Emerging Contaminants and Membrane Technology

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Emerging contaminants will affect existing and future treatment technologies utilized by the drinking-water community. Existing, pending, or potential emerging contaminants can be classified as disinfection by-products (DBPs), pathogens, and synthetic or natural organic compounds. Membrane technology offers the most versatile and universal treatment technology for water treatment and can meet pending and future treatment challenges.

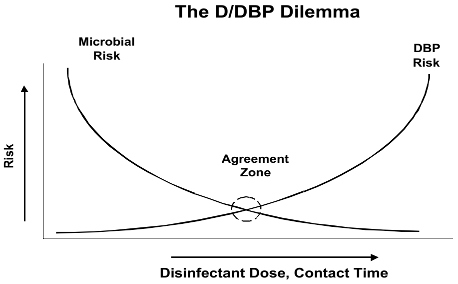

Figure 1

DBPs

Although DBPs have challenged the water community's treatment capability since the late 1970s, changes in the Disinfection By-Product Rule will force many utilities to modify water treatment to meet the Stage I or II Maximum Contaminant Level (MCL), which is 80 μg/L THMs and 60 μg/L HAAs. The Stage I and II DBP MCLs differ by method of calculation. Stage I has a MCL of 80 μg/L THMs and 60 μg/L HAA_5 and allows utilities to use a four-quarter running average for all sampling points in the distribution system. Stage II requires a four-quarter running average for each point in the distribution system.

Although 120/100 will be the initial Stage II MCL, six years after Stage II implementation, each utility will eventually have to meet 80/60 at each point in the distribution system. The impact is significant, as the highest DBP four-quarter average concentration will control DBP treatment technology.

DBPs are typically formed during disinfection and represent a paradox for water treatment. As shown in Figure 1, DBP formation varies inversely with disinfection efficiency; hence, there is a limited region for meeting DBP and disinfection regulations. Chloramines, the most popular treatment technique for controlling THMs, cannot feasibly meet the "CT" requirement for primary disinfection in surface-water systems, affecting more than 20 water plants in the state. It is probable that groundwater treatment facilities will have to meet CT requirements in the pending Groundwater Disinfection Rule, which will exclude chloramines as a primary disinfectant; therefore, membranes, ozone, and ultraviolet disinfection become desirable choices for meeting emerging DBP regulations. (Chellam and Taylor, 2001)

Pathogens

Regulations for cysts, bacteria, and viruses significantly affect drinking-water treatment. The size ranges of cysts, bacteria, and viruses vary and are approximately 3-15 μ, 0.3 to 3 μ and 0.05 to 0.008 μ respectively. Cryptosporidium is the current microorganism of concern and is regulated by the Interim Enhanced Surface Water Treatment Rule (IESWTR), which uses turbidity removal criteria stating 2.5 logs of removal will be given to surface-water plants that achieve less than 0.3 NTU 95 percent of the time with no occurrences over 0.5 NTU and have less than 2 NTU coming from the sedimentation basin. The pending Long-Term Two IESWTR (LT2IESWTR) is tied to a 12-month average over a 24-month data-gathering period raw-water average and requires the source to have less than 0.075 cysts/100 L in order to avoid additional treatment requirements, which include membranes. Regulations have also been proposed that require as much as 6-log removal in the treatment processes, based on raw-water cyst concentration. (Lisle and Rose, 1995)

Groundwater plants will also be affected by Cryptosporidium regulations; however, specific CT requirements have not been listed in the Groundwater Disinfection Rule. (Hong et al, 2001) Although Cryptosporidium regulations are not finalized, pathogen regulations for surface and groundwater sources will undoubtedly be tightened in the current decade.

Pesticides, PHACs, and EDRs

Pesticides, pharmaceutically active compounds (PHACs), and endocrine disruptors (EDRs) are synthetic organic compounds (SOCs) that have emerged as probable candidates for regulations in the near future. Currently pesticides are more stringently regulated in Europe than in the United States. European regulations require that no more than 0.1 μg/L of one and 0.5 μg/L of all regulated pesticides is allowed in finished drinking water. (Taylor and Jacobs, 1996) Pesticide regulation is under review by the U.S. Environmental Protection Agency. The structure and molecular weight of the regulated pesticides of most concern in the European community are shown in Figure 2.

