 | <1.0 | <1.0 |
| Ibuprofen | 70350 | 641 | 3.95 | 5.3 | 8.9 | <1.0 |
| Diclofenac | <100 | 5.6 | 15 | 17 | 1.1 | <1.0 |
| Triclosan | 4030 | 176 | 7.55 | 11 | 6.9 | <1.0 |
| Gemfibrozil | <100 | 331 | 35.5 | 270 | <1.0 | <1.0 |

Microfiltration followed by Reverse Osmosis and Electrodialysis Reversal:

Treatment trains consisting of microfiltration (MF) followed by RO and MF followed by electro dialysis reversal (EDR) were evaluated at the pilot scale to remove EDC/PPCP compounds present in tertiary treated wastewater. The tertiary treated wastewater used in this study is characterized by relatively high levels of total dissolved solids, hardness and alkalinity, with moderate levels of organic material and low turbidity. Table 13 presents typical feed water quality at the pilot site.

Table 13. Pilot Feed Water Quality (Tertiary Treated Wastewater)

| Parameter | | |
|---------------------------|--------|----------|
| Cl- (chloride) | 188 | mg/L |
| NO3-N | 7.1 | mg/L |
| SO4 | 96 | mg/L |
| Ca | 59.1 | mg/L |
| Cr (Total) | <0.002 | mg/L |
| Fe | 0.07 | mg/L |
| Mg | 31.7 | mg/L |
| SiO2 | 24.0 | mg/L |
| Na | 156 | mg/L |
| Conductivity | 1200 | umhos/cm |
| pH | 7.3 | SU |
| TOC | 9 | mg/L |
| Turbidity | 0.7 | NTU |
| Hardness, total (CaCO3) | 250 | mg/L |
| Alkalinity, total (CaCO3) | 190 | mg/L |
| TDS | 720 | mg/L |
| UV-254 | 0.109 | Abs/cm |

The trial equipment consisted of a modified US Filter “H” series RO, model number ROSLH 3180. The pilot system was capable of utilizing up to 12 vessels, but for the purposes of this study, 3 vessels were used, configured in a 2:1 array with a feed water recovery (FWR) of 50 – 75 percent (10 – 15 gpm permeate flow). The membrane elements were Dow Filmtec brackish water membranes, part number BW30-4040. Each vessel housed four RO membrane elements.

Membrane pretreated water was continuously fed to the RO pilot system at a flow rate of approximately 20 gpm. The pilot system utilized DOW FilmTec BW30-4040 membrane elements. Four elements were placed in series in each of the three pressure vessels in a two-stage, 2:1 array configuration. Sodium bisulfite and anti-scalant were added to the MF pretreated water to control RO membrane fouling and protect the membrane elements from chemical damage due to free chlorine or chloramines.

The EDR equipment consisted of a Aquamite V with a bipolar membrane stack. The capacity of the Aquamite V is 15,000 – 35,000 gpd. The maximum feed flow for this unit was 60,000 gpd. The Aquamite V supported an electric power supply of

480/460/380/220 Volts, 50/60 Hz, 3 phase and was supplied by direct current (DC) at 3 phases, full wave with silicon diode rectifiers.

The EDR operated at a range of flows (22-27 gpm) to continually produce demineralized water without constant chemical addition during normal operation. Current was supplied at 2-4 amps depending on the specific water quality goals to be achieved. Membrane fouling and scaling was controlled by using electrical polarity reversal every fifteen minutes.

Typically, EDR systems are configured using multiple stages to provide the maximum membrane surface area and retention time to remove a specified fraction of salt from the demineralized stream. Two types of staging are used: hydraulic and electrical. For this study, the Aquamite V pilot unit operated as a single stack with two electrical stages that could be independently controlled to achieve a desired water quality. Electrical staging was accomplished by inserting additional electrode pairs into the membrane stack to provide maximum salt removal rates while avoiding polarization and hydraulic pressure limitations.

Results for the UF/RO/EDR piloting are shown in Table 14.

