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Procesvand – online overvågning af rengøringskvalitet, vandkvalitet og biofilm-dannelse

Mejeribrugets
ForskningsFond

MARTS 2015

Slutrapport

for samarbejdsprojekter under MFF

1. Projektets titel

Procesvand - online overvågning af rengøringskvalitet, vandkvalitet og biofilm-dannelse

2. Projektleder

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3. Øvrige medarbejdere

Søren Balling Engelsen, KU.FOOD.SPECC, sb@food.ku.dk

Christian Lyndgaard Hansen, KU.FOOD.SPECC (Post Doc → Industry)

Jannie Krog Jensen, KU.FOOD.SPECC (PhD student, successfully defended 28-05-2015 → Industry)

4. Projektperiode

January 2012 - December 2014 (integrated with inSPIREfood co-financing).

5. Projektresume

Rengøring af membranfiltreringsanlæg er særdeles resursekrævende mht. vand, tid, varme og rengøringsmidler, men metoder til at evaluere rengøringseffektiviteten er sparsomme. En række indledende feltundersøgelser af rengøringsprocedurerne, Clean-In-Place på Arla Foods Ingredients ledt til formulering af følgende: Langtidsvariationer i rengøringskvalitet af industrielt UF anlæg. API i Nr. Vium har opsamlet prøver hver dag under forskellige CIP trin på et UF/MF anlæg. Ultrafiltrerings- og mikrofiltrerings-membraner bliver i høj grad brugt af mejeriindustri. De største begrænsende faktorer for disse enheder er flux og nedgang i effektiviteten som følge af irreversibel fouling på membranerne og samtidig den effektivitet hvormed den reversible fouling kan fjernes/rengøres. Formålet med dette projekt er at undersøge residual foulingen (tilbageværende protein, fedt og mineraler efter endt rengøring) som er deponeret på ultrafiltrerings- og mikrofiltrerings-membraner efter brug. Membranoverfladerne er undersøgt ved at bruge infrarød spektroskopi i kombination med en attenuated total reflectance prøveenhed. Produktionsmembraner der har været benyttet i forskellige stadier hos Danmark Protein, Arla amba, var målet for vores undersøgelser. Informationen kan bruges til at undersøge og overvåge residual fouling og kan bidrage til udformning af nye membraner samt grafting af membraner som kan optimeres til specifikke formål.

6. Projektets formål

Mejeriindustrien omsætter enorme mængder af vand. Genanvendeligheden af disse store vandmængder afhænger af mængden af de næringsstoffer de indeholder. Dette projektet har til formål at skabe et forbedret grundlag for bæredygtig anvendelse af procesvand i mejeriindustrien. Projektet vil undersøge mulighederne for oprensning af procesvand fra forskellige mejeriprocesser til en kvalitet som muliggør at vandet kan anvendes og behandles som rent vand på lige fod med brøndvand i produktionen. Målsætningen er dels (1) at udvikle sensorer, som kan anvendes online til måling af små koncentrationer af indholdsstoffer i "forholdsvis rent" RO permeat samt at pre-screene mulige oprensningsprincipper til anvendelse i industrielle processer og dels (2) at analysere data fra produktionsfaciliteter for at skabe en multivariat modellering af variation og renhedsgrad med henblik på at kunne designe og styre oprensningsprocessen til at opnå den tilstrækkelige renhed.

