# Characterisation of membrane fouling by IR spectroscopy

**Thygesen Ole[1*], Zarebska Agata[1], Hassing Søren[1], Qu Haiyan[1], Hedegaard Martin[2]**
*(1)University of Southern Denmark, Niels Bohrs Allé 1, 5230 Odense M, DK*
*(2) Imperial College London, London, UK*
*Corresponding author:olt@kbm.sdu.dk

**Abstract**
Separation of nutrients from animal manure into fractions with a high concentration of N, P and K, respectively, is one of managing the nutrients so that they in the most efficient way as fertilizers to the crops in the fields. One of the main plant nutrients are ammonia, which can be removed from the liquid fraction of separated animal slurry by membrane distillation. The main objective of this study is to identify the composition of membrane fouling from ammonia recovery from the liquid fraction of separated pig slurry and to visualise the distribution of fouling on the membrane using FT-IR spectroscopy and multivariate data analysis. The study identified IR bands at 1280, 1536 and 1656 $cm^{-1}$ which were assigned to proteins and at 1112 and 1736 $cm^{-1}$ which were assigned to carbohydrates. The distribution of fouling was visualised using the N-FINDR algorithm and it was shown that the fouling was uniformly distributed on the membrane.

**Introduction**
One of the big challenges in current livestock production is the management of the manure. Through separation of the manure into fractions with a high content of N, P and K, respectively, the redistribution of the nutrients can be made easier and the nutrients can be applied in the most optimal way.
This study focuses on the concentration of the ammonium nitrogen from pig manure. First step in the concentration is the separation of the pig slurry into a liquid and a dry-matter-rich fraction, this is currently(2010) done at 33 pig farms in Denmark[3]. The liquid fraction contains most of the ammonium nitrogen.
A method that has shown promising results for concentrating ammonia from liquid fraction of animal slurry is membrane stripping using a membrane contactor and an acidic strip solution. The main obstacle when using a membrane contactor is the deposition of fouling on the membrane; the fouling has been shown to mainly consist of organic components[2]. By using FT-IR mapping, we aim to obtain more knowledge of the distribution and composition of the fouling on the membrane which could in turn lead to better ways to clean the membranes or an optimisation of the membrane to minimise the fouling propensity.

**Material and Methods**
The membrane set-up consists of a tubular PP membrane, with an average pore size of 0.2 μm and a porosity of 70%, from Microdyn-Nadir Gmbh. The liquid fraction from the pig slurry separation is pumped through the inside of the membrane and the strip solution on the outside of the membrane.
FT-IR analysis measurements was carried out using a Perkin Elmer Spectrum 100 spectrometer coupled with an autoIMAGE FT-IR microscope. The spectra were recorded using 15x15 μm aperture and 10 scans. The FT-IR will give spectroscopic information on the fouling composition.
Data analysis was conducted with software developed in-house for use in the Matlab (Mathworks) environment, and with the multivariate statistical analysis using the PLS toolbox (Eigenvector Research). The data analysis consisted of removal of the background signal from the sample, this was done by applying a k-means cluster analysis where the spectra are assigned to different clusters by minimizing the difference within each cluster and maximizing the difference between the different cluster, the clusters that contain the background signal was then subtracted from dataset. Afterwards a spectral unmixing algotith called N-FINDR was used, the algorithm gives as an output the n spectra (endmember spectra) that are most different from each other and spans the most of the dataset. Then each spectrum in the dataset is described as a linear combination of the endmember spectra. Now a map was constructed by assigning different colours to the different spectra, each spectrum got mix of colours showing how much it resembled each of the endmember spectra[1].

This data analysis produced a map that shows which parts of the membrane is covered by components with similar FT-IR spectra, hence giving a map of the distribution of the different components in the membrane fouling.

*Embedding and cutting of the PP membrane*
The samples were placed in a well plate and covered with 100% ethanol for 10 minutes. The ethanol was removed from the well plate and a 50:50 mixture of 100% ethanol and Polyester Wax 360704E(VWR international, PA, USA). The samples were left overnight at 45C and then transferred to a clean well where pure polyester wax at 45 ˚C was added. The sample was left for 2 hours and then transferred to a clean well and add pure polyester wax at 45˚C. Place in a vacuum chamber at 75 kPa for 2 hours. The sample was left to harden at room temperature for 3 days. 4µm sections were cut on a rotary microtome, keeping blocks cooled on ice. One sample was cut in perpendicular to the surface of the membrane and one sample was cut close to parallel to the surface. The sections were moved to a $MgF_2$ slide using distilled water, and dried upright at room temperature overnight. The wax was removed by immersion in histoclear for 2 times 15 minutes.

