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A Comparison of Silver- and Copper-Charged Polypropylene Feed Spacers for Biofouling Control

Richard Hausman, Isabel C. Escobar
Department of Chemical and Environmental Engineering, The University of Toledo, Toledo, Ohio 43606-3390
Correspondence to: I. C. Escobar (E-mail: isabel.escobar@utoledo.edu)

ABSTRACT: Implementation of nanofiltration (NF) and reverse osmosis (RO) processes in treating traditional water sources can provide a steady-state level of removal that eliminates the need for regeneration of ion exchange resins or granular activated carbon. Moreover, RO can help meet future potable water demands through desalination of seawater and brackish waters. The productivity of membrane filtration is severely lowered by fouling, which is caused by the accumulation of foreign substances on the surface and/or within pores of membranes. Microbial fouling, or biofouling, is the growth of microorganisms on the membrane surface and on the feed spacer as present between the envelopes. The fouling of membranes has demanded and continues to demand considerable attention from industry and research communities. Many of these applications use membranes in a spiral wound configuration that contains a feed spacer. The goal of this project was to develop low-biofouling polypropylene (PP) spacers through the functionalization of PP by a spacer arm with metal chelating ligands charged with biocidal metal ions, investigate the use of this metal-charged polypropylene (PP) feed spacers that target biofouling control, and to use some traditional and one novel techniques to autopsy the membranes after filtration to gain a better understanding of the biofouling mechanism and how the modified spacers are affecting it.

KEYWORDS: feed spacer; biofouling; silver; copper

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INTRODUCTION

Membranes for water treatment are usually characterized into four main classifications that can be based solely on pore size. These classifications are, from the largest pore size ($\sim$ 1 μm) to the smallest ($\sim$ 0.001 μm): microfiltration (MF) and ultrafiltration (UF), which are considered low-pressure membranes, and nanofiltration (NF) and reverse osmosis (RO), which are considered high-pressure membranes. RO membranes have also been considered to be nonporous membranes resulting in a solution-diffusion based separation. Much advancement has been made in membrane performance, permeability and durability, but there are still many problems with membrane performance and lifetime, which restrict them from more widespread uses. One such challenge, that is common to both low- and high-pressure systems, is membrane fouling.[1]

Fouling can be described as the undesirable accumulation and/or formation of deposits at the membrane surfaces, on the membrane pores, or within the pores. Membrane fouling categories include: colloidal fouling, inorganic fouling, organic fouling, and biological fouling, which is often referred to as biofouling. The accumulation of foulants hinder the membrane filtration process by decreasing the flux of permeate and increasing the hydraulic resistance of mass transport. This accumulation can come in the form of cake/gel layer formation or physical pore blocking.

Biofouling is the accumulation and growth of microorganisms onto the membrane surface and on the feed spacer, as present between the envelopes in spiral wound reverse osmosis membrane modules. This accumulation of microorganisms, along with the presence of nutrients that are common in many membrane applications, forms biofilms. For spiral-wound reverse osmosis and nanofiltration membranes, biofouling is the major type of fouling leading to pressure drop.[2–4] It has been shown that biofouling causes a flux decline by increasing hydraulic resistance.[5,6] Furthermore, biofouling is particularly significant because membrane replacement due to fouling is the single largest operating cost in water separation.[1] For this reason, research on altering the chemical, and possibly antimicrobial, properties of the feed spacer is the focus of much attention.

In biofilms, organisms are embedded in a matrix of microbial origin, consisting of extracellular polymeric substances (EPS). These matrices are often very complex and difficult to remove.

For this reason, much effort goes into the prevention of biofilm growth, rather than its removal. This prevention is usually attempted through the use of pretreatments, nutrient removal, maximizing shear forces at the membrane surface, and backflushing. The problem with pretreatment methods is that even if 99.9% of microorganisms are removed, those left remaining can proliferated and cause irreversible fouling. Furthermore, biocides, such as free or combine chlorine, can only be used with certain chlorine-resistant membranes, and since biofouling is such a common problem, use of biocides eventually destroy the membrane. Biofouling starts at the membrane/feed spacer interface suggesting that biofouling might be a feed-spacer problem.[7] Feed spacers, which usually have the form of nonwoven crossed cylinders, serve to separate adjacent membrane leaves and create flow passages, but also to promote flow unsteadiness and enhance mass transport.

By creating such turbulence, the undesirable fouling and concentration polarization phenomena are mitigated.[8] Research has also shown that little work has been focused on feed spacers for biofouling control.[9] The work that has been conducted on feed spacers has been focused on feed spacer geometry, generally to reduce pressure drop and increase permeate flux.[8,10] These works have shown that altering the feed spacer geometry can alter wall shear stresses and that such stresses have maxima significantly higher than those corresponding to empty channels. The nonuniformity of shear stresses was also shown to have the ability to be manipulated which may have implications on membrane fouling. It is apparent that anti-fouling properties were not the primary focus of these studies and biofouling resistance, specifically, was not even mentioned. The only studies found regarding feed spacer surface modifications consisted of methods for bulk modifications of the entire membrane module/membrane/spacer rather than specifically the feed spacer.[11,12] The lack of research being conducted on feed spacer modifications to control biofouling, coupled with the unique role the feed spacer plays in this type of fouling, has led to the research that has been conducted in this work.