Table 14. Results from UF/RO – EDR Pilot Testing

| | Raw Influent | Tertiary Effluent | Electrodialysis | Microfiltration | Reverse Osmosis |
|-------------------------------|--------------|-------------------|-----------------|-----------------|-----------------|
| Analyte | ppt | ppt | ppt | ppt | ppt |
| Hydrocodone | 35 | <1.0 | <1.0 | <1.0 | <1.0 |
| Trimethoprim | 213 | <1.0 | <1.0 | <1.0 | <1.0 |
| Acetaminophen | 14200 | 2.5 | 3.4 | 2.4 | <1.0 |
| Caffeine | 32500 | 1.9 | 2.0 | 2.4 | <1.0 |
| Erythromycin-H ₂ O | 79 | <1.0 | <1.0 | <1.0 | <1.0 |
| Sulfamethoxazole | 360 | <1.0 | <1.0 | <1.0 | <1.0 |
| Fluoxetine | 10 | 8.5 | 5.8 | 4.7 | <1.0 |
| Pentoxifylline | <10 | <1.0 | <1.0 | <1.0 | <1.0 |
| Meprobamate | 124 | 75 | 71 | 67 | <1.0 |
| Dilantin | 51 | 52 | 47 | 31 | <1.0 |
| TCEP | 244 | 133 | 127 | 127 | <5.0 |
| Carbamazepine | 78 | 19 | 18 | 17 | <1.0 |
| DEET | 154 | 122 | 112 | 100 | 4.2 |
| Atrazine | <10 | <1.0 | <1.0 | <1.0 | <1.0 |
| Diazepam | <10 | <1.0 | <1.0 | <1.0 | <1.0 |
| Oxybenzone | 657 | 5.8 | 3.8 | 4.9 | <1.0 |
| Estriol | 137 | <5.0 | <5.0 | <5.0 | <5.0 |
| Ethinylestradiol | <10 | <1.0 | <1.0 | <1.0 | <1.0 |
| Estrone | 49 | <1.0 | <1.0 | <1.0 | <1.0 |
| Estradiol | 33 | <1.0 | <1.0 | <1.0 | <1.0 |
| Testosterone | 47 | <1.0 | <1.0 | <1.0 | <1.0 |
| Progesterone | <10 | <1.0 | <1.0 | <1.0 | <1.0 |
| Androstenedione | 52 | 5.8 | 5.2 | 5.2 | <1.0 |
| Iopromide | 17 | 42 | 51 | 34 | <1.0 |
| Naproxen | 4480 | <1.0 | <1.0 | <1.0 | <1.0 |
| Ibuprofen | 2270 | 6.0 | 5.4 | 2.7 | <1.0 |
| Diclofenac | <10 | <1.0 | <1.0 | <1.0 | <1.0 |
| Triclosan | 564 | 1.2 | <1.0 | 1.2 | <1.0 |
| Gemfibrozil | 1220 | <1.0 | <1.0 | <1.0 | <1.0 |
| Galaxolide | 544 | 931 | 587 | 617 | <10.0 |
| Musk Ketone | 119 | 65 | 45 | 45 | <10.0 |