**Results and discussion**

*FT-IR mapping*
For the sample cut close to parallel to the fouling layer a model with four endmembers was produced using the N-FINDR algorithm. The spectra showed that the fouling layer was uniformly distributed over the surface of the membrane. Three of the four endmember spectra showed a combination of fouling and membrane spectra, the difference being the ratio of membrane:fouling band intensities, the endmember spectra of the pure membrane and the highest intensity of fouling band intensities are shown in figure 1.

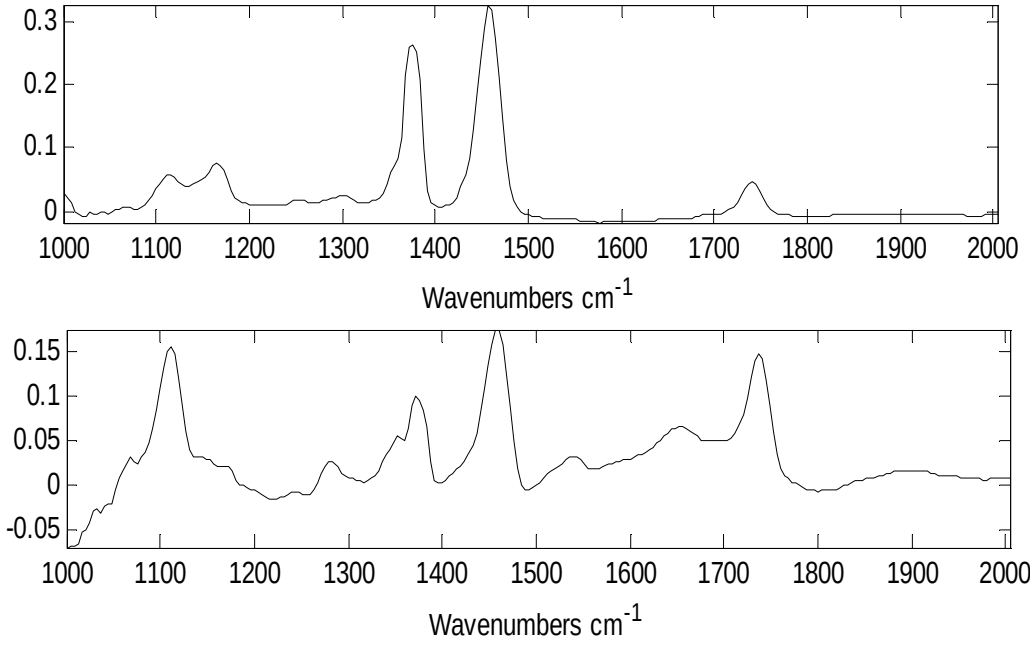


**Figure 1- The endmember spectra of the PP membrane(top) and the PP membrane with fouling(bottom)**

A picture of the membrane slice and the map produced based on the result from the N-FINDR algorithm are shown in figure 2