Grafting of unsaturated vinyl monomers onto PP is a convenient route to develop new polymeric materials with synergistic properties.[13] Polymer–metal complexes have been extensively studied and successfully employed in several fields.[14] As in low-molecular-weight compounds, a polymer ligand must donate unshared electrons to the metal ion to form metal-ligand bonds. Among the multidentate ligands, iminodiacetic acid (IDA) possesses one aminopolycarboxylate and provides a reactive secondary amine hydrogen to react with alternate functional groups.[14] Hence, IDA can be more easily introduced to the side chain of a polymer or vinyl monomer via an SN2 epoxy group reaction of glycidyl methacrylate (GMA) and IDA.[15] This reaction has two advantages, (1) GMA is a commercial industrial material that is cheaper than any other vinyl monomers that possess an epoxy ring in the side chain; and (2) it produces a vinyl monomer that can be polymerized in the presence of an initiator and can be grafted to activate polymer surfaces. The chemical modification of polypropylene feed spacers to allow metal chelation, increase antimicrobial properties, and ultimately control membrane biofouling has been studied.[15,16] In these studies, PP was functionalized with copper (Cu) to demonstrate that Cu-charged PP could be used to make low biofouling feed spacers for spiral wound elements. The functionalized PP contained grafted GMA with the metal chelating ligand (IDA) to which copper was chelated.[15] Many studies have been conducted on the use of copper ions to disinfect water against microbial biofilms with effective dosages of a few tenths of 1 mgL^{-1}.[17] Copper is thought to be cytotoxic by causing changes in the plasma membrane permeability or efflux of intracellular K^+ during the entry of Cu^{2+} ions.[18] Copper is known to coordinate with Cys residues which, in turn, may lead to changes in enzyme activity and intracellular trafficking.[19] It can also participate in Fenton-like reactions generating reactive hydroxyl radicals, which can cause cellular damage imparted via oxidative stress.[18] Copper may damage many proteins, both on the microorganism envelope or within the cell. Conformational changes in the protein structure or in the protein active site may occur, resulting in the inhibition or neutralization of the proteins' biological activities.[20] Silver ions also posses antimicrobial properties as they are known to have strong interactions with thiol (sulfydryl, —SH) groups.[21] Cytoplasmic proteins and DNA are targets of silver through interaction with these thiol groups in proteins, causing enzymatic inactivation.[22] Additionally, cytosines in DNA form stable C—Ag—C structures.[23]

The goal of this project was to develop low-biofouling PP, which can used for numerous applications such as food packaging, medical devices, but mainly, reverse osmosis feed spacers, through the functionalization of PP. The functionalized PP contained a spacer arm glycidyl methacrylate (GMA) with a metal chelating ligand, iminodiacetic acid (IDA). Many studies have been conducted on the use of copper and silver ions to disinfect water against microbial biofilms.[17,24] These ions are believed to interfere with enzymes involved in cellular respiration and bind DNA at specific sites.[25] For this reason, the metal chelating ligands were charged with either copper or silver ions to increase PP biofouling resistance.

EXPERIMENTAL

Membranes

The membranes used were TFC-S polyamide membranes that were commercially available nanofiltration thin film composite (TFC) membranes manufactured by Koch Membranes (San Diego, CA). These polyamide membranes, described in greater detail in Chennamsetty and Escobar,[26] consisted of a polysulfone support layer covered by aromatic polyamide selective layer. The functional groups were carboxylate/carboxylic acid. The film layer was $\sim$ 1000–2000 Å thick and the molecular weight cutoff was around 200–300 Da.[27,28] The membrane had a slight negative charge with a contact angle of 55°.[29] The typical operating pressure was 5.5 bar, with the maximum operating pressure being 24 bar. The maximum operating temperature was 45°C and the allowable pH range was 4–11. Chlorine tolerance was low, with the maximum continuous free chlorine concentration being <0.1 mgL^{-1}.

Polypropylene Feed Spacers

Homopolymer polypropylene sheets of thickness 0.030 inches were purchased from Professional Plastics (Fullerton, CA) and

were used as received unless otherwise noted. Homopolymer polypropylene 0.026" feed spacers, produced with 100% FDA grade (CFR 21) polypropylene, were donated by Delstar Technologies (Middleton, DE).

Materials

Glycidyl methacrylate (GMA) was purchased from Fisher Scientific (Hampton, NH) and vacuum distilled before use. Sodium iminodiacetate disbasic (IDA) hydrate 98% and methylene chloride were purchased from Aldrich Chemistry (St. Louis, MO) and used as received. Humic acid was purchased in the form of a 50–60% sodium salt, as well as reagent grade tannic acid, from Acros Organics, NJ, USA. *Pseudomonas fluorescence* cells, ATTC#12842 were purchased from ATTC and were freshly cultured on R2A agar (BD, Franklin Lakes, NJ) before each inoculation. Benzoyl peroxide, toluene, acetone, copper sulfate, silver nitrate, sodium chloride, calcium chloride, magnesium chloride, ferrous sulfate, sodium acetate, sodium thiosulfate, glucose, and ethylenediaminetetraacetic acid (EDTA) were purchased from Fisher Scientific (Hampton, NH) also used as received.