PHACs and EDRs are a new class of SOCs that the Environmental Protection

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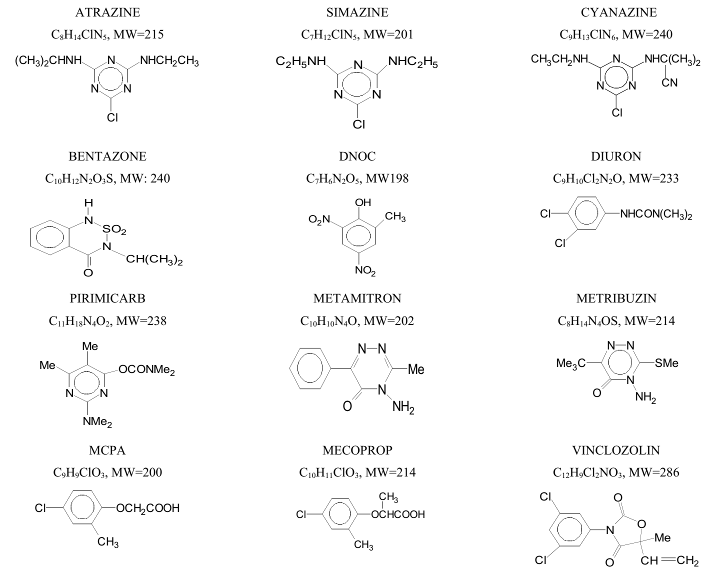

Figure 2

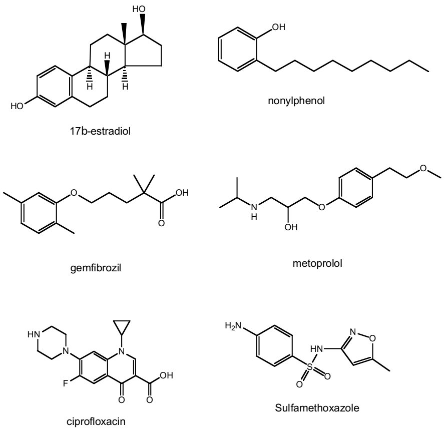

Figure 3

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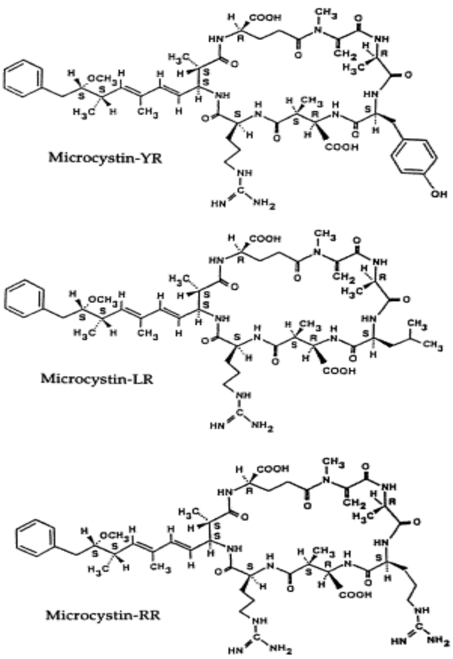
Agency has put forth for potential regulations. PHACs and EDRs are essentially drugs or other SOCs that have been discharged into our water supplies and adversely affect consumers' health. The structure and name of some PHACs and EDRs affecting the water community are shown in Figure 3. All these compounds are similar in that they are organic with similar size and structure.

Algal Toxins

Algal toxins are by-products of algae and are typically associated with algal blooms common in surface waters used for water supply in Florida. They are natural organic contaminants. Algal toxins are also organic compounds with typical ring structure and are larger than PHACs or EDRs. Fish kills, livestock deaths, and alligator deaths have been attributed to algal toxins, which are of three major types: Microcystins, Cylindrospermopsins and Anatoxins.

