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EVALUATION OF MEMBRANE PERFORMANCE AND FOULING BY PYROLYSIS-GC/MS

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INTRODUCTION

The loss of membrane efficiency due to fouling is one of the main impediments to the development of membrane processes for use in drinking water treatment. Membrane fouling is dependent on the water quality and the membrane properties and construction. In general, fouling is defined as the accumulation of material on the surface, or in the pores, of a membrane that decreases the water flux through the membrane. The consequences of fouling can be severe, fouling can reduce the water flux through a membrane up to 90 percent (1). There are five broad fouling categories: sparingly soluble inorganics, colloidal or particulate matter, dissolved organics, chemical reactants, and microorganisms.

Dissolved organics and colloidal matter are considered to be the most serious of the foulants due to the difficulty in removing them with pretreatment processes. Membranes can be fouled either by cake-layer formation or adsorption. Cake-layer formation refers to a layer of material on top of the surface of the membrane. Cake-layer fouling can be removed hydrodynamically. Adsorption refers to materials attached within the pores of the membrane. This type of fouling is generally considered irreversible although chemical cleaning can be effective in some cases. The nature of the organic molecules that foul nanofiltration membranes is not known. Knowledge of the characteristics of the natural organic matter responsible for membrane fouling may lead to optimal membrane and pretreatment selection. Improved nanofiltration performance will lead to an increased use of nanofiltration as a drinking water treatment method.

Pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS) has the ability to elucidate natural organic matter characteristics. Pyrolysis is used to thermally cleave organic molecules into volatile fragments that are then separated by gas chromatography and identified by mass spectroscopy. The Py-GC/MS method used herein was developed by Bruchet et al. (2) at the Lyonnaise des Eaux in Paris, France. Bruchet's method categorizes natural organic matter in terms of polysaccharides, proteins, polyhydroxyaromatics, and aminosugars. The fractions are calculated relative to a known standard mixture of dextran, bovine serum albumin, cellulose acetate, and Fluka humic acids. A simple empirical algorithm was developed for computing relative peak areas among the various classes of biopolymers (2).

The objective of this research is to relate the productivity of membrane systems that treat different waters to natural organic characteristics as determined by Py-GC/MS. Membrane studies will be completed with a cellulose acetate membrane that has a nominal molecular-weight cutoff of 500 Daltons (Amicon YC05), and a thin-film polyamide membrane (Fluid Systems) that has a nominal molecular-weight cutoff of 200 Daltons. Waters from the Ohio River (southern Ohio), East Fork Lake (southern Ohio), and Manatee County (Florida) were used. The three waters have very different characteristics. The Manatee County water (MCW) has a very high dissolved organic carbon (DOC) concentration (near 20 mg/L). It also has very low alkalinity (12 mg/L as $CaCO_3$) and hardness (29 mg/L as $CaCO_3$). Py-GC/MS results indicate that the Manatee County water is very aromatic in nature. The Ohio River water (ORW) is low in DOC (approximately 2.5 mg/L). It is moderately hard (110 mg/L as $CaCO_3$), and has a moderate alkalinity (56 mg/L as $CaCO_3$). Preliminary Py-GC/MS results suggest that it has aromatic and proteinaceous character. The East Fork Lake water (EFLW) has a moderate DOC (approximately 5 mg/L), and has the highest hardness (126 mg/L as $CaCO_3$) and alkalinity (100 mg/L as $CaCO_3$) of the three waters. The EFLW Py-GC/MS results indicate a polysaccharide nature.

METHODOLOGY

The membrane experiments were conducted in a 450 ml dead-end pressure vessel that was stirred. The membrane experiments were run until the flux decreased to approximately 50 percent of the initial flux, or until a steady flux was obtained. At the end of each experiment, the concentrate was collected and rotoevaporated to a concentration that allowed for adequate organics to be spiked into 50µl pyrolysis tubes. Likewise, the feed and the permeate streams were rotoevaporated to a similar concentration. The membrane was then turned over and approximately 100 ml of organic-free water was used to backflush the membrane. Finally, the membrane was turned back over and a short run with organic-free water was completed to check the flux recovered after backflushing. The backflush sample was also rotoevaporated to the same concentration as the other samples. The Manatee water experiments had a layer of material on top of the membrane that did not come off with backflushing. This material was physically scraped off and analyzed.

The DOC, total dissolved solids (TDS), and ultraviolet @254nm (UV) of the feed, concentrate, and numerous permeate samples were assessed. These results allowed for a mass balance to be completed over the membrane experiment. Also, small aliquots of the rotoevaporated samples were taken and diluted into 100 ml of organic-free water. DOC, TDS, and UV of the diluted samples were assessed. This was completed to determine the volume of the samples to be spiked into the pyrolysis tubes to obtain the same total DOC in all of the tubes (130 µg). It also allowed for determination of the amount of organics that adhered to inorganic precipitation during rotoevaporation. Rotoevaporation losses of organics may be important with regard to the pyrolysis results if the organics removed were not similar in make-up to the organics that remained in solution.