Membrane processes and CIP in dairy processing in numbers:

- In use since the 1960s, the dairy industry has always been the main driving force in developing membrane technology for the food industry.
- The (refined) whey powers global market was estimated at €5.5 billion in 2011, forecast to reach €6.6 billion in 2015.
- Estimated areas (m^2) in dairy processing for 2009, worldwide: Ultra Filtration: 400,000; Nano Filtration: 300,000; Reverse Osmosis: 100,000; Micro Filtration: 50,000.
- The food industry represents 20-30% of the €250 million annual turnover of membranes used in the manufacturing industry worldwide (yearly growth ~7.5%).
- It is estimated that ARLA alone will operate a combined MF and UF area of 400,000–500,000m^2 by 2018.
- Membrane cleaning is a costly process that requires time, chemicals, energy, plus a lot of water! It has been estimated that the cost for CIP chemicals in full scale membrane cleaning is around €17-24 per m^2 per year, while additional costs (electricity, cooling, heating, water, waste water treatment, manpower, membrane wear) typically amount to €33-43 per m^2.
- ARLA Foods Ingredients alone has currently (2014) around 200.000m^2 of membrane area installed which is expected to grow by 75-100% in the next 5 years. It can be estimated that the total annual cleaning costs in 5 years could amount to €17,500,000-26,800,000 – an attractive target for process optimization!

7. Projektets delaktiviteter i hele projektperioden

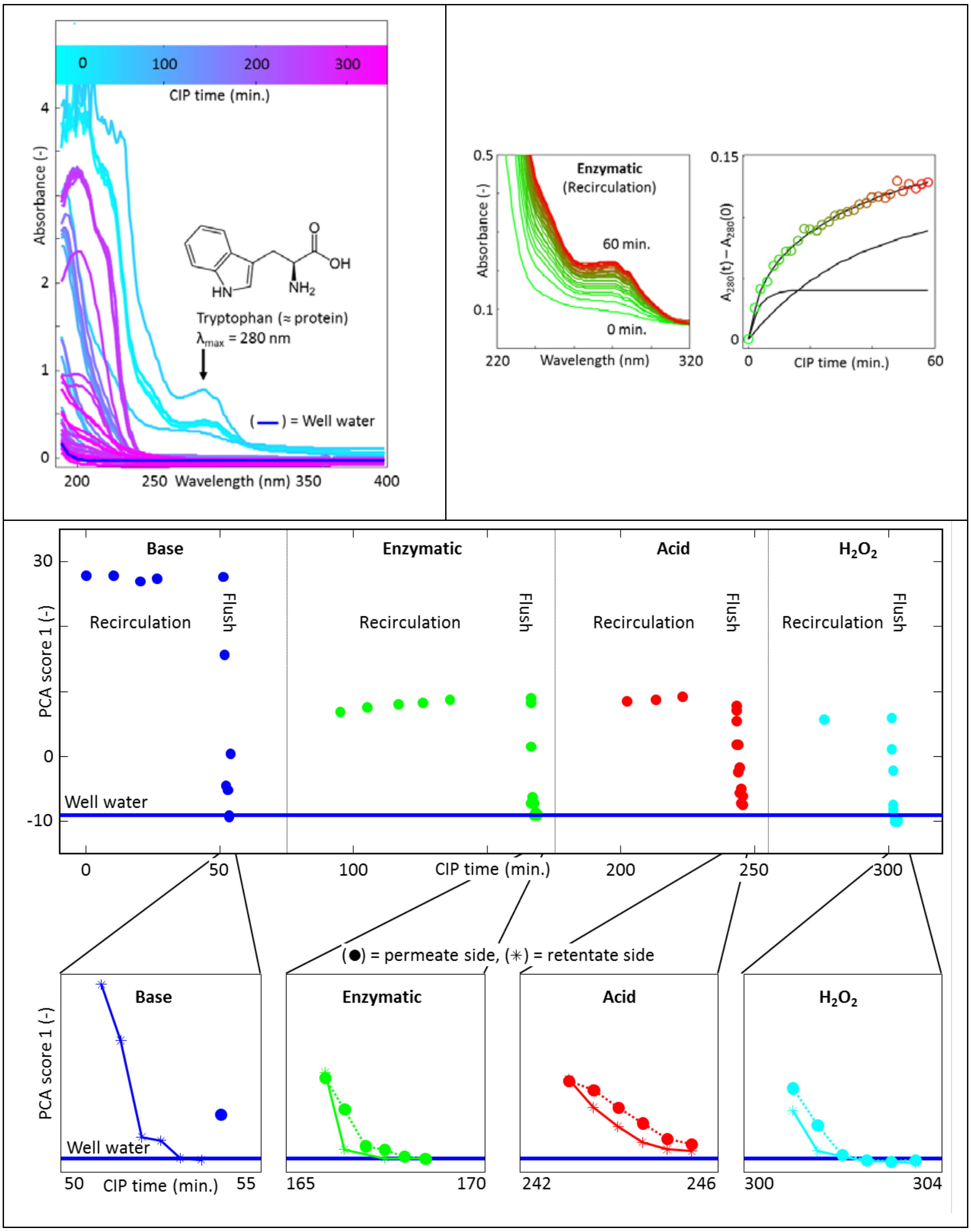
The project activities can be divided in three (overlapping) labors: (1) a Post Doc investigation into "measurement based CIP", a PhD study on residual foundling distribution for dairy membrane systems, finding funding for future research in CIP/Cleaning. The first two are summarized under point *8. Projektets resultater/faglige forløb i perioden* and *11. Formidling og vidensdeling vedr. projektet*, while the last point is evidenced under point *12. Nye kontakter.*

