**FF as tool for membrane fouling potential**

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**CEERS 23 April 2010**

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- Conclusions

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**Brief background**
- While the causes of membrane fouling are many and complex, organic and inorganic micro pollutants present in water is responsible for membrane fouling.
- Organic fouling is seen as the most significant of all membrane fouling.
- SDI and MFI is widely used for evaluating the fouling potential of feed water.
- Limitations of traditional fouling indicators SDI/MFI include standard test conditions which does not simulate the actual crossflow filtration system.
- Moreover these indices are non-linear with foulant concentrations and has very poor reproducibility. These indicator and particularly MFI is related mainly to particulate fouling and not organic fouling.
- Flow field-flow fractionation (FF) is used for separation of particles however, its many similarities with the crossflow filtration system is a motivation for studying this tool for fouling indicator of organic foulant species.

**Research objectives & Scopes**
- Evaluate the application of Flow field flow fractionation (FF) as a tool for membrane fouling indicator.
Background on FIFFF:

What is FFF?
- Like chromatography, Field-flow fractionation (FFF) is a flow based separation technique used to separate broad range of macromolecules ranging from 1 nm to 100 µm
- Invented by Dr. J.C. Giddings in the late 1960s
- Retention and separation of particles in FFF is caused by the action of field applied at right angle to the horizontal flow

Background on FIFFF: Sub-classes

- What is Field: any externally generated influence capable of causing relative displacement of components
- Depending on the type of field applied, FFF family has been invented and named accordingly
- Flow FFF (FFF) is one family of FFF that uses crossflow as the field

Background on FIFFF: Separation principles

- FIFFF has a thin ribbon like horizontal channel flow which has a laminar flow and a parabolic velocity profile
- Crossflow is applied as a field perpendicular to the channel flow to retain the particles
- Separation is based on the relaxation of particles achieved at differential heights from the channel wall (membrane), which depends on physicochemical properties of particles such as diffusion coefficients and hydrodynamic size
- Smaller particles with larger diffusion coefficients fall within the middle or faster velocity region and are carried out first followed by larger particles

Concept of membrane fouling study using FIFFF

\[ M_1 = M_e + M_s + M_a \]
\[ M_2 = M_e + M_{ir} \]

Where:
- \( M_e \): Mass of sample injected
- \( M_s \): Mass of sample eluted from channel
- \( M_a \): Mass of sample filtered through membrane
- \( M_{ir} \): Mass of sample reversibly adsorbed on the membrane
- \( M_{ir} \): Mass of sample irreversibly adsorbed on membrane
Experimental
- Organic foulant
  - Humic Acid as NOM
  - Bovine Serum Albumin (BSA) as protein
- Membrane cleaning agents
  - 0.1 N NaOH
- Membranes:
  - UF 20 kDa PS (NTR 7410, Nitto Denko, Japan)
- Carrier: 1.0 & 10 mM NaCl with 0.1 mM NH₃ as bactericide
- AF2000 Focus (Postnova Analytics, Germany)

Results and Discussions
UV signal sensitivity and consistency: PSS standards
- Very good correlation between sample concentration and, peak intensity and peak integral area
- Peak integral area (mV·s) used as it provides more information and moreover the R² was higher

Results and Discussions
UV signal sensitivity and consistency with HA and BSA foulant concentration
- Integral area for HA and BSA foulant increased with increase in concentration
- Very strong correlation between sample concentrations and UV signal integral area

Results and Discussions
UV signal sensitivity and consistency: detector flow rates versus integral area
- Integral area decreased linearly with increase in detector/ channel flow rates
- At higher channel flow rates samples elute earlier
- Higher detector flow rates is synonymous to higher crossflow rates in the actual crossflow filtration system
Results and Discussions

UV signal sensitivity and consistency: Crossflow versus signal integral area

- Increase in crossflow field decreased integral area exponentially but reaching constant values after certain concentration
- Higher crossflow rate in FIFFF is synonymous with higher permeate flow rates in the actual crossflow filtration system

Results and Discussions

Membrane fouling interpretation using FIFFF

- Two approaches has been used in correlating FIFFF analysis data to membrane fouling potential
  - Moment/ statistical analysis of FIFFF fractogram as suggested by previous authors
  - Evaluating quantitative adsorption of foulant using FIFFF as proposed in this study

Results and Discussions

Fouling interpretation using Moment analysis

Potential relationship between common moments in RTD functions and membrane fouling. (Wright, 2002)