Experimental Methods and Characterization

Preparation of Copper (Cu) and Silver (Ag) Charged PP-graft-GMA-IDA. Polypropylene sheets were cut into squares with and area ranging from 2 to 4 cm^2, or PP feed spacers were cut to the appropriate size, rolled and tied with Teflon tape, and sonicated in ethanol for 30 min to clean and remove anything on their surfaces. The sheets were then vacuum-dried at 60°C for 24 h before being placed into the reaction vessel. The nitrogen used was from an ultra high purity 300 cm^3 tank (Air Gas, Independence, OH).

The initial weights (W_o) of the sheets were determined before they were placed in a round bottom flask containing toluene as a solvent/interfacial agent, the radical initiator benzoyl peroxide (BPO), and GMA. Polymerization occurs via C—C double bond cleavage and results in a graft material with the original reactivity of the epoxy ring. Thus, the epoxy group can be effectively used to anchor the desired species. After the sheets soaked in the toluene/GMA monomer solution in which the toluene slightly swells and etches the PP, the reaction vessel was purged with nitrogen and the temperature was increased to 80°C to activate the BPO and the simultaneous homopolymerization of GMA and its grafting to PP was allowed to occur. The sheets were then taken out and washed with acetone to remove all unbound GMA homopolymer. The sheets were placed in a 50/50 DMSO/H_2O solution containing 0.5 iminodiacetic acid (IDA) for 90 min. The DMSO, as a polar aprotic solvent, stabilizes the transition state of the SN2 reaction between the epoxy group of the GMA and the imine group of the IDA. Also, a mixed solvent system is used so that the IDA salt can be dissolved by the water. After the reaction with IDA, DI water was used to rinse the sheets before they were vacuum dried and again analyzed by an ATR-FTIR spectrometer. The PP-graft-polyGMA-IDA sheets were placed into either 0.2*M* copper sulfate or 0.6*M* silver nitrate solution for 30 min to allow IDA to chelate Cu(II) or Ag(II) ions, respectively.

Investigation of Antimicrobial Properties of Charged PP-graft-GMA-IDA. Two 150 mL Erlenmeyer flasks of LB Broth (Difco/Becton, Dickinson and Company, Sparks, MD) containing *E. coli* ATTC#10798 bacterium cells at a concentration of 3.0 $\times$ 10^5 cells mL^{-1} were prepared. Three sheets of both virgin PP and Cu(II) or Ag(II) charged PP-graft-GMA-IDA were added to the each flask and they were then incubated at 35°C, which is near the maximum growth temperature of 37°C, to increase cellular growth. At 24, 96, and 168 h sheets were taken from each flask. Cells were detached from the sheets using a Stomacher 400 Circulator (Seward, London, England). Detached cells were stained with Quant-iT PicoGreen dsDNA stain and counted using an Olympus BX51 fluorescent microscope (Tokyo, Japan) and an Olympus DP-70 digital camera (Tokyo, Japan). Triplets of each sample were taken, counting 10 fields each time.

Release of Chelated Metal Ions from Modified PP. Atomic absorption analysis was performed on solutions that had been exposed to the Cu(II) charged PP sheets in batch experiments. Samples collected during filtration runs using Ag-charged feed spacers were sent to the United State Department of Agriculture Agricultural Research Service at the University of Toledo. The amount of silver in solution was quantified using a Thermo Scientific XSeries 2 ICPMS, which is capable of accurately measuring silver in the parts per billion (ppb) range.

The batch experiments consisted of 2 cm^2 sheets of Cu- or Ag-charged PP placed in 500-mL solutions of 5 m*M* EDTA, with pH adjusted to 11 and 50 mgL^{-1} ferrous sulfate, both of which were prepared in DI water. The solutions were shaken for 212 h at room temperature. About 2-mL samples of the solutions were collected throughout the experiment, which ran for 212 h, to be analyzed for copper or silver content.

Performance of Modified Feed Spacers During Crossflow Filtration. Modified and unmodified spacers were tested in full recycle mode with the use of identical nanofiltration TFC-S membranes. In full recycle mode, a 55-L container was filled with feed solutions and tubes for the pump inlet, permeate outlet, and concentrate outlet placed into it. Water was pumped through a Poly Science KR-60A heater/chiller (Niles, IL) to maintain isothermal conditions. Each membrane was subjected to 8 h of precompaction using DI water. The fluxes of membranes using both modified and unmodified feed spacers were measured throughout a 48-h period of filtration.

The feed water was composed of *Pseudomonas fluorescens* Migula cells, which were freshly grown on an R2A agar plate, added to the reservoir so that the initial cell concentration was 10^6 cells mL^{-1}. Filtration was carried out at 34°C and 6.89 bar (100 psi). The fluxes of membranes using Cu-charged, Ag-charged, and unmodified feed spacers were measured throughout four filtration runs each: one 4-h run, one 24-h run, and two 48-h runs (except in the case of the Ag-charged spacer which had one 48-h run). Cell counts, following the same protocol listed for live/dead counting of cells detached from the membrane, were performed on the solution in the feed reservoir throughout filtration.