8. Projektets resultater/faglige forløb i perioden

Our work explores the potential of using Ultra-Violet spectroscopy (UV) as an analytical technique for monitoring and optimization CIP of dairy processes. UV spectroscopy is a candidate method because it is sensitive down to the ppm level for many compounds and because it is able to measure on-line with speeds of less than a second. Whey protein quantification in dairy UF by UV is possible through the indirect marker tryptophan, which is a strong UV chromophore. Modeling methods using UV spectra can be divided into two categories. The first is single-wavelength or univariate models that correlate absorbance at one chosen wavelength to a concentration by Beer’s law. However, in complex mixture samples such as observed during UF membrane CIP, it can be challenging to distinguish the individual UV absorbance contributions. The second category of multi-wavelength models (or more general multivariate models) has the advantage that they can be used to investigate process dynamics despite the presence of interfering species. Explorative multivariate classification methods such as Principal Component Analysis (PCA) can be powerful tools for investigating latent patterns in UV spectral data sets.

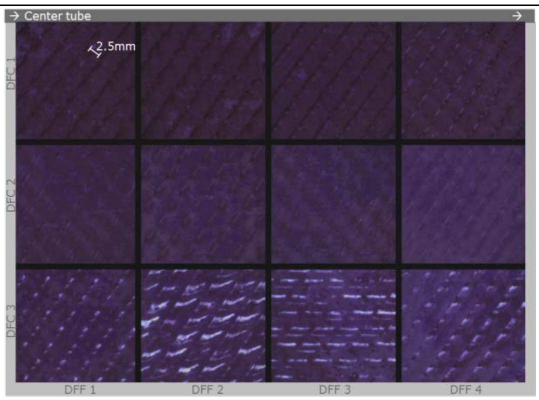
Real-time measurement of CIP liquids - cleaning agents and dissolved contaminants in water - during cleaning can provide valuable insight on the progress of cleaning. This is the first step towards actively controlling the process. At present the CIP procedures applied in industrial UF membrane filtration operations are almost exclusively recipe-driven where the procedure is fixed, disregarding variations in the nature and extent of fouling. Two concepts of active control of cleaning based on measurements can be envisioned: (1) stopping a cleaning step when the system does not increase in concentration of the fouling material and (2) stop a flushing step when the rinsing water stops decreasing in concentration of the fouling material or cleaning agents. Measurement based control of CIP requires that the technique has an acceptable limit of detection of the fouling material and/or cleaning agents and is sufficiently fast to provide results which can be acted upon within the time-scale of the different cleaning and flushing steps. Samples were collected from a nine-loop whey UF unit with spiral wound polyethersulfone membranes. The total dead volume in the nine loops is estimated to be 5.5m^3 and the average production time before CIP was around 20 hours. The applied CIP program consists of four main steps – caustic, enzymatic, acid and hydrogen peroxide – each involving a long recirculation and short flushing part (the later done one loop at the time). UV spectra (10 mm path-length) of the samples from a full CIP sequence are shown below. The individual CIP processes can easily be identified from the score development highlighting that the combined soil and cleaning agent composition of each CIP process has a unique UV signature. The score development during the flushing steps shows an exponential decrease, but at different rates for the successive steps. E.g., the flushing of the acid cleaning agent is slow compared to the flushing of other cleaning agents. Collectively, the PCA plots demonstrate that UV spectroscopy is an effective monitoring sensor of the dynamics of a CIP procedure. This is attractive because it indicates that each CIP step can be monitored and potentially controlled and optimized based on process measurements rather than according to fixed regimes.