ACTIVATED CARBON TESTING

Granular Activated Carbon Adsorption

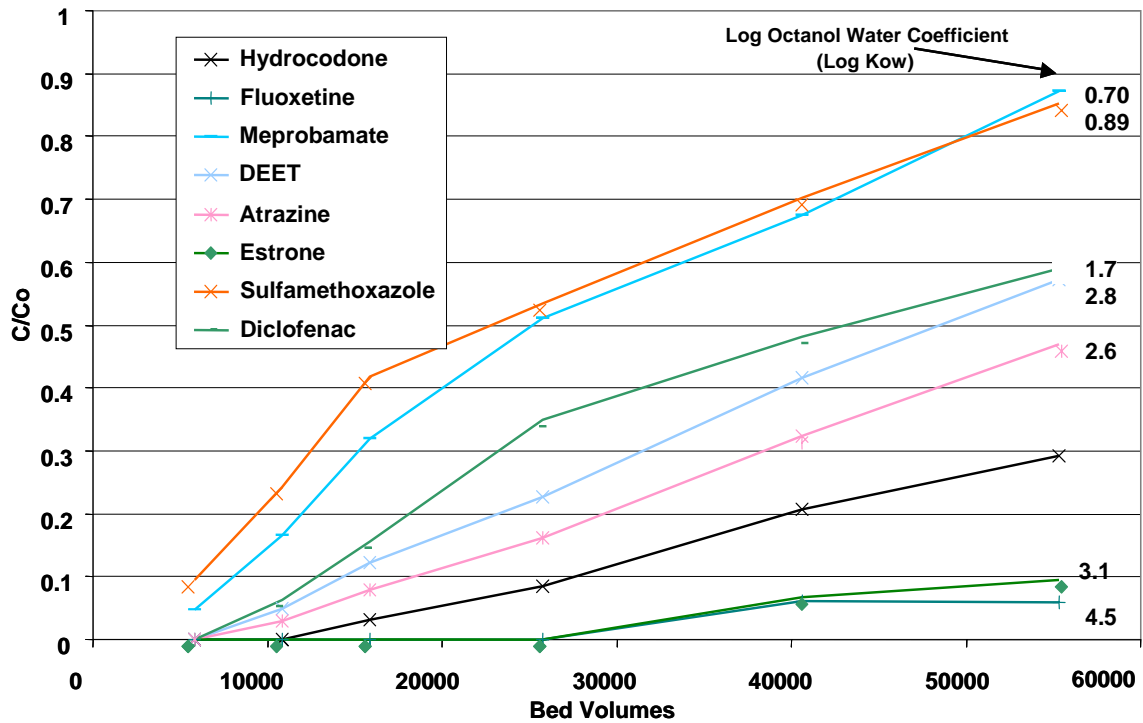
Bench-scale testing was conducted using rapid small-scale column tests (RSSCTs) to predict granular activated carbon (GAC) performance. Tests compared two lignite-based GACs, HYDRODARCO 4000 (HD4000) and a steam-treated version of the same (S16L). Steam treatment involved a 16% pyrolyzed mass loss at 1000°C resulting in a pore structure distinct from that of HD4000. RSSCTs simulated a full-scale column that operates at a 7.6 minute empty bed contact time (EBCT). Only Colorado River water was utilized for these experiments. Target compounds were spiked into Colorado River water to achieve a 100-200 ng/L mixture. Tests were conducted at 20-25°C. Results of one RSSCT is shown in Table 15 and represented graphically in Figure 8.

Table 15. Results of RSSCT GAC Test with Representative EDCs/Pharmaceuticals

| | 20,000 BV | 27,500 BV | 35,000 BV | 45,000 BV | 65,000 BV | 90,000 BV |
|-------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Analyte | ppt | ppt | ppt | ppt | ppt | ppt |
| Hydrocodone | <2.0 | <2.0 | <2.0 | 4.1 | 11 | 45 |
| Trimethoprim | <2.0 | <2.0 | <2.0 | <2.0 | 8.3 | 37 |
| Acetaminophen | <2.0 | <2.0 | 7.6 | 17 | 45 | 108 |
| Caffeine | <20 | <20 | <20 | <20 | 29 | 90 |
| Erythromycin-H ₂ O | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 | 2.8 |
| Sulfamethoxazole | 25 | 46 | 80 | 103 | 119 | 184 |
| Fluoxetine | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 | 7.3 |
| Pentoxifylline | <2.0 | <2.0 | <2.0 | 2.7 | 11 | 41 |
| Meprobamate | 12 | 29 | 56 | 93 | 131 | 217 |
| Dilantin | <2.0 | 5.8 | 12 | 25 | 45 | 96 |
| TCEP | <20 | 24 | <20 | 40 | 78 | 159 |
| Carbamazepine | <2.0 | <2.0 | <2.0 | 4.0 | 14 | 51 |
| DEET | <2.0 | 9.0 | 4.6 | 27 | 51 | 121 |
| Atrazine | <2.0 | <2.0 | <2.0 | 13 | 31 | 93 |
| Diazepam | <2.0 | <2.0 | <2.0 | <2.0 | 8.2 | 36 |
| Oxybenzone | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 |
| Estradiol | <10 | <10 | <10 | <10 | 7.3 | 35 |
| Ethinylestradiol | <2.0 | <2.0 | <2.0 | <2.0 | 4.5 | 22 |
| Estrone | <2.0 | <2.0 | <2.0 | 2.5 | 5.0 | 20 |
| Estradiol | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 | 12 |
| Testosterone | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 | 9.4 |
| Progesterone | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 |
| Androstenedione | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 | 8.7 |
| Iopromide | 20 | 38 | 61 | 96 | 126 | 191 |
| Naproxen | <2.0 | 2.2 | 5 | 10 | 30 | 63 |
| Ibuprofen | 12 | 26 | 45 | 70 | 103 | 154 |
| Diclofenac | <2.0 | 2.8 | 6.3 | 14 | 36 | 72 |
| Triclosan | <2.0 | <2.0 | <2.0 | <2.0 | <2.0 | 7.6 |
| Gemfibrozil | <2.0 | <2.0 | 4.7 | 12 | 36 | 84 |