Fouled Membrane Autopsies

SEM Imaging of Fouled Membranes. Samples of each membrane, one used with the unmodified/virgin spacer, one used with the Ag-charged spacer, and one used with the Cu-charged

Table I. FTIR Wave Numbers and Band Assignments of Biofilm Components

Wave number (cm^{-1})	Band assignment	Associated biomolecule	References
970	C—O stretch	Polysaccharides	34
1053	C—O or C—O—C stretch	Polysaccharides	34-36
1380	Symmetric stretch of carboxylate Ion	Polysaccharides	37
1450	C—H bending of CH2	Lipopolysaccharides	36, 37
1535	NOH bend of amide II	Protein	34-39
~1635	C=O stretch of amide I	Protein	34-39
1735	C=O stretch of esters	Polysaccharides, fatty acids, phospholipids, lipopolysaccharides	34, 36, 37

spacer, were taken from identical locations on the membrane surface after the filtration period. These membranes were vacuumed dried at ambient temperature to remove all water and were then coated using a gold-palladium target for 30 s to aid in electron imaging and prevent charging. Scanning electron microscopy (SEM) imaging (Hitachi S-4800 High Resolution Scanning Electron Microscope, Japan) of membrane samples was performed.

FTIR Spectroscopy of Fouled Membranes. FTIR analysis using an attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Digilab UMA 600 FT-IT, Holliston, MA) microscope with a Pike HATR adapter and an Excalibur FTS 400 spectrometer, Ge crystal with a refractive index of 4.0 and a long wave length cut-off of 780 cm^{-1}) was performed on an unfouled membrane, as well as membranes fouled using virgin and Ag and Cu modified feed spacers in 21 locations on each membrane and averaged. To determine the depth of penetration during ATR-FTIR, the eq. (1) was used,[30] where DP is the depth of penetration of the evanescent IR wave, $\ominus$ is the angle of incidence (45°), λ is the wavelength (μm), n_1 is the refractive index (RI) of the Ge Crystal (4.0), and n_2 is the RI of sample being analyzed in this case polyamide with a RI of 1.56[31]

$$\mathrm{DP} = \frac{\lambda}{2\pi n_1 \left[\sin^2 \emptyset - \left(\frac{n_2}{n_1}\right)^2\right]^{\frac{1}{2}}} \quad (1)$$

This equation is valid when the refractive index of the sample is uniform throughout the depth of penetration. If one considers a case where there are two layers in the path of the IR penetration, as in the case of a biofouled membrane (biofilm and membrane layers), this equation must be altered to eq. (2),[32] where n_3 is the refractive index of the biofilm layer, t_b is the thickness of the biofilm layer which is seen by the IR, and t_m is the thickness of the membrane, which is seen by the IR.

$$\mathrm{DP} = \frac{\lambda}{2\pi n_1 \left[\sin^2 \emptyset - \left(\frac{n_2\left(\frac{t_m}{DP}\right)+n_3\left(\frac{t_b}{DP}\right)}{n_1}\right)^2\right]^{\frac{1}{2}}} \quad (2)$$

To determine t_m an FTIR spectra of an unfouled membrane must be acquired and a prominent peak that is characteristic of the membrane, but does not appear in the biofilm, is located. The peak at 1238 cm^{-1} (8.08 μm) was identified as such, and the area under it was determined. Once a biofilm layer of thickness t_b is accumulated on the membrane, the area under this peak decreases. The area under the peak of the fouled membrane is then divided by the area of the initial membrane, and the resulting value is multiplied by the DP calculated using the unfouled membrane to determine t_m. This is summed up in eq. (3), where A_1 is the area under the characteristic membrane peak of the unfouled membrane and A_2 is that of the fouled membrane.

$$t_m = \frac{A_2}{A_1} \times DP \quad (3)$$

The DP can simply be substituted with ($t_b + t_m$) in eq. (2), since the depth of penetration through the two-component system is obviously the sum of the thickness of penetration through both. From literature, n_3, the refractive index of the biofilm, is 1.38.[30] The values of every variable expect t_b are now known so it can be determined.

Once the thickness of the biofilm has been determined, information about the concentration of components in the biofilms can be investigated. The FTIR spectra of *Pseudomonas fluorescens* biofilms have been studied,[30] and the locations of peaks for different components are known. A list of these components and their locations are shown in Table I. For the peaks on the biofilm that do not interfere with peaks from the membrane, the area under a peak of interest can be determined by integration. Varian Resolutions Pro Version 4.1.0.101 was used to integrate under the peaks of interest. This area is then divided by the thickness of the biofilm, t_b, on the membranes to get a concentration with units (amount μL^{-1}). The unit in the numerator is not known since extinction coefficients are unknown, and therefore only relative quantitative information can currently be gained from this technique; that is, the concentration of a species in a biofilm on a membrane used with a modified spacer versus that fouled with virgin spacer. Because Beer–Lambert's law states that concentration is directly proportional to absorbance, much insight about the difference in biofilm formation when using a copper-charged feed spacer can still be obtained. To determine the area under biofilm component peaks, which