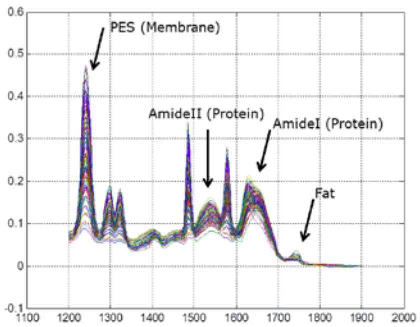
Based on the systematic increase in PCA scores during the enzymatic cleaning it was decided to investigate this cleaning step in more detail via more frequent sampling. The development in absorbance clearly indicates the progress of the membrane cleaning process via the absorbance at 280 nm. This can be interpreted as protein removal from the membrane. As expected, when fouling deposit is removed from the membrane into the surrounding liquid (thereby increasing UV absorbance of the liquid), the rate of deposit removal steadily decreases with time in an asymptotic way. The cleaning development was tested for first and second order reaction models, but none of these models were found adequate based on residual inspection. Instead, the suggested model summing two simultaneously occurring first order reactions was found to fit the observed data very well (R^2 = 0.994). From the parameters of the fitted model the contributions of the individual first order cleaning reactions was calculated and plotted. We suggest two underlying cleaning processes: an early/fast phase associated with the removal of the cake from the surface and a later/slower phase associated with the removal of the in-pore trapped proteins. The data does clearly demonstrate that UV spectroscopy is a capable PAT sensor for monitoring enzymatic cleaning kinetics. Together with conventional membrane flux recovery measurements it is a valuable tool in investigating and understanding how CIP factors such and detergent concentration, temperature and transmembrane pressure influence the rate of different cleaning mechanisms.