Each Py-GC/MS sample was run in triplicate. The pyrolysis tubes were weighed before and after pyrolysis to confirm that similar sample sizes were being used, and to show that similar amounts of the samples were being pyrolyzed. The three waters being used were each concentrated on two separate occasions to confirm that each water's characteristics were not changing over time.

After the fouling of the membranes, a small (0.3mg) sample of each of the fouled membranes was pyrolyzed. The membrane sample was measured on a balance sensitive to 0.01mg. As with the previously discussed samples, each Py-GC/MS sample was run in triplicate. Clean membranes were also pyrolyzed in triplicate to determine the background pyrograms.

The analytical procedure for Py-GC/MS entailed ramping the pyrolysis sample from 35°C to 750°C at 20°C/ms in a heated-filament pyrolysis probe. The final temperature was held constant for 20 seconds. Splitless injection to the GC was used. The GC was ramped from 35°C to 260°C at a rate of 2°C/min. A 60-meter Supelco WAX-10 column was used.

RESULTS

Table 1 contains the flux decline results for the matrix of experiments performed in this study. The Manatee County water showed the greatest flux reduction for the Amicon membrane experiments.

The East Fork Lake water showed the greatest flux reduction for the Fluid System membrane experiments. The reason for this behavior is made clear by electron microscope analysis. Electron microscopy of the fouled Amicon membranes showed no inorganic deposits. This indicates that the fouling agents were organic in nature. Electron microscopy of the Fluid System membranes for the EFLW and ORW experiments, however, showed large deposits of calcium (most probably calcium carbonate). The Manatee County water showed no inorganic fouling with the Fluid System membrane.

TABLE 1. FLUX DECLINE RESULTS FOR MATRIX OF EXPERIMENTS

Membrane/Water	Liters of Water Passed	Percentage Flux Decline
Amicon/Manatee County Water	7.8	35
Amicon/Ohio River Water	21.5	30
Amicon/East Fork Lake Water	18.6	15
Fluid System/Manatee County Water	6.8	55
Fluid System/Ohio River Water	6.8	60
Fluid System/East Fork Lake Water	3.9	68

As mentioned above, the Amicon membranes were fouled by organics. Therefore, it is not surprising that the Manatee County water, which had the highest DOC concentration, showed the greatest amount of fouling. The organic nature of the foulant was also confirmed by the UV, DOC, and TDS balances of the membrane run. The Amicon membrane had a large enough molecular-weight cutoff to pass inorganic ions while rejecting most of the organic molecules.

The Fluid System membrane rejected both organics and a great deal of the inorganic ions. This was shown by UV, DOC, and TDS mass balances over the membrane experiments. This was expected because of the Fluid System membrane's designation as a "softening" membrane. The East Fork Lake water had the greatest concentration of hardness and alkalinity, and hence the greatest amount of inorganic fouling. The Fluid-System/MCW experiment showed a lack of inorganic fouling as mentioned above. This was due to the water's extremely low hardness and alkalinity. This was visually confirmed by noticing that the final concentrate solutions of the Fluid-System/EFLW and the Fluid-System/ORW experiments were salty in appearance, whereas the Fluid-System/MCW concentrate was clear.

Py-GC/MS of the Manatee County water showed that the water is primarily polyhydroxyaromatic in nature. Polyhydroxyaromatics accounted for over half of the organics. Proteins, polysaccharides, and aminosugars accounted for a much lower percentage of the total. The pyrolysis results for the feed water, concentrate, permeate, and membrane scrapings showed that the concentrate had a marked decrease in polysaccharides as compared to the feed water. The pyrolysis results of the other fractions were roughly similar to the feed-water results.

Figure 1 contains the mass balance for the Amicon/MCW experiment. The mass balance shows that the biopolymer groups were primarily found in the concentrate stream as expected due to the high organic rejection. The permeate, backflush, and membrane scrapings contained small amounts of all the biopolymers. The mass balance closed very well for the protein, polyhydroxyaromatic, and aminosugar groups. However, a large amount of the polysaccharides fed to the system was not accounted for. When the membrane was pyrolyzed, the unaccounted for polysaccharides were found. Figure 1 also shows the amount of polysaccharides found in the membrane. This additional amount of polysaccharides closes the mass balance reasonably well. Therefore, these results suggest that polysaccharide material was irreversibly adsorbed (operationally defined) to the membrane, and was responsible for the membrane fouling.