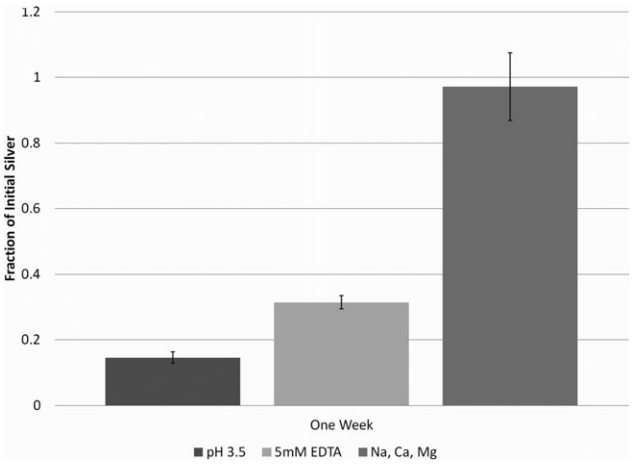

Figure 1. Fraction of silver remaining on modified PP during batch leaching study.

do overlap peaks coming from the unfouled membrane, the absorption coming from the membrane in the specified region must be subtracted. To do this, the area of this region is determined from the spectrum of the unfouled membrane, multiplied by, and then subtracted from the area integrated under the same region on the fouled membrane.

RESULTS

The chemical modification of polypropylene feed spacers to allow Cu(II) chelation, increase antimicrobial properties, and ultimately control membrane biofouling has been studied.[15,16] Analysis showed that the number of cell attached to virgin PP sheets, over a 168-h time span, was approximately an order of magnitude higher than those attached to the copper(II) charged PPgraft-GMA-IDA sheets. The chelation of copper to the feed spacer was determined to be preferential only to EDTA in batch leaching studies. Thus, environmental impacts from copper leaching when using Cu-charged PP feed spacers would be minimal. More significantly, use of the copper-charged feed spacer led to a consistently lower rate of flux decline during filtration. This increased resistance to fouling, and more specifically, biofouling, was hypothesized to be attributed to the hindrance of cell adhesion to the membrane/feed spacer interface. FTIR analysis verified the presence of greater levels of polysaccharides on membranes fouled while using the unmodified polypropylene feed spacers compared to membranes fouled using copper charged feed spacers. Polysaccharides are known to make up the largest portion of EPS, and are related to cell adhesion during initial stages of biofilm formation.[33] It is believed that the antimicrobial property, as well as the increased hydrophilicity, of the Cu-charged feed spacers aided in hindering cell adhesion and, consequently, biofilm formation and biofouling. The work presented here focuses on modifying membrane feed spacers with silver(II), a known biocide,[34] instead of copper. Previous results using copper are presented for comparison.

Metal Leaching

To determine the extent to which the silver would leach from the feed spacers, compared to copper, as well as to determine that silver's affinity to the IDA modified feed spacer was indeed less, a batch study similar was conducted. Modified PP that was charged with silver was exposed to the same three solutions (high salt, pH 3.5, and 5 m*M* EDTA at pH 11) for 1 week. From Figure 1, it was observed that significantly more silver leached under identical conditions as compared to copper. While, after 1 week, both silver and copper did not appear to leach in the presence of the high salt solution, after exposure to solution at a pH of 3.5 and the 5 m*M* EDTA solution at pH 11, only $\sim$ 17% and $\sim$ 32% of the silver remained on the surface of the modified PP. Therefore, silver had a lesser affinity to the IDA modified PP than copper, and was more prone to leaching as compared to copper since after exposure to these same solutions, $\sim$ 75% of copper remained chelated to the IDA modified PP.[15,16]

While copper concentrations taken at different times, as well as the average copper concentration, show that little copper leached from the Cu-charged PP, the same was not true for silver. US EPA drinking water regulations stipulate a primary standard of 1.3 mgL^{-1} for copper and a secondary standard of 1.0 mgL^{-1} for copper, while for silver, only a secondary standard of 0.1 mgL^{-1} exists.[35] However, leaching to the drinking water might not be an issue for application; since any leached copper or silver would be in the retentate stream since these should be partially or completely rejected by the reverse osmosis membrane.

Performance of Silver Modified Feed Spacers

Permeate flux was measured throughout one 4-h, one 24-h, and one 48-h experiments, and normalized to the initial flux values after precompaction under a pressure of 6.89 bar. *Pseudomonas fluorescens* Migula cells, which were freshly grown on an R2A agar plate, were added to the reservoir so that the initial cell concentration was 10^6 cells mL^{-1}. Filtration was carried out at 34°C and 6.89 bar. The flux data, alongside the previously reported data,[15,16] is shown in Figure 2. As the filtration data illustrates, the silver charged feed spacer appeared to control biofouling as well as, or better than, the copper charged feed spacer at short time increments (4 h or less). As filtration time