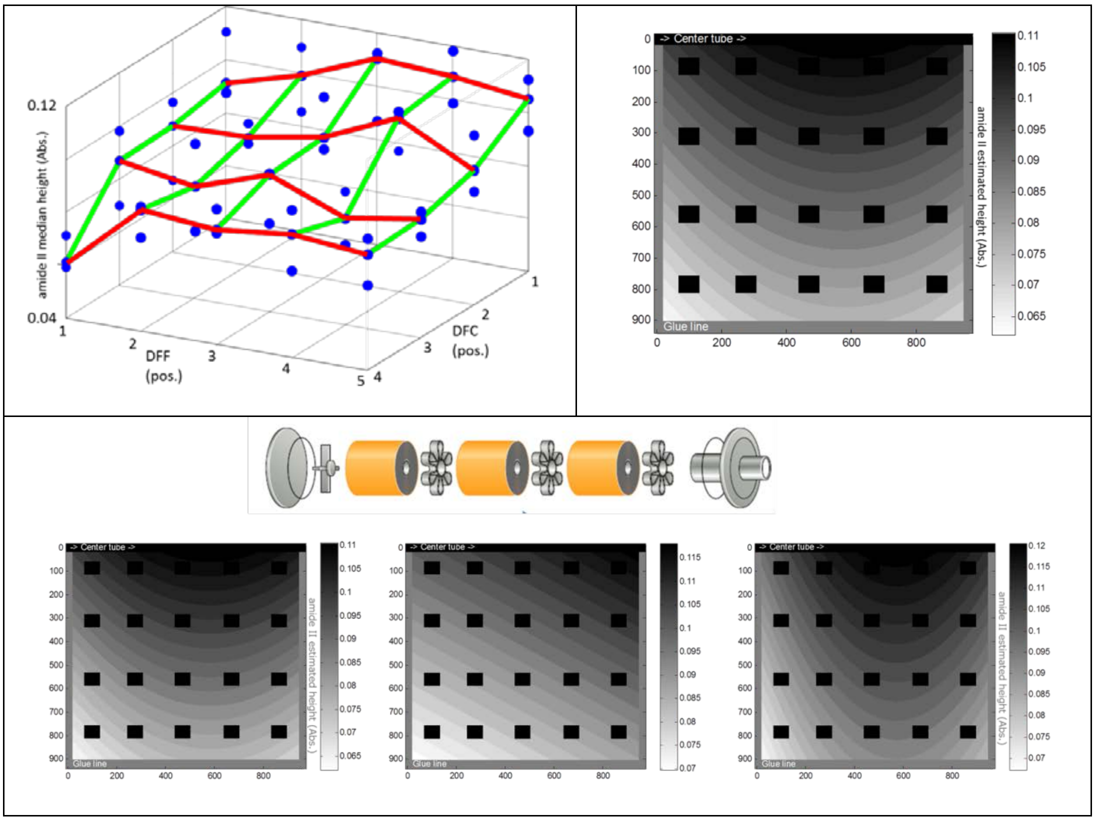


An extensive investigation on the residual fouling of UF and MF membranes in full-scale dairy processing has been conducted. Successful measurement and data analytical methods have been developed to describe the residual fouling on membranes. ATR-FT-IR has demonstrated to be an appropriate analytical technique for measuring the different molecular components originating from the residual fouling compared to the staining method. The staining for proteins and visual inspection aided in describing and understanding the spatial distribution of residual fouling on the membrane and helped identify the inhomogeneity that can cause large variation in the measurement results. The observations were in agreement with the (sparsely available) references on full-scale production investigations, providing confidence in our method of analyses. ATR-FT-IR is a more suitable method as it is a fast and non-destructive method that provides chemical selectivity on the residual fouling. Tukey's HSD test showed that three cartridges steaming from one housing are significantly different, which indicates that there is no repeatability between the cartridges concerning residual fouling, even though they are positioned in the same steel housing and have experienced the exact same production and CIP cycles over the 5-month period of use. These statistically significant differences between leaves will most likely not occur spontaneously inside a closed production and CIP system; all leaves within one cartridge are expected to experience the same flows. This indicates that the leaf has been less (or more) exposed to the environment in the cartridge during whey processing (and cleaning). The large variability between the leaves within one cartridge and between the cartridges is suspected not only to be a result from the use at the dairy but also caused by the manufacturing and assembly of the membrane cartridges. The investigation showed that both protein and fat show a characteristic residual fouling pattern over the leaves. The conclusion is that ATR-FTIR is a strong (albeit labor intensive) method for semi-quantitative evaluation of the complex process of membrane filtration at an industrial scale. The two directions as main and/or quadratic effects have a significant influence on the findings in all the ANOVA calculations performed on amide II and fat bands. There is a clear, non-homogeneous distribution on the membrane sheets with the concentration of residual fouling the highest at the center tube and decreases toward the glued edge along the distance-from-center direction.

Overall shared tendencies can likely be explained by spatial flow and pressure differences caused by the design aspects of spirally wounded modules and steel housings in UF/MF. The permeate flux can be credited the higher fouling concentration closer to the center tube as the flux is higher here since permeate has the shortest distance to travel. Similarly there is an increase in fouling at the feed inlet of the membrane cartridge due to TMP being at the highest at this point. Despite the clear common trends as evidenced by a large leaf-to-leaf variation is observed from, and a cartridge-to-cartridge variation. A systematic nearest neighbor pattern for the leaves inside one cartridge was not observed. These differences in cleaning (and probably capacity performance) can most likely be attributed to manufacturing and assembly variations in the complex structure of spirally wound membrane units.