Some Microcystins are shown in Figure 4. These toxins are cyclic peptides containing unique hydrophobic amino acids and have molecule weights from 900 to 1,000. These algal toxins can not be destroyed by digestion. They are transported through the gastrointestinal tract and concentrated in liver cells by a bile acid-type carrier mechanism. (Steffensen et al., 1999)

Figure 4



Cylindrospermopsin is shown in Figure 5 and was identified from a culture of the blue-green algae present in a dammed reservoir that poisoned livestock. It is stable to boiling and is more stable than microcystin-LR and anatoxin-a. The effects of chronic toxicity from continued ingestion of this organism are not yet known, but can be expected to involve all tissues that rapidly synthesize proteins, such as the pituitary gland, epithelia including the gut lining, the pancreas, lymphoid tissue, and the prostate gland, as well as the kidneys and liver. (Falconer, 1999)

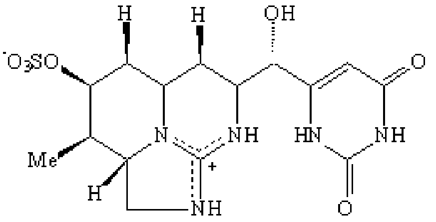


Figure 5

Anatoxins algal toxins are shown in Figure 6. A major bloom of *Anabaena circinalis* that covered 1,000 kilometers of the Darling River in Australia in the summer of 1990-1991 was associated with considerable numbers of sheep and cattle deaths and these algal toxins. These neurotoxins are well-characterized blocking agents of sodium channels in nerve axons; they cause progressive paralysis and death from respiratory failure (Falconer, 1999). Anatoxin-a has been identified as the most common cause of dog and sheep deaths by neurotoxic cyanobacteria in Northern Australia. (Falconer, 1999) Anatoxin-a is a guanidinium methyl phosphate ester with molecular weight of 252. A third neurotoxin from *Anabaena* is anatoxinas. It is likely that other neurotoxins will be identified in blue-green algae.

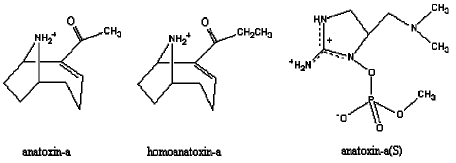
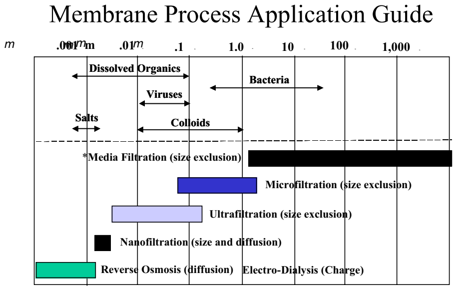


Figure 6

Membrane Technology

A general understanding of potable-water membrane technology can be achieved by associating minimum size of contaminant with membrane processes using Figure 7. (Taylor, 1989) Although there are several mechanisms affecting contaminant removal by membranes, size exclusion is very significant and can be used to describe membrane capability. If the contaminant is too large to pass through the membrane pore, then it is removed from the filtrate stream.



*Media Filtration (not a Membrane Process) Is Shown for Reference Only.

*Electrodialysis removes only ionic species

Figure 7

Contaminants can be categorized as pathogens, organic solutes, and inorganic solutes. Pathogens can be subdivided into cysts, bacteria, and viruses. Organics can be subdivided into DBPs or their total organic carbon (TOC) precursors, SOCs and NOCs. Inorganic parameters are total dissolved solids, total hardness, heavy metals, and other inorganic contaminants. (Taylor and Wiesner, 1999)

Reverse osmosis (RO) and nanofiltration (NF) are pressure-driven membrane processes that can remove contaminates to 0.0001 µ and 0.001 µ respectively. Electrodialysis (ED) and electrodialysis reversal (EDR) processes are capable of removing contaminants to 0.0001 m, but a charge is required. Consequently, ED and EDR are limited to treatment of ionic contaminants and are ineffective for pathogen removal and most organic applications, contrary to RO and NF.

RO and NF can remove any pathogen and organic contaminants to nearly undetectable levels, which is why log rejection is used for pathogen regulations. RO and NF are both diffusion-controlled and size-exclusion processes; however, no process is capable of absolute removal. RO and NF processes have the broadest span of treatment capability but require the greatest degree of pretreatment. (Taylor and Mulford, 1989)

UF can achieve greater than six-log removal of all pathogens from drinking water, whereas MF can achieve greater than six-log removal of cysts. (lovins, Taylor and Hong, 2002; Jacangelo et al., 1991) Consequently, membrane processes are ideal for removing turbidity and microbiological contaminants, and they are well suited for treating the majority of drinking-water sources in the United States. Membrane processes do