BV = Bed Volumes

Figure 8. RSSCT Results Shown with Log Kow



GAC was also evaluated at two full-scale installations. In the first installation (drinking water), the GAC was regularly thermally regenerated (Table 16). At the second installation (water reuse), the GAC was not regenerated/replaced on a regular basis and was clearly no longer effective (Table 17). Also, Table 17 demonstrates the ineffectiveness at UV disinfection for the removal of these contaminants.

Table 16. Results from Full-Scale Drinking Water GAC (Regenerated)

| Analyte | GAC Influent ppt | GAC Effluent ppt |
|------------------|---------------------|---------------------|
| Caffeine | 17 | <10.0 |
| Erythromycin | 1.8 | <1.0 |
| Sulfamethoxazole | 6.0 | <1.0 |
| Meprobamate | 1.2 | <1.0 |
| Dilantin | 1.8 | <1.0 |
| TCEP | <10.0 | <10.0 |
| Carbamazepine | 2.2 | <1.0 |
| DEET | 1.8 | <1.0 |
| Atrazine | 650 | 6.1 |
| Oxybenzone | 1.0 | <1.0 |
| Iopromide | 3.3 | <1.0 |
| Ibuprofen | 1.1 | <1.0 |
| Gemfibrozil | 1.2 | <1.0 |

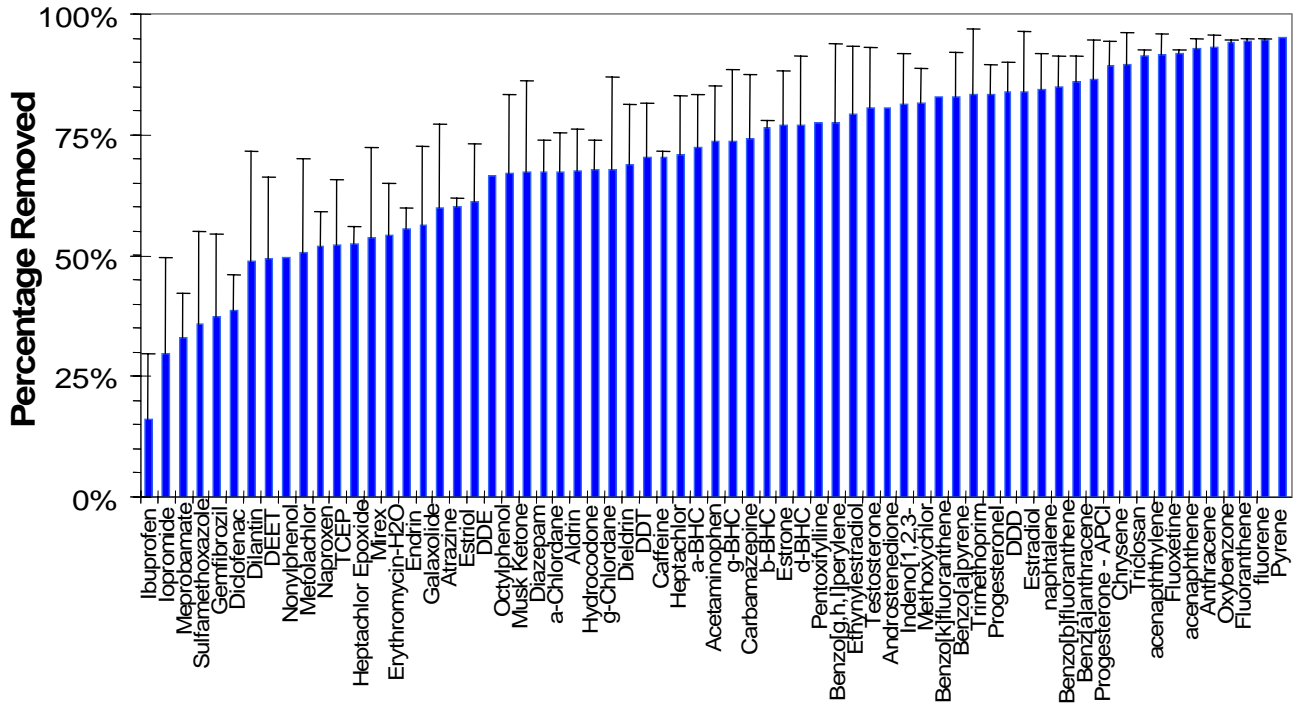
Table 17. Results from Full-Scale Water Reuse GAC (Not Regenerated)