9. Afvigelser

9.1 Fagligt

Almost all activities started in this project are continued in other research projects!

9.2 Økonomisk

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9.3 Tidsplan

The PhD study in this project was delayed (approximately 6 months). The costs for this delay were carried by KU.FOOD.SPECC.

10. Planer for næste halvår

No new activities planned.

11. Formidling og vidensdeling vedr. projektet

1. J. Thygesen, F.W.J. van den Berg 'Subspace methods for dynamic model estimation in PAT applications' Journal of Chemometrics 26(2012)435-441

2. Populærvidenskabelig artikel i Mælkeritidende nr. 19, 23. september 2011 s.6-7. "PAT i Mejeriindustrien - Optimering af mejeriproduktion gennem sensor teknologi og kemometri" (v/Christian B. Lyndgaard).

3. Presentation EFFoST, November 2011, Berlin "Process analytical Technology in the Dairy Industry" (Ch. B. Lyndgaard)

4. Poster presentation Danish Water Forum Annual Meeting January 2012, Copenhagen, “Process Water - Minimizing Industrial Water Use by In-process Cleaning Diagnostics” (Ch. B. Lyndgaard, J. K. Jensen, S. Knøchel and F. van den Berg)

5. H. Babamoradi, F.W.J. van den Berg, Å. Rinnan ‘Comparison of bootstrap and asymptotic confidence limits for control charts in batch MSPC strategies’ Chemometrics and Intelligent Laboratory Systems 127(2013)102–111

6. F.W.J. van den Berg, Ch.B. Lyndgaard, K.M. Sørensen, Søren B. Engelsen ‘Process Analytical Technology in the Food Industry’ Trends in Food Science and Technology 31(2013)27-35

7. Ch.B. Lyndgaard, M.A. Rasmussen, S.B. Engelsen, D. Thaysen, F.W.J. van den Berg ‘Moving from recipe-driven to measurement-based cleaning procedures: monitoring the Cleaning-In-Place process of whey filtration units by ultraviolet spectroscopy and chemometrics’ Journal of Food Engineering 126(2014)82–88

8. Th.H.A. Berg, J.C. Knudsen, R. Ipsen, F. van den Berg, H.H. Holst and A. Tolkach “Investigation of Consecutive Fouling and Cleaning Cycles of Ultrafiltration Membranes Used for Whey Processing” International Journal of Food Engineering 10(3)(2014)367-381

9. J.K. Jensen, N. Ottosen, S.B. Engelsen and F. van den Berg “Investigation of UF and MF Membrane Residual Fouling in Full-Scale Dairy Production Using FT-IR to Quantify Protein and Fat” Int. J. Food Eng.11(1)(2015)1-15

10. J.K. Jensen, J.M.A. Rubio, S.B. Engelsen, F. van den Berg ‘Resolving ATR-FT-IR spectra of Protein Residual Fouling on Membranes using MCR’ Chemometrics and Intelligent Laboratory Systems 144(2015)39-47

11. J.K. Jensen ‘ATR-FT-IR/surface measurements on Membrane systems (working title)’ in preparation (2015)

12. F.W.J. van den Berg, H.H. Holst, S.B. Engelsen ‘Water reuse and saving in the food industry: A new frontier in food manufacturing’ New Food 17/6(2014)49-53

12. Nye kontakter

- A new major research project (REWARD) was initiated based on the investigations conducted in this project.

- A (smaller) research project concerning water (re)use and cleaning in the meat industry has started (RENPÅNY).

- A three year industrial Post Doc in the area of (membrane) cleaning (Thilo Berg) was financed by the ministry and API.