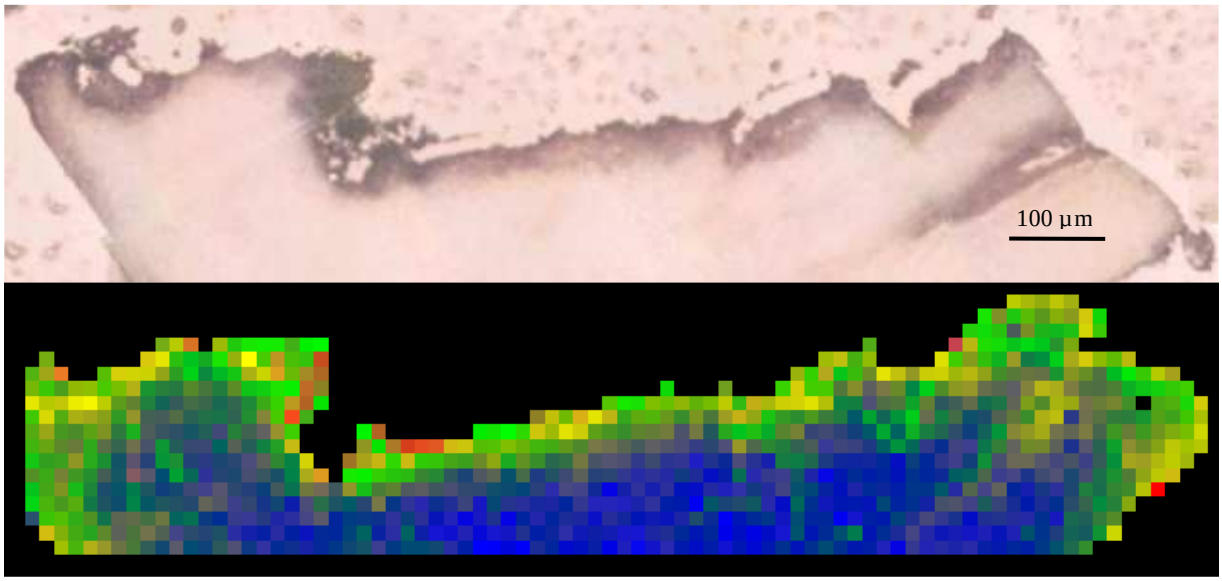


**Figure 2- Slice of the 4 µm thick slice of fouled membrane(top) and the corresponding map made based on the model from the N-FINDR algorithm(bottom). The blue is the pure PP membrane, the other colours in order of the most intense of the fouling bands red>yellow >green**

The five bands found in figure 1) bottom that cannot be assigned to the membrane are positioned at 1112, 1280, 1536, 1656 and 1736 $cm^{-1}$. Three of these: 1280, 1536 and 1656 $cm^{-1}$ can be assigned to the amide I, II and III vibrational modes of the peptide bonds in proteins[4] which are known to have a large propensity for fouling of hydrophobic membranes [5]. The band at 1352 $cm^{-1}$ has been assigned to $CH_2$ wagging[4]. The bands at 1112 and 1736 $cm^{-1}$ can be assigned to the C-O and C=O stretching in carbohydrates, respectively[4]. Carbohydrates have as proteins been reported to be one of the main foulants of membranes[6]. The band assigment is summarized in table 1.

**Table 1- Band assigment in the membrane fouling**

| **Wavenumber [$cm^{-1}$]** | **Band assignment** | **Reference** |
|---|---|---|
| **1112** | C-O stretch, Carbohydrates | [4] |
| **1280** | Amide III, Proteins | |
| **1352** | $CH_2$ Wagging | |
| **1536** | Amide II, proteins | |
| **1652** | Amide I, proteins | |
| **1736** | C=O stretching, carbohydrates | |

For the sample cut perpendicular to the fouling layer a model with three endmembers was produced using the N-FINDR algorithm. The spectra showed that the fouling layer was uniformly distributed over the surface of the membrane and that the fouling only to a very small extend penetrated more than 15 µ into the membrane. Two of the three endmember spectra showed a combination of fouling and membrane spectra, the difference being the ratio of membrane:fouling band intensities, the endmember spectra of the pure membrane and the highest intensity of fouling band intensities resembles the spectra shown in figure 1.

The map of the fouling distribution for the membrane cut perpendicular to the membrane surface is shown in figure 3.