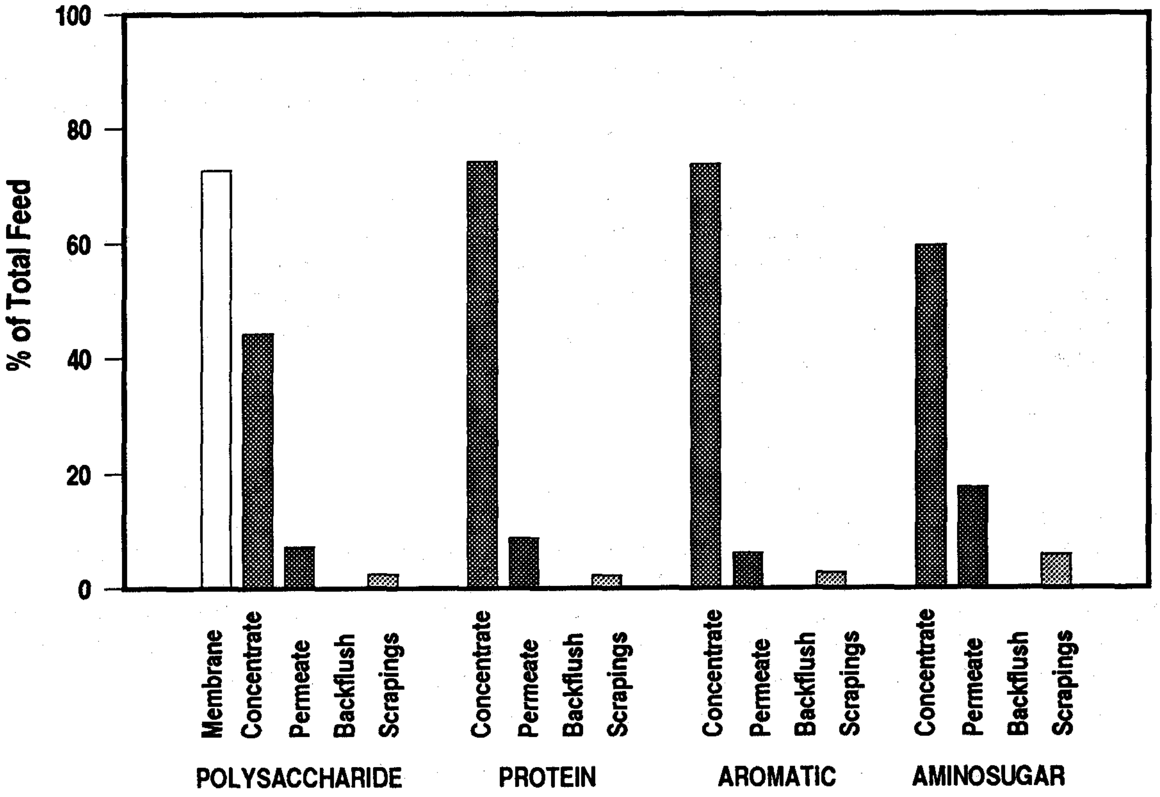

Figure 1. Pyrolysis-GC/MS mass-balance results for Amicon-YC05 membrane run with Manatee County water.

The Amicon/MCW results agree with the work of Mallevialle et al. (3) who showed that polysaccharides were one of the fouling agents for ultrafiltration membranes. Mallevialle et al. (3) indicated that inorganics also were present in the fouling mechanism. In this work, however, the electron microscopy results do not show an inorganic presence.

The Fluid-System/MCW results show that all of the Bruchet et al. (2) groups were rejected, and thereby remained in the concentrate. However, the mass balance indicates that significant portions of all four groups remained unaccounted for. Co-elution problems with membrane pyrolysis fragments obscured the membrane pyrolysis results for polysaccharides and polyhydroxyaromatics. Therefore, it is unknown as to whether they were irreversibly adsorbed to the membrane.

The EFLW results are unique. For the Amicon experiment, all four Bruchet et al. (2) groups were rejected by the membrane and thereby remained in the concentrate solutions. The mass balances suggest that no significant amounts of organics were adsorbed to the membrane. Direct pyrolysis of the membrane showed a similar result. The very low flux drop over the course of the Amicon/EFLW experiment also suggests that the membrane was not significantly fouled. The membrane run was stopped because TDS, UV, and DOC broke through the membrane at elevated levels. The lack of fouling was surprising because of the high polysaccharide concentration in the East Fork Lake water.

The Fluid System/EFLW pyrolysis results suggest that proteinaceous material was adsorbed onto the membrane. The percentage of flux reduction that was caused by the proteinaceous material in relation to that caused by the above mentioned inorganic foulant is unknown. The combined mixture of inorganic and organic foulants corresponds to the results of Mallevialle et al. (3).