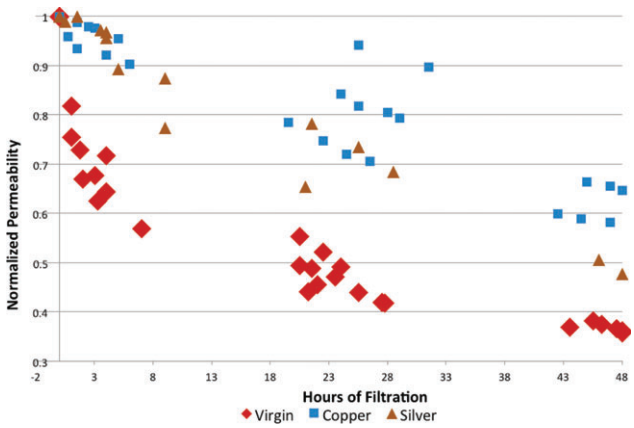

Figure 2. Normalized flux data for *Pseudomonas fluorescens* containing feed water with copper and silver charged feed spacer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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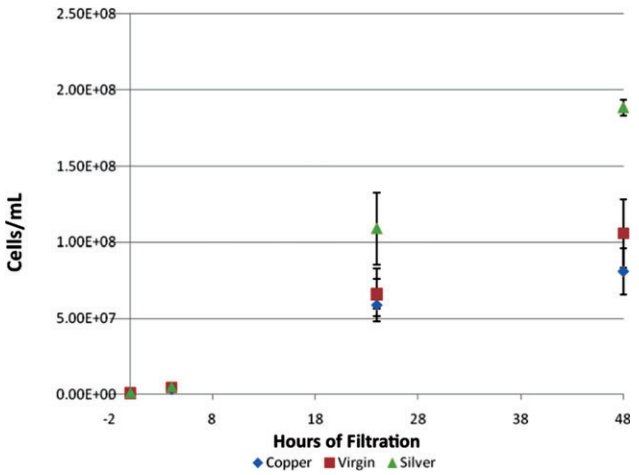

Figure 3. Total cells in solution during filtration with copper and silver charged feed spacers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

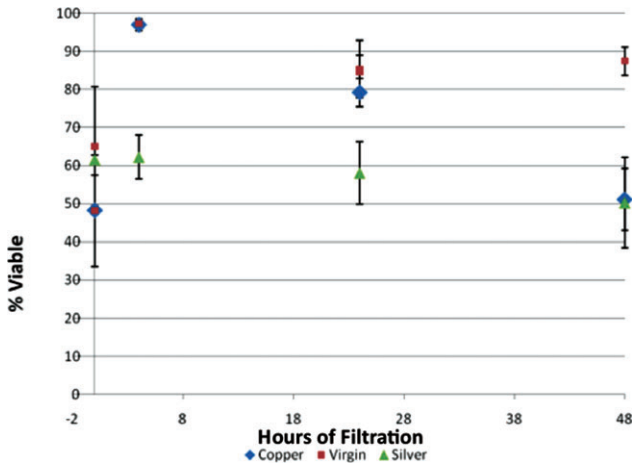

Figure 4. Viable cells in solution during filtration with copper and silver charged feed spacer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased, the ability of the silver feed spacer to control fouling and maintain a constant flux deteriorated, and after 48 h the percentage of initial flux fell between that of the virgin and copper charged feed spacers (∼ 47%). To investigate this performance, counts of live/dead, as well as total, cells in the feed reservoir were performed just as they were for the virgin and copper charged feed spacer experiments. This total number of cells in solution vs. filtration time is shown in Figure 3, and the percentage of viable cells in the feed reservoir vs. filtration time can be seen in Figure 4. Both have been shown next to previously presented data (copper and virgin spacers) for comparison purposes. Figure 3 shows that after 24 h of filtration, the total number of cells present in water using silver charged feed spacers was significantly higher than when using copper charged or virgin feed spacers. On the other had, viable cells are always lower when using silver charged feed spacers (Figure 4); thus, the high number of total cells associated with silver charged feed spacers is likely due to dead cells.

Membrane Autopsy After Using Silver Modified Feed Spacers

After filtration using unmodified, copper charged and silver charged feed spacers, membrane coupons were taken from identical locations on the membrane, vacuum dried, sputter coated with cold and imaged using a SEM. These images are shown in Figure 5. With respect to the membrane tested using the unmodified feed spacer, after 24 h, a biofilm covered the surface entirely, and a small amount of contour was observed in the biofilm. After 48 h, the biofilm looked similar to what it did at 24 h but the contour was much greater, indicating that the