<table>
<thead>
<tr>
<th>Moment</th>
<th>Characteristic definition</th>
<th>Relationship with solute properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (M1)</td>
<td>Arithmetic average</td>
<td>Average size of the sample/solute</td>
</tr>
<tr>
<td>Variance (M2)</td>
<td>Average squared standard deviation</td>
<td>Solute-solute (electrostatic) interactions</td>
</tr>
<tr>
<td>Skew (M3)</td>
<td>Degree of asymmetry of values around the mean in a data set</td>
<td>Solute-membrane interactions</td>
</tr>
<tr>
<td>Kurtosis (M4)</td>
<td>Relative peakedness of a data set distribution</td>
<td>Solute shape and surface characteristics. Solute-membrane electrostatic interactions</td>
</tr>
</tbody>
</table>

Results and Discussions

Fouling interpretation using Moment analysis. FIFFF Fractogram

FIFFF fractogram of HA of different concentrations

FIFFF fractogram of BSA of different concentrations
Results and Discussions

Fouling interpretation using Moment analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Toc (mg/L)</th>
<th>1st NaOH</th>
<th>2nd NaOH</th>
<th>3rd NaOH</th>
<th>4th NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA1</td>
<td>3.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>HA10</td>
<td>3.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>HA15</td>
<td>3.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>HA20</td>
<td>3.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

- At higher HA concentration, retention time slightly increased, an indication of increased solute-solute and solute-membrane interactions.
- Average size of HA decreased at higher ionic strength. Increase in ionic strength enhances electrical double layer compression and charge shielding effect resulting in weaker charge repulsion effect. HA structure becomes coiled from linear at higher ionic strength.
- Smaller sized coiled HA reduces rejection and enhances adsorption within the pores forming denser cake layer thereby increasing fouling potential of HA.

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Results and Discussions

Fouling interpretation through quantitative adsorption

- Figure shows the elution profile of retained and unretained HA.
- The first peak refers to elution of HA under retained mode and its integral area relates to the amount of sample eluted.
- After the sample is eluted under retained mode, crossflow field is released.
- NaOH is injected to remove adsorbed HA under unretained mode.
- HA removed by cleaning is recorded in the form of unretained fractogram.
- The integral area of this fractogram relates to the amount of HA adsorbed on the membrane.

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Results and Discussions

Fouling interpretation: quantitative adsorption

- Relative adsorption refers to integral area (mV·s) of the signal response of unretained elution.
- Relative adsorption increased with increase in foulant concentration but only up to certain extent due to a limit to which a membrane can adsorb foulant during single injection.
- Relative adsorption decreased when higher detector/channel flow rates were used (linear correlation) for both HA and BSA.

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Results and Discussions

Fouling interpretation: quantitative adsorption

- Relative adsorption increased linearly with increase in crossflow field rates for both HA & BSA

![Graph showing relative adsorption vs. crossflow field rates with linear trend lines for HA and BSA.]

Conclusions

- FIFF is a promising tool for evaluating the fouling potential of foulant samples on any type of membrane
- Moment analysis of FIFF fractogram indicated that only first moment (mean) was consistent and statistically reliable in correlating to membrane fouling while the 2nd, 3rd, and 4th moments varied widely
- It is also found that it is possible to quantify the reversible foulant adsorbed on the membrane using FIFF
- The combined data of moment analysis is a useful technique for evaluating and interpreting membrane fouling potential of certain foulant sample
- However further studies are necessary to develop this fouling potential study into a suitable fouling index for actual cross flow membrane filtration system and confirm with the actual crossflow RO filtration.

- Ionic strength had a significant influence on the adsorption
- For HA, adsorption increased at higher ionic strength
- This supports our earlier explanation by moment analysis that at higher ionic strength, charge repulsion decreases and HA becomes more coiled, leading to enhanced adsorption on the membrane

![Graph showing relative adsorption vs. Humic Acid concentrations with different NaCl concentrations showing increased adsorption with higher NaCl concentrations.]

- However, for BSA, adsorption decreased with increase in ionic strength
- This supports our earlier explanation by moment analysis that, increase in ionic strength decreases attractive forces between oppositely charged BSA functional groups resulting in a slightly larger molecule.
- This can lead to a reduction in BSA adsorption density as ionic strength increases

![Graph showing relative adsorption vs. BSA concentrations with different NaCl concentrations showing decreased adsorption with higher NaCl concentrations.]

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THANK YOU!