The ORW results are also unique. The concentrates for both the Amicon-YC05 experiment and the Fluid System experiment show high concentrations of polysaccharides. The pyrolysis mass balances, however, give inaccurate results. The inaccurate results suggest that the high ratio of salts to organics affected the pyrolysis results. The ORW concentrate solutions had the greatest amount of organics removed by salt precipitation during rotoevaporation.

The varied fouling results for the different waters and different membranes suggest that it may be possible to choose a pretreatment process that delays flux reduction. For inorganic contaminants, acid addition or antiscalent agents can be used, as they are currently. For organic foulants, Py-GC/MS can identify the major foulant and a pretreatment process could be selected to remove the foulant. Also, if membrane properties can be related to fouling agents, the choice of the optimal membrane can be made from analysis of the water.

CONCLUSIONS

The cellulose-acetate-based Amicon-YC05 membrane was fouled to the greatest extent by the Manatee County water which had high organic levels. The polysaccharide fraction of the Manatee County water was determined to be responsible based on a mass balance over the membrane experiment and by direct evaluation of the fouled membranes. The East Fork Lake water did not foul the Amicon-YC05 membrane severely. The pyrolysis-GC/MS results for the East Fork Lake experiment confirmed that organics were not adsorbing onto the membrane. The Ohio River water results were inconclusive, probably due to the presence of salts. Electron microscopy results showed that there was no inorganic fouling of the Amicon membranes by any of the waters.

The polyamide-based Fluid-System membrane was fouled to the greatest extent by the East Fork Lake water which had the highest hardness and alkalinity. Calcium carbonate precipitation was deemed to be the causative fouling agent by electron microscopy for both the East Fork Lake water and Ohio River water. The East Fork Lake water pyrolysis results suggest that proteins also adsorbed to the membrane with the inorganic foulants. The Ohio River water pyrolysis results were inconclusive probably due to the presence of salts. The Manatee County membrane experiment showed no inorganic fouling, The pyrolysis-GC/MS results for the Manatee County water experiment suggest that all four biopolymer classes may be involved in the observed fouling.

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BIOFILTRATION FOR CONTROL OF VOLATILE ORGANIC COMPOUNDS (VOCS)

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INTRODUCTION

Air biofiltration is a promising technology for control of air emissions of biodegradable volatile organic compounds (VOCs). In conjunction with vacuum extraction of soils or air stripping of ground water, it can be used to mineralize VOCs removed from contaminated soil or groundwater. The literature (1) describes three major biological systems for treating contaminated air bioscrubbers, biotrickling filters and biofilters. Bioscrubbers, which are not evaluated here, use counter current gas-liquid spray columns with microorganisms freely suspended in the aqueous phase. Biofilters and biotrickling filters use microbial populations in biofilms immobilized on support media to degrade or transform contaminants in air. Filter media can be classified as: bioactive fine or irregular particulates, such as soil, peat, compost or mixtures of these materials; pelletized, which are randomly packed in a bed; and structured, such as monoliths with defined or variable passage size and geometry. The media can be made of sorbing and nonadsorbing materials. Nonbioactive pelletized and structured media require recycled solutions of nutrients and buffer for efficient microbial activity and are thus called biotrickling filters. Filters with bioactive fine or irregular particulates as media, referred to as biofilters, usually do not recycle solutions of nutrients and buffers to prevent media compaction and gas channeling. All filters humidify the contaminated air before biotreatment.

Soil biofilters are relatively large because soil pores are smaller and compounds have low permeability in soil. They also have limited bed depths, required for maintaining humidity in soil and minimizing pressure drop. Peat/compost biofilters, used commercially, are suitable for treating large volumes of air containing biodegradable VOCs at low concentrations (<200 ppmv). However, both soil and peat/compost biofilters are susceptible to channeling and maldistribution of air and require periodic media replacement.

Extensive work has been conducted to improve biofiltration by EPA's Risk Reduction Engineering Laboratory and the University of Cincinnati in biofilters using pelletized and structured media and improved operational approaches. Representative VOCs in these studies included compounds with a range of aqueous solubilities and octanol-water partition coefficients. The compounds include iso-pentane, toluene, methylene chloride, trichloroethylene (TCE), ethyl benzene, chlorobenzene and perchloroethylene (PCE) and alpha (α-) pinene. Comparative studies were conducted with peat/compost biofilters using isopentane and α-pinene. Control studies were also conducted to investigate adsorption/desorption of contaminants on various media using mercuric chloride solution to insure the absence of bioactivity.

MATERIALS AND METHODS

The typical experimental set-up of a biofilter bed (Figure 1) packed with support media was operated at steady-state conditions to characterize process performance. Contaminated air, synthesized by injecting VOC stock solutions into a controlled air stream, was passed through the biofilter bed. The inlet air was humidified