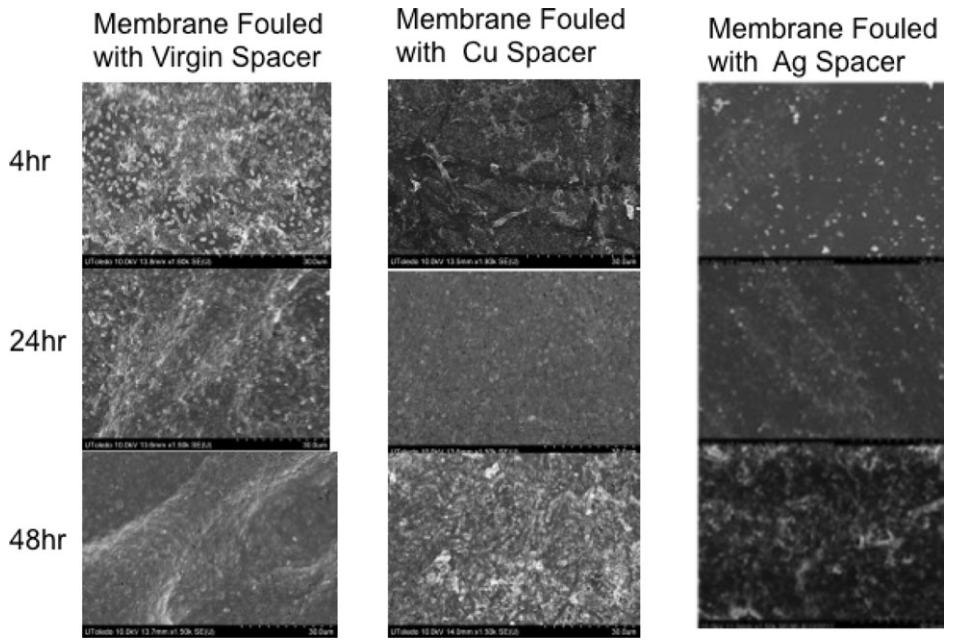

Figure 5. SEM images of fouled membranes using copper and silver feed spacers.

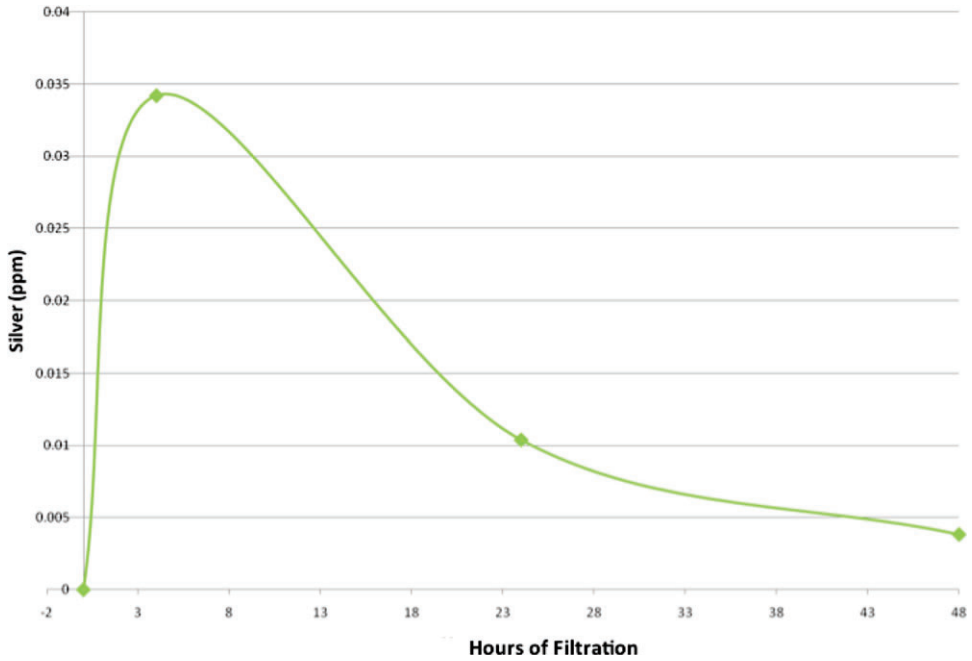

Figure 6. Amount of silver in solution vs. filtration time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thickness of the fouling layer was likely greater. The membrane fouled with the copper-charged spacer showed little or no cellular attachment after 4 h, slightly more at 24 h, and, at 48 h, an image similar to the one taken from the membrane fouled with the virgin spacer after 4 h was observed. When the flux from the membrane used with the virgin spacer after 4 h was compared to that of the membrane used with the modified spacer at 48 h, there was visual agreement. From Figure 5, it also appeared that the silver charged feed spacers caused more colloidal fouling of dead cells, rather than the EPS mediated biofouling when the virgin feed spacer was used. This was consistent with the lower percentage of dead cells observed in the feed reservoir during filtration with the silver feed spacer. Also, this agreed with the amount of silver that was detected in the feed reservoir water vs. filtration time.

As seen in Figure 6, the amount of free silver in solution is high after 4 h of filtration time. The amount of free silver in solution then decreases with filtration time. It is hypothesized that the silver, having a lower affinity to IDA, leaches rapidly during the beginning hours of filtration, resulting in fewer viable cells in solution. The amount of available silver on the feed spacer surface is then depleted, while the silver that has leached stays bound to components of dead bacteria. This results in less free silver in solution, a higher number of total cells in solution, a higher percentage of viable cells, and ultimately a faster rate of flux decline.