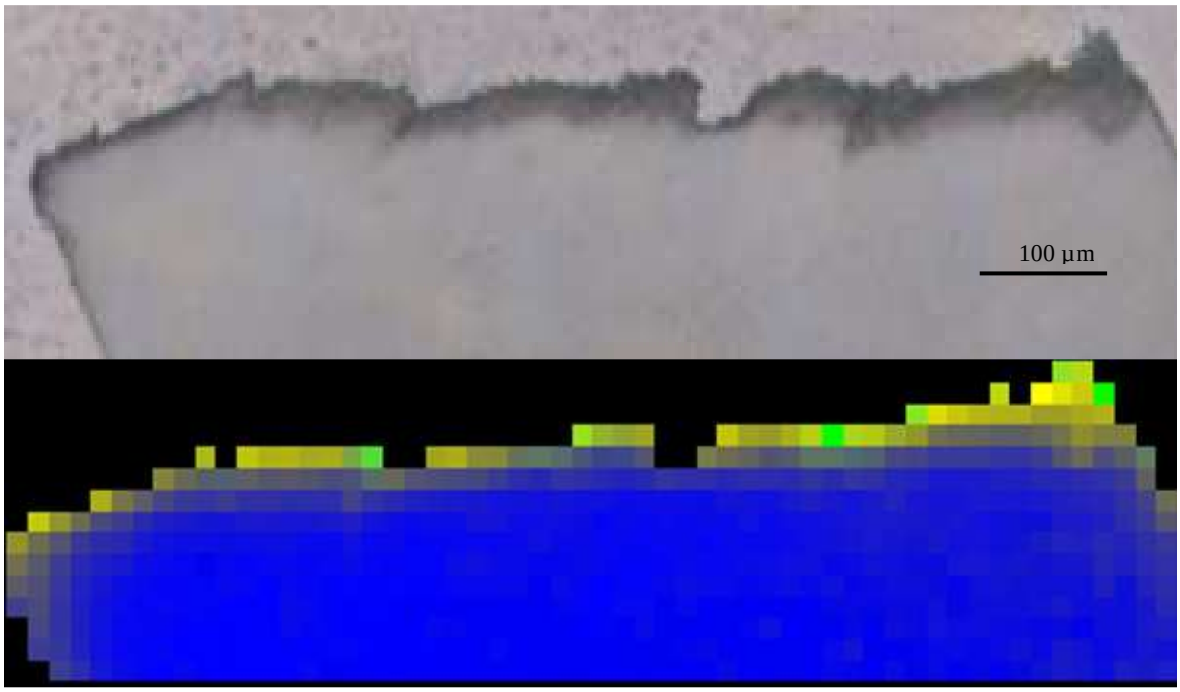


**Figure 3- Slice of the 4 µm thick slice of fouled membrane(top) and the corresponding map made based on the model from the N-FINDR algorithm(bottom). The blue is the pure PP membrane, the other colours in order of the most intense of the fouling bands green>yellow**

## Conclusion and perspectives

The study confirmed that the membrane fouling from the stripping of ammonia from the liquid fraction from pig manure consists of organic compound at that proteins and carbohydrates are the most predominant compounds in the fouling. The study showed that the distribution of fouling components on the membrane surface is uniform.

## Acknowledgements

The study was supported by a grant from the Danish Council for Strategic Research under the work program "Clean and environmentally friendly animal waste technologies for fertilizer and energy production (CLEANWASTE)."

## References

[1] Hedegaard M., Matthäus C., Hassing S., Krafft C., Diem M. and Popp J., 2011, Spectral unmixing and clustering algorithms for assessment of single cells by Raman microscopic, Theor Chem Acc (2011) 130:1249–1260 imaging

[2] Zarebska A., Norddahl B. and Christensen K. V. Fouling characterization of membrane contactors used for the recovery and concentration of ammonia from undigested pig slurry. I: 11th World Filtration Congress & Exhibition Abstract Book. red. / Wilhelm Höflinger; Gerd Mauschitz. Vol. 1 Graz, Austria : Filtech, 2012. s. 209.

[3] Birkmose T., and O. Thygesen. 2010. Status of application of slurry separation in Denmark, May 2010 (in Danish). Skejby, Denmark: Danish Agricultural Advisory Centre. Available at: www.landbrugsinfo.dk/Tvaerfaglige-emner/Gylleseparering/Sider/pl_10_187.aspx .Accessed March 2013.

[4] Movasaghi, Z., Rehman, S., and Rehman, I. ur, 2008. Fourier Transform Infrared (FTIR) Spectroscopy of Biological Tissues, Applied Spectroscopy Reviews, 43: 134–179

[5] Zhao Y.-H., Wee K.-H. and Bai R., 2010 Highly hydrophilic and low-protein-fouling polypropylene membrane prepared by surface modification with sulfobetaine-based zwitterionic polymer through a combined surface polymerization method, Journal of Membrane Science 362, 326–333

[6] Trussel R.S., Jang N., Merlo R.P., Kim I.S., Hermanowicz S.W. and Jenkins D., Changes in mixed liquor and organic foulant properties affect membrane fouling for non-nitrifying and nitrifying biological conditions, Water Environ Res. 2009 Mar;81(3):255-64