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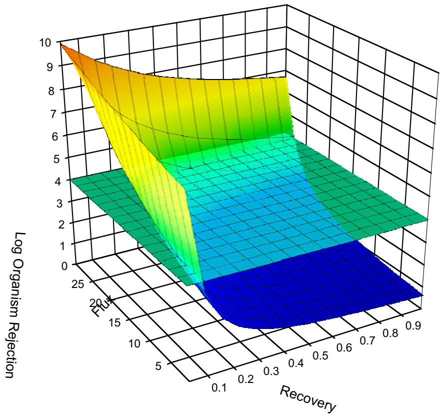

Figure 8

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not remove dissolved gases like H_2S and CO_2.

Mechanism

As previously noted, contaminant removal by membrane processes can be generalized to diffusion-controlled and size-exclusion mechanisms. Simple models describing those mechanisms are shown in Table 1.

These mechanisms are significantly different, as illustrated by log rejection for varying flux and recovery, shown in Figure 8. Permeate water quality changes significantly for varying flux and recovery in a diffusion-controlled mode, as illustrated by the curved plane in Figure 8. The flat plane shown in Figure 8 is representative of water quality from a size-exclusion process. Log rejection will increase as flux increases and decrease as recovery increases in diffusion-controlled processes, where no change will occur in size-exclusion processes. (Lovins and Taylor, 1997)

Pathogen removal by NF or RO is controlled by a size-exclusion mechanism, whereas ion removal is diffusion controlled. Removal of organic compounds exhibits both mechanisms. Diffusion-controlled processes would have the flexibility of decreasing recovery to produce a higher water quality, given that more water could be drawn to meet demand. (Shetty, Sharma and Chellam, 2002)

$$C_p = \frac{K_s C_f e^{\frac{F_w}{k}}}{K_w \Delta P \left(\frac{(1-r)(2-2R)}{2+2r-R} \right) + K_s e^{\frac{F_w}{k}}} \quad \text{or} = \phi C_f$$

C_p = Permeate stream solute conc (M/L^3)
F_w = Water flux (L^3/L^2t)
K_w = Solvent MTC (L^2t/M)
K_s = Solute mass transfer coefficient (L/t)
k =Back diffusion coefficient(L^3/L^2t)

C_c = Concentrate stream conc (M/L^3)
C_f = Feed stream solute conc (M/L^3)
R = Recovery
r = Recycle ratio
ϕ = Convection coefficient

Table 1

DBP Control

Only RO and NF processes are membrane processes used for DBP control. The pores in UF and MF membranes are too large to reject the DBP precursor (TOC). Reduction of THM, HAA and TOC from conventional surface-water treatment and NF is shown in Figure 9. This data was generated in the American Water Service Company's (AWSC's) East St. Louis water-treatment plant and shows the conventional coagulation process removed little of the TOC relative to the three NFs. Two of the NFs had a polyamide composite thin film (CTF) and one had a cellulose acetate (CA) thin film.

Historically, CTF membranes have outperformed CA membranes, as was the case here, although both removed DBP precursors very well. This data indicates that RO and NF membrane processes will be able to meet the Stage II MCL of 80/60 for THMs and HAAs. Granular activated carbon (GAC) can also be used to control DBPs. A typical guideline for selecting membranes or GAC on the basis of cost is: Removal of less than 1 mg/L TOC favors GAC, while removal of more than 1 to 3 mg/L TOC requires close study, and removal of more than 3 mg/L TOC favors membranes. (USEPA, 1996)