A novel method allowed for monitoring of biofilm thickness versus filtration time and made it possible to compare biofilm component concentrations on membranes fouled with virgin and modified spacers versus time. This FTIR based technique has the ability to both absolutely quantify the biofilm thickness and quantitatively related biofilm components on fouled membrane surfaces. As can be seen in Figure 7, the biofilm thickness appeared to grow to the maximum measurable level (that is, when DP $= t_b$) at a faster rate when the virgin spacers were used. Silver-charged feed spacers led to a slower increase in biofilm thickness during the early hours (<24 h) of filtration, which was consistent with flux data, again pointing toward silver staying chelated and preventing biofilm formation in the similar fashion as the copper-charged feed spacer. At later times (>24 h) however, the rate of biofilm thickness increased to greater than the copper-charged feed spacers. This was consistent with the faster rate of flux decline seen during this period when using the silver charged spacer compared to the copper charged spacer.

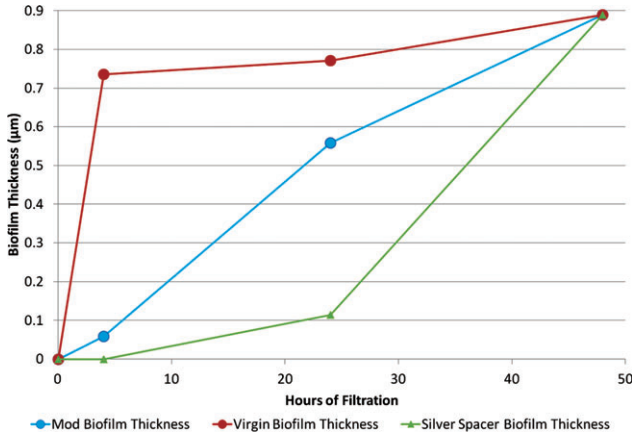

Figure 7. Biofilm thickness vs. filtration time with copper ("mod biofilm thickness") and silver charged feed spacer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

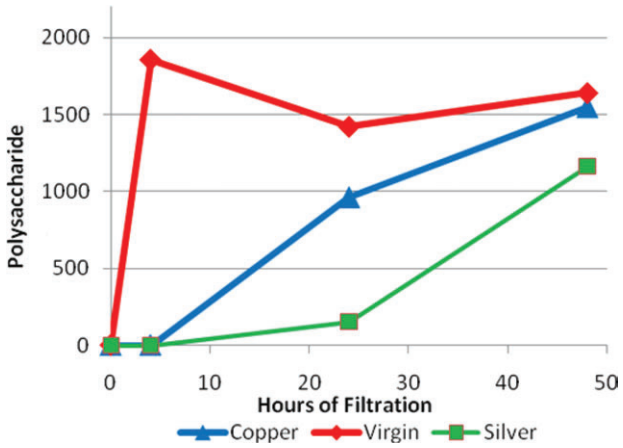

Figure 8. Polysaccharide concentration on membrane vs. filtration time with silver charged feed spacer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Once the biofilm thickness was calculated, the polysaccharide amount on the membranes fouled with the unmodified, copper-charged and silver-charged spacers could be calculated. This data is presented in Figure 8. When the polysaccharide (region from 900 to 1200 cm^{-1}) amount was compared between the virgin and copper-charged feed spacers, a higher amount after 4 h of filtration with the virgin spacer was observed. In contrast to the comparison between copper-charged feed spacers and virgin feed spacers, the amount of polysaccharide on the surface of the membrane was not indicative of the extent of fouling, and ultimately flux decline, which had occurred. The amount of EPS present on the surface of the membranes fouled using the silver charged feed spacer was less, after 48 h, than both the virgin and copper charged feed spacers. The flux decline, however, after 48 h was between that of when using copper charged and when using virgin feed spacers, pointing toward a fouling mechanism that was not dependent on EPS excretion.

Figures 7 and 8 indicate that the copper-charged feed spacers affected the cellular attachment of the bacteria by hindering the EPS (polysaccharide) secretion. This decreased cellular attachment ultimately resulted in lower flux decline observed. On the other hand, as the cell counts observed in Figures 3 and 4 and SEM images (Figure 5) indicate, a higher number of dead and total cells caused extensive colloidal fouling after 48 h of filtration using the silver-charged feed spacer. The hypothesis to explain this was that the silver was leaching from the feed spacer, contaminating the feed reservoir and killing cells. This caused the number of dead cells to increase, but since there was an abundance of carbon source, the cells stayed in a log growth phase longer, resulting in an overall increase in cell numbers.

CONCLUSIONS

The use of silver, as a chelated, antimicrobial metal, instead of copper was investigated, as it is known to be biocidal. As expected, it was shown that silver does not chelate as strongly to the IDA modified PP as copper. Leaching studies showed much greater levels of silver release, compared to copper, when exposed to solutions a membrane and feed spacer will commonly encounter. During cross flow filtration using silver charged feed spacers, it appears that during the first few hours, before a critical amount of silver had leached from the feed spacer, the silver-charged feed spacers performed as well, or better than the copper charged feed spacers. After this time it appears that this increased leaching resulted in a higher percentage of dead and total cells in the feed reservoir compared to identical runs with copper charged feed spacers. This resulted in higher levels of colloidal fouling, which ultimately resulted in a feed spacer whose performance fell between the virgin and copper-charged feed spacers during these studies. The presence of colloidal fouling, instead of traditional EPS controlled biofouling, was supported by FTIR analysis which showed lower levels of polysaccharides on the surface of the membrane fouled during the use of the silver charged spacer compared to other spacers.

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