| | GAC Influent | GAC Effluent | UV Disinfection |
|-------------------------|---------------------|---------------------|------------------------|
| Hydrocodone | 66 | 54 | 49 |
| Trimethoprim | 147 | 129 | 125 |
| Acetaminophen | 26700 | 10300 | 9440 |
| Caffeine | 36300 | 40600 | 41200 |
| Erythromycin | 143 | 136 | 147 |
| Sulfamethoxazole | 198 | 409 | 365 |
| Pentoxifylline | <25 | 31 | 29 |
| Meprobamate | 190 | 213 | 209 |
| Dilantin | 97 | 104 | 100 |
| Carbamazepine | 177 | 189 | 195 |
| DEET | 229 | 674 | 728 |
| Atrazine | 31 | 30 | 32 |
| Oxybenzone | 96 | <25 | <25 |
| Estriol | <50 | 8.3 | 11 |
| Ethinylestradiol | <10 | 1.0 | <1.0 |
| Testosterone | 54 | 147 | 134 |
| Progesterone | <10 | 1.3 | 1.7 |
| Androstenedione | 88 | 176 | 181 |
| Iopromide | <10 | 5.1 | 4.6 |
| Naproxen | 4340 | 3340 | 3410 |
| Ibuprofen | 7550 | 8370 | 9210 |
| Diclofenac | 12 | 3.0 | 1.5 |
| Triclosan | 297 | 3.5 | 2.0 |
| Gemfibrozil | 4090 | 3450 | 3500 |

Powdered Activated Carbon Adsorption

Powdered activated carbon (PAC) adsorption studies were conducted in the laboratory using AC800 (Acticarb, Dunnellon, FL, USA) and WPM (PAC form of F400, Calgon Carbon Corp., Pittsburgh, PA, USA). The PACs were hydrated for 24 hours in distilled water prior to use and added as a slurry (1000 mg/L) to the samples. The experiments were performed in a six-place jar tester using 2-L glass beakers filled with 1.5-L of source water. The doses and contact times were based upon full-scale WTPs that frequently use PAC contact times of 1 to 5 hours and PAC dosages of 5 to 50 mg/L. Sampling and filtration procedures were followed as described for the coagulation and chemical softening experiments.

Figure 9. Average Removal using PAC at Bench-Scale



CONCLUSIONS

Clearly, RO filtration is a superior technology for the removal of organic contaminants. However, at trace levels (i.e., ng/L) some compounds can still be detected in the RO permeate. UF was not effective for the removal of most compounds; however, many steroid hormones showed significant removals through the UF membrane. The MBRs investigated provided marginal improvement in the treatment of organic contaminants as compared to the activated sludge. However, the effect of SRT was not clearly evaluated in the studies shown here.

Activated carbon is effective for the majority of organic contaminants studied. Removal using activated is dependent upon regeneration/replacement in the case of GAC. Also, hydrophobic compounds are more readily sorbed by activated carbon than hydrophilic compounds. This effect was observed in both PAC and GAC experiments.

Without question, membranes and activated carbon can provide efficient barriers to the passage of micropollutants. However, no single process can remove every contaminant. For maximum removal of organic pollutants, a multi-barrier treatment train containing membranes, activated carbon, and a strong oxidant (i.e., ozone) would be ideal.