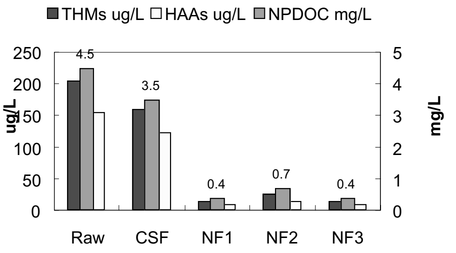


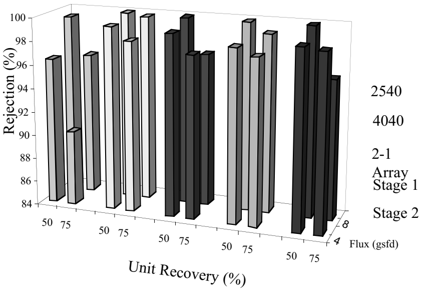
Figure 9

Pesticides And Other Organic Contaminates

The average removal of the 12 pesticides shown in Figure 2 for different sizes of pilot plants is shown in Figure 10. These 12 pesticides were fed at a concentration of 10 µg/L each or total pesticide concentration of 120 µg/L to a 2.5"x40" single element, 4"x40" single element and a two-stage pilot plant in a 2-1 configuration with three elements in each pressure vessel. These results indicate that nearly complete pesticide removal was achieved at the high flux (8 gsfd) and low recovery (50 percent), and that more than 90-percent recovery was achieved for all operational conditions.

All the observations shown in Figure 2 for the 4"x40" membranes easily met the European pesticide regulations for total and individual pesticides. These results indicate that elements smaller than 4"x40" did not offer comparable performance to 4"x40" elements, due to the difference in configuration of the spiral-wound modules. The variation in pesticide concentration with flux and recovery shows pesticide removal is diffusion controlled, and that membranes are a very effective process for removing SOCs. (Chen and Taylor, 1997)

Figure 10



Very little work has been done on PHACs, EDRs and algal toxin removal by membrane processes; however, the molecular weights of these organic compounds are greater than the molecular weights of the pesticides just discussed. The largest pesticide molecular weight was Vinclozolin (288), which was rejected below detection at feed concentrations of 10 µg/L. The PHACs, EDRs, and algal toxins shown in Figures 3, 4, and 5 are larger than pesticides and will be effectively removed by RO or NF membranes. There is some probability that UF or MF membranes can remove algal toxins.

Pathogens

The median log rejection values (LRV) for cysts, bacteria, and viruses are shown in Figure 11. The same membranes that were reference previously at the AWSC plant at East St. Louis in addition to MF and UF membranes are referenced in Figure 11. The organisms used for challenge testing were *Giardia lamblia* cysts (12 mm), *Cryptosporidium parvum* oocysts (4 mm), *Clostridium perfringens* (3 mm), PRD-1 phage (0.1 mm), and MS-2 phage (0.025 mm).

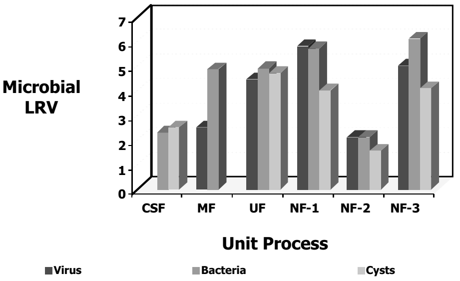


Figure 11

The data shown in Figure 11 is conservative in that more than half of the observations resulted in no organisms passing the membrane, which is infinite rejection. These challenges were assigned one organism in the permeate so that LRV could be calculated. Even at that, the LRV from the UF, NF 1, and NF 3 is twice the LRV credited to conventional coagulation-sedimentation-filtration (CSF) treatment, which indicates these processes reject a thousand times (three orders of magnitude) more organisms than CSF.

The MF passed viruses as expected, and the CA NF 2 was significantly less effective than other membrane processes; however, other than MF passage of viruses, the rejection of pathogens was independent of microorganism size for the pathogens investigated in this study. The data shown in Figure 11 indicates that membranes are a very effective process for removing microorganisms. (Lovins, Taylor and Hong, 2002) Other investigations have shown MF processes are capable of 5 LRV of cysts or more with in process verification. (Miller, 1999)

Summary

Membranes offer distinct treatment advantages against emerging contaminates: RO or NF membranes are capable of meeting the Stage II DBP MCL by removing enough TOC or DBP precursors so that free chorine can still be used for disinfection. Pressure-driven membrane processes can reject five to six logs of viruses, bacteria, or cysts, which exceeds most, if not all, treatment capacities of any other single process. RO or NF membranes can reject small molecular-weight pesticides, are used to meet the stringent European standards, and will likely reject the higher molecular-weight PHACs, EDRs, and algal toxins.

There are no water quality disadvantages to membrane utilization. Significant membrane disadvantages are cost and concentrate disposal.

Membranes can meet or exceed all water-quality regulations; the question many of us have to answer is, “How much are we willing to pay for that water